Controlled, self-assembly of silica nanoparticles
into uniform mesostructured glass

A thesis submitted in fulfillment of the requirements for the degree of

Master of Philosophy (Science)

by

Victor Akpe

School of Chemistry, The University of Sydney

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Dedication

Mrs. Victoria Akpe (Wife)
Statement of Originality

I declare that this thesis submission contains no material presented for a degree at this or any other university and, to the best of my knowledge and belief, contains no copy or paraphrase of work published by another person, except where the author has been duly acknowledged.

Victor Akpe
Sydney, February 28, 2017
Thesis contributions

Professor John Canning supervised the experiment in chapter 4.1 and partly supervised the second experiment in chapter 4.2. He also suggested to the idea of fabricating silica microwires in the cold temperature range in chapter 4.5 and also furnished me with previous thesis work to start with the thesis writing. Professor Canning wishes it known that he did not get to see the thesis prior to its submission.

Professor Maxwell Crossley supervised and edited the first draft of the thesis work presented in chapters 4.1 to 4.6. He also gave valuable suggestion for doping of the microwires with sugar solution.

I received occasional assistance with the SEM imaging, and Mr Hadi Sabouri helped with the DLS instrument set up reported in chapter 4.6.

The final thesis amended in line with the examiners comments.

This thesis describes studies conducted from June 2015 - February 2017 in the Interdisciplinary Photonics Laboratory and the School of Chemistry at the University of Sydney.
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Abstract

Crucial to the next generation technologies is exploring ways of making nanoparticles bind with incompatible materials. These possibilities include the inclusion of a variety of chemical or biological species into colloidal suspension of silica (SiO₂) nanoparticles. For example, the assembled materials may potentially serve as platforms for optical sensing, protein storage, and as super-capacitors to power electronic devices. This thesis presents microwires produced from colloidal droplet of silica nanoparticles on a glass substrate during evaporation. Some of the challenges that stems from microwire fabrication include variable size dimensions and pore sizes, knowing the optimal volume of liquid droplet to add to the surface per unit area, temperature and humidity conditions, and glass surface conditions. The follow up studies focus on clarifying some of these optimal conditions in the fabrication process. Other studies include to understand the nanostructured surfaces of these wires, and to explore sugar and protein inclusion into silica nanoparticles.

The aim of the first experiment (Chapter 4.1) was to evaluate glass substrate that gives a reproducible surface. Here, contact angles of water droplets measured on specialty glass surfaces (SuperFrost Ultra Plus microscope glass slide) gave a consistent contact angle (39 ± 1) °. Routinely used microscope glass slides gave inconsistent contact angle values at the different surface positions. In this section, the ultrasonication method proved to be more effective for glass surface cleaning. The mechanism of ultrasonication method is through a process known as cavitation. Ultrasonic waves are released in succession along the glass surface, which then forms large bubbles use for scrubbing the surface to remove particulate matter and oil films.
In the second experiment (Chapter 4.2), the aim was to demonstrate the importance of surface control and drop deposition to produce a uniform nanostructured surface of silica microwire. By manipulating the surface properties, such as coating the surface, limit the drop’s volume ($V= 1 \, \mu\text{L}$) (to reduce size deformation caused by gravity upon evaporation), optimise silica nanoparticles concentration during the evaporative process, microwires with less variable size dimensions were produced. The emphasis here is that Au-coated surface enhances the spatial ordering of nanoparticles in a more controlled manner to hcp/bcc configuration states. The evaporation of liquid droplets on Au-coated and non-coated surfaces in chapter 4.3 further showed that Au-coated surface retained less water than the uncoated surface of the same glass material. Consequently, at ambient temperature, Au-coated surface gives a faster evaporative process, less time for nanoparticles to form aggregate clumps, uniform dispersion and less time for water to interact with the surface. Additionally, the orderly packing leads to uniform and thinner wires. The study also confirms the superior flow behaviour of a gold-coated surface over a non-coated surface.

In the fourth experiment (Chapter 4.4), the aim was to compare the structural differences of nanostructured surfaces of microwires fabricated both below and above ambient temperatures. Based on the current findings from these studies, the following arguments have been summarised: 1. Metastable states may exist in silica nanoparticles rearrangements; 2. The particles of these metastable states may be smaller than the average nanoparticle size ($<< \phi \sim 20–30 \, \text{nm}$). 3. Below ambient temperature, capillary lines may split into dendritic microchannel pots, use primarily to bring together nanoparticles to form new confined domains - metastable configuration; 4. Also below ambient temperature, surface tension increases and fluid motion decreases. This is because the force of adhesion between
the drying droplet and Au-coated surface becomes stronger. The capillary process involves the active transport of water to the edge of the droplet. However, at ambient temperature, water moves at a very slow rate. The water gradually permeates the spongelike boundary network at the Au-coated surface (see micrographs of Au-coated and uncoated surfaces in chapter 4.2, figure 5). By so doing, microchannel pots are created, and through intermolecular forces, nanoparticles within the restricted domains come together to form the metastable configuration state. Conversely, above ambient temperature, surface tension decreases, so that the adhesive interaction of the liquid at the Au-coated interface becomes weaker, causing fluid to move rapidly from inside of the drop to be replaced at the periphery. In chapter 4.5, the aim of the section was to recognise the phase patterns of the different nanostructured surfaces of microwires at different temperatures.

Lastly, the sixth section (Chapter 4.6), presents preliminary studies of the inclusion of protein (protease enzyme), sugar- D-(+)-glucose (reducing sugar), D-(+)-trehalose dihydrate (TRE) (non-reducing sugar) into colloidal suspension of silica nanoparticles. The aim of this section was to explore the stable environment for protein storage. From the study, the slow movement allowed nanoparticles to intermingle with other molecules in the vicinity, and through van der Waals interaction, phase separation into hcp/ bcc structures and other close-packing configurations (metastable) along with boundary network emerged. SNP_PRO addition produced hcp in the entire network after drying. The hcp/bcc mean size of the nanocluster size was measured, \( c_l \approx (127) \text{ nm} \) and pore size diameter \( \approx (\rho \approx 5-6) \text{ nm} \). The SNP_TRE and SNP_TRE_PRO produced metastable states, and mean diameter of their nanocluster sizes were measured at \( c_l \approx 127 \text{ nm} \) and 133 nm respectively.
Compiled Research Reports

The following experimental works listed below were carried out in the school of chemistry:

1. Evaluation of glass surface cleaning methods to obtain reproducible contact angle measurements for the control of self-assembly processes using drops.

2. Controlled and reproducible fabrication of self-assembled silica microwire from spherical caplet drops on glass surface sputtered with gold particles.

3. Analysis of the spherical cap approximation of a liquid droplet on Au-coated and non-coated surfaces.

4. Fabrication of silica microwire on an Au-coated surface below ambient temperature.

5. Understanding the structural networks in silica microwires with a 3D-Phase contrast variation tool.

6. Preliminary studies of protein integration into mesostructured glass, fabricated by controlled, self-assembly of silica microwires.

Acronyms

(SEM) Scanning electron microscopy
(OM) Optical microscopy
(Silica NPs or SNP) Silica nanoparticles
(hcp) hexagonal close packing
(bcc) body-centered cubic
(fcc) face-centered cubic
(3D-PCV) 3D-Phase contrast variation
Nomenclature

$S$  Surface area of the spherical cap, mm$^2$

$R_v$  Rate of volume change, mm$^2$s$^{-1}$

$\gamma_{sv}$  Solid-vapour interfacial energy, J.m$^{-2}$

wt.%  Weight expressed in percentage

$\gamma_{sl}$  Solid-liquid interfacial energy, J.m$^{-2}$

$\gamma_{lv}$  Liquid-vapour interfacial energy, J.m$^{-2}$

$\theta$  Contact angle, °

$r_{philc}$  Drop-base radius of a hydrophilic surface, m

$r_{phobic}$  Drop-base radius of a hydrophobic surface, m

$V_0$  Volume of liquid droplet dispensed onto the surface, m$^3$

$h_0$  Initial height of liquid droplet dispensed on the substrate’s surface.

$T$  Temperature (°C)

t  time (seconds)
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1. Introduction

This thesis deals with the development of strategies to control the self-assembly of silica microwires produced from colloidal dispersion of silica nanoparticles on a glass substrate during evaporation. Generally, microwires have compact, robust surfaces and low-loss structures. [1, 2]. The unique properties they exhibit on the nanoscale have attracted much attention to consider them as smart materials for future technology [3]. The nanostructured surface has been identified as a potential surface that can be used to replace conventional materials used in sensor [4, 5], solar cells [6, 7], and battery applications [8, 9]. By composition, they may have single elemental structures – Si, Ge, Cu, Au, and Ag – or multicomponent structures – GaAs, GaN, InP, CdS, SiC, Si₃N₄, SiO₂, Al₂O₃, ZnO, SnO₂, and In₂O₃ [10]. The tensile strength of some of these wires, combined with their thermal and conductive or optical properties, makes them suitable for use in a number of applications [11, 12]. For example, in photonic applications, microwires with compact, low-loss structures and high evanescent field are useful in a broad range of applications spanning sensing, lab-in-a-fiber, and nanophotonics through to optical interconnects for faster computing and signal processing with reduced thermal footprint computing [1].

Recently, there has been the growing interest to find a simple, inexpensive method to fabricate microwires [13-17]. As a result, a wide range of techniques is used; examples include laser ablation solid techniques [18], electron beam lithography [19], template-based method [20], bottom-up methods (such as chemical and physical vapor deposition [21] and solgel technique [22]), and top-down techniques [23]. For silica (SiO₂) materials, the two most successful approaches are “top-down” and “bottom-up methods”. The top-down method deals with the various methods of lithography to pattern materials to the desired micro or
nanosize dimensions. Examples are the top-down tapering of optical fibers [2] using self-modulated taper drawing, flame-brushing technique, and modified flame brushing technique (flame source: microheater or a sapphire capillary tube heated by CO\textsubscript{2} laser beam, and direct drawing from the bulk. On the other hand, the bottom-up method involves arranging atoms and molecules to produce a defined nanostructure material greater than 2 nm [24, 25]. This method borrows its techniques from polymer science, colloid chemistry and molecular synthesis. Some of the challenges that arise from these two methods (top-down and bottom-up) include:

- The maximum resolution of the patterns formed by the top-down method is significantly coarser than the dimensions of the patterns formed by the bottom-up method.
- The nanosize material fabricated from the bottom-up method using polymer science, colloid chemistry and molecular synthesis can sometimes be identical and usually do not have long-range order when integrated into extended materials.
- The top-down method is usually expensive and very tedious. A practical example is a typical microfiber drawn from glass during preform that requires high temperature (800 –1000) °C [26]. Integrating specialty chemicals or biological probes into the core fiber structures is almost impossible. The self-assembly of materials from nanoparticles provides that bridging strategy that allows the fabrication of structural nanomaterial with the bottom up method- to organize into regular patterns by intermolecular forces, while using the top-down platforms - to guide the self-assembly processes.

The stages involved in microwire formation and characterisation are shown Figure 1-1.
Figure 1-1. The stages involved in microwire formation and characterisation techniques. 1. Images of the evaporative process of silica microwire at room temperature from silica nanoparticle drop dispensed on a hydrophilic glass substrate [Naqshbandi, M.; Canning, J.; Gibson, B. C.; Nash, M. M.; Crossley, M. J., Room temperature self-assembly of mixed nanoparticles into photonic structures. Nature Communications 2012, 3, 1188]. 1. Dispersion and deposition of nanoparticles is along the perimeter of the drop through capillary flow to produce a dense ring (“coffee-ring stain”), also responsible for the initial pinning process at the edge of the drop. 2. As the evaporation process continues, water molecules lost at the perimeter of the drop must be drawn from the centre to the perimeter of the drop to keep the contact line fixed, indicated in the optical micrographs of (a) and (b). 3. Through convective flow, microwires rise up from the surface. 4. As the volume recedes completely, microwires overcome surface tension. Beneath the four stages, 1-4 (a) and (b) show line tensions that lead to bifurcation in the initial stages. On the right: 14 cm long microwire fabricated from 10 x 1 mL drop on a glass mirror.

In many ways, the self-assembly process is advantageous. First, the method allows aggregation of structures too small to manipulate into ordered patterns to give function to the materials. Second, the method enables the fabrication of hierarchical structures of composite materials on different nanoscale dimensions, each having unique properties of their own. Further, the self-assembly process can generate 3D structures, which most times can be inexpensive. Lastly, the self-assembly of mixed nanoparticles with biological moieties
hold promising applications in the discovery of more exotic structures for technologies of the future. The possibilities to self-assembled microwires from nanoparticles at room temperature have expanded enormously, potentially enabling many sensor, lab-in-a-fiber, and nanophotonics platforms [1].

SEM micrographs of microwire images show a highly robust surface, and a few reports on the surface arrangement of these wires indicate hcp/bcc for silica nanoparticles, with average distribution: ~20–30 nm [1]. Some micrographs of silica microwire structures are presented in Figures 1-2 and 1-3, and in expanded form beneath the each Figure.

Figure 1-2. Morphology of silica microwire structures and challenges: a. Optical micrograph of variable wire dimensions during the last stage of drying; b. Optical micrograph of uniform wires produced only in the middle section of the wires instead over the entire structure (exception is the coffee-ring region); c. SEM micrograph: variable packing structures; d. SEM micrograph: aggregation and crowded packing structures.
Expanded images from Figure 1-2 c and d with scale bars:
Figure 1-3. Assembled microwire. a. Optical micrograph. b. SEM micrograph

Expanded image of Figure 1-3b with a scale bar:
Generally, the robust surface areas that nanoparticles (NPs) exhibit, size regimes within their domains, and surface curvatures influence both the activity of protein and protein structure [27, 28].

This thesis also explores the robust surface area of silica microwire for use in preserving protein structure. For example, some biological molecules such as lyophilized monoclonal antibodies are often unable to stay outside their non-native environment over a period because of denaturation to the non-native structure of a lyophilized cake [29]. Recent studies use sugar molecule in the presence of water to stabilize quaternary protein structure in glass-matrix form, to prevent degradation over the recommended expired shelf life [29-33]. The self-assembly of silica microwires using bottom-up method, provides an insoluble host in water, and the problems with charging of the surface may be avoided using this method. In an alternative approach, spray-drying methods reported in this paper [29] involve a tedious process, where optimal storage for proteins at best, to be stable at 40 °C within glass-matrix state. The glass-matrix structure of the proposed silica microwires provides an insulating environment, and it is possible to extend the thermal performance well beyond previously reported. Other possible methods involve solgel method. The disadvantage with this method is that it uses some organic precursors in the formulation, which may adversely affect the stability of protein. Lastly, one application of interest of this composite material: glass matrix of protein and silica microwire is the transportation of vaccines to and within countries with high climate temperatures that exceed temperature $T > 45$ °C.

The follow up studies on the evaporative self-assembly of silica nanoparticles using the bottom-up method aim to clarify the optimal conditions in the fabrication process,
understand the nanostructured arrangements of these microwires, and explore possible strategies for sugar and protein inclusion in silica nanoparticles.

The study objectives include the following:

1. To adopt a simple and efficient cleaning method, and to use the contact angle measurements to demonstrate the importance of complete control of surface properties and drop deposition.

2. Understand the structural arrangements of wires at different temperatures, both at cold temperature range and at ambient conditions. In addition, to use the 3D-Phase contrast variation tool in conjunction with the SEM micrographs of the wires, to understand their different nanostructured surfaces.

3. Study the nanophase structure of sugar and protein inclusion into silica nanoparticles at room temperature. Additionally, explore the nanostructured surface to preserve and avoid protein denaturation.

The review on contact angle measurements of different microscope glass types in the literature [34-39] shows variety of methods for cleaning microscope glass slides. The present thesis only looks at the physical aspect of cleaning that excludes the use of chemical treatments. The first experiment, chapter 4.1 was to evaluate glass slide that gives a reproducible surface by the contact angle method. The argument is that if the contact angle provides information of the interaction of liquid droplet with glass surface (Young’s equation). Then a consistent contact angle with least error value may produce microwires with fewer variations in size dimensions and structure.
Chapter 4.2 deals with the importance of surface control and drop deposition. By manipulating the surface properties, such as coating the surface, limit the drop's volume \( V = 1 \, \mu\text{L} \) (to reduce size deformation caused by gravity upon evaporation), optimize silica nanoparticles concentration upon evaporation; microwires with less variable size dimensions may be achieved. Here, the use of glass surface sputtered with Au particles plays an important step in the fabrication process. In chapter 4.3, the table (Table 1) shows the rate of water on Au coated and the uncoated surfaces of the same glass material, where Au-coated surface retained a lesser amount of water on the surface than non-coated surface. The implication of low water retention surfaces at ambient temperature is faster evaporative process, less time for nanoparticles to form aggregate clumps, uniform dispersion and less time for water molecules to interact with the surface. Besides that, configuration of well-ordered hcp/bcc arrangements will lead to uniform and production of thinner wires that are more controlled on the glass surface. This disparity confirms the superior flow behaviour of Au-coated surface over non-coated surface during the evaporative process at ambient temperature.

Chapter 4.4 deals with the fabrication of silica microwires below ambient temperature (0, 5, 10, and 15) °C. As outlined in the study objectives above, the aim was to compare the nanostructured surface difference between microwires produced from cold temperature range with the ones obtained at ambient temperature. According to Deegan R.D et al. (Nature, 1997), for a drying droplet at ambient temperature: when liquid droplet dry on the surface, the contact line of the drying drop is pinned to the edge of the drop, so that as the liquid evaporates from the edge, the liquid from the center of the drop moves to replenish the lost liquid. These mutually inclusive events during evaporation form the basis for the
coffee-ring deposition and capillary lines observed for a drying droplet. Below ambient temperature, microwires produced on Au-coated surface shows prominent boundary networks. The 3D-phase contrast variation tool (introduced in chapter 4.5) functions as an auxiliary characterization tool for SEM micrographs of microwires produced for this type of nanostructured surface.

Chapter 4.6, presents preliminary studies for the inclusion of protein (protease enzyme) and sugar- D- (+)-glucose (reducing sugar), D- (+)-trehalose dihydrate (TRE) (non-reducing sugar) into colloidal suspension of silica nanoparticles. The aim of this section was to explore the stable environment for protein storage.

The block diagram in Figure 1-4 outlines the thesis structure. Chapter 1 (Introduction) provides the overall objective for pursuing the study on silica microwires along with the silica hybrids produced (doped microwires). Chapter 2 provides the background related to the complete control of surface properties and their application in producing uniform microwires. It also provides the direct link to the experimental work carried out in Chapter 4. Chapter 3 (Methodology and Characterization Techniques) provides a brief summary of the methods and surface characterization techniques, with a greater detailed report included in the compiled chapter that follows. Chapter 4 (Experimental Section) provides a compiled research report of all the experiments carried out in the course of the program, presented in six sections. Each of these sections is a stand-alone compilation with incorporated references. Chapter 5 provides the concluding remarks and future directions. Appendices and the bibliography follow this.
Figure 1-4. Block diagram of thesis structure.
2. **Background: Contact angle, wetting, adhesion**

The contact angle of a liquid on the surface is the boundary at the interface where the liquid-vapor meets a solid support, and it depends on the extent of interaction between the solid surface and liquid, defined by the Young equation (Figure 2-1). When the same drop volume of a liquid is placed on different surfaces, the interaction will contain unbalanced energies. For equilibrium on the surface to be established, a thermodynamic driving force is always present to minimize the surface energy. The contact angle provides information of the surface parameters that needs measurement and is a useful inverse measure of spreading and wettability [40].

Figure 2-1. Schematic illustration of the Young-Dupre model of a three-phase contact line of a liquid droplet. $\gamma_{sv}$, $\gamma_{sl}$ and $\gamma_{lv}$ are in thermodynamic equilibrium. The “three-phase contact line” is the point where the solid surface, liquid and vapour co-exist.

2.1 **Theory of contact angle**

A drop of liquid on a flat horizontal surface may remain as a definite drop or spread [41]. The plausible surface types include:

1. A smooth homogeneous surface;
2. A smooth heterogeneous surface;
3. A rough, homogeneous surface; and
4. A rough, heterogeneous surface.
On a plane geometrical area, the contact angle defines the intersection of the liquid-solid and the liquid-vapour interfaces, drawn at a tangent line from the contact point of the end of the drop.

The classical Young equation described in equation 1 makes the following assumptions:

1. The solid surface is smooth and homogeneous;
2. The liquid droplet is static and the drop geometry is finite;
3. There is no gravitational effect of the liquid droplet on the solid surface;
4. There is no spreading; and
5. Equilibrium contact angle exists.

Figure 2-1 shows the expression of a hydrophilic surface for a three-phase contact line for a droplet [41]:

\[ \gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \]  \hspace{1cm} (1)

Similarly, for a hydrophobic surface, Figure 2-1, the equation is:

\[ \gamma_{sl} = \gamma_{sv} + \gamma_{lv} \cos(180 - \theta) \]  \hspace{1cm} (2)

\( \gamma_{sv} \), Solid-vapour interfacial energy

\( \gamma_{sl} \) Solid-liquid interfacial energy,

\( \gamma_{lv} \) Liquid-vapour interfacial energy and \( \theta \) is the contact angle between the liquid-vapour interface and the solid surface.
For spreading to occur (hydrophilic surface), the following inequality in equation 3 must be satisfied:

\[ \gamma_{sv} - \gamma_{sl} > \gamma_{lv} \cos \theta \]  

(3)

The spreading that a liquid droplet makes on a smooth solid surface using the work of adhesion on the surface, \( W \), is the work that is required to separate two adjacent phases within the boundary of intersection of the contact angle. The energy required for spreading to take place at the surface is the work done at the surface per unit area (Jm\(^{-2}\) or mN.m\(^{-1}\)). This is without the gravitational force effect.

The work of adhesion of the liquid droplet by the solid surface per unit area in Figure 2-1 is the interplay of the interfacial tensions of the three-phase contact line, given by:

\[ W = \gamma_{sv} + \gamma_{lv} - \gamma_{sl} \]  

(4)

Substitution of equation 1 into equation 3 gives:

\[ W = \gamma_{sl} + \gamma_{lv} \cos \theta + \gamma_{lv} - \gamma_{sl} = \gamma_{lv} \cos \theta + \gamma_{lv} \]

\[ W = \gamma_{lv} (1 + \cos \theta) \]  

(Hydrophilic surface)  

(5)

In addition, substitution of equation 2 into equation 4 gives:

\[ W = \gamma_{sv} + \gamma_{lv} - \gamma_{sv} \cos(180 - \theta) = \gamma_{lv} + \gamma_{lv} \cos(180 - \theta) \]

\[ W = \gamma_{lv} [1 - \cos(180 - \theta)] \]  

(Hydrophobic surface)  

(6)
The implication from equation 5 is that when the $\theta$ of liquid on a smooth solid surface tends to 0 on a hydrophilic surface, $W$ is less than $2\gamma_{lv}$, or the work of adhesion is less than twice the interfacial tension of the liquid-vapour phase. However, as $\theta$ increases on a hydrophobic surface, the work of adhesion tends to $\gamma_{lv}$ (equation 6) (Figure 2-2). This means that the work of adhesion requires twice as much effort to overcome surface tension in the liquid-vapour phase on a hydrophilic surface than on a hydrophobic surface.

Figure 2-2. The shapes of liquid droplets on different surfaces. The work of adhesion decreases as $\theta$ increases. The model also describes the wettability condition on the surface. The wettability of a liquid on a substrate is the ability of an aqueous system to align the hydrophilic group in the aqueous system.

D. M. Spori [42] derived two useful equations to predict the drop size of a liquid droplet formed by both hydrophilic and hydrophobic surfaces (Figure 2.3). Equations (7) and (8) predict the maximum spatial resolution for contact angle measurements.

Figure 2-3. Schematic illustration of a drop’s footprint from the dispensed volume of a liquid droplet on substrate surfaces – modification of Young’s model [Spori, D. M., Structural influences on self-cleaning surfaces. 2010, Thesis ETH, Zurich].
\[ r_{\text{philic}} = \left( \frac{6V_0 \sin^3 \theta}{\pi(1 - \cos \theta)(3 \sin^2 \theta + (1 - \cos \theta)^2)} \right)^{1/3} \] (7)

\[ r_{\text{phobic}} = \left( \frac{-3V_0 \sin^3 \beta}{\pi(1 - \cos \theta)^2(2 + \cos \beta - 4)} \right)^{1/3} \text{ where } \beta = 180 - \theta \] (8)

\( r_{\text{philic}}, r_{\text{phobic}} \) are the drop-base radii of hydrophilic and hydrophobic surfaces respectively.

\( V_0 \) - Initial volume of liquid droplet dispensed on the substrate’s surface.

\( h_0 \) – Initial height of liquid droplet dispensed on the substrate’s surface.

2.1.1 Methods of measuring contact angle

There are various methods for measuring the contact angle of a given liquid droplet, but the two common techniques are - the static and dynamic contact angle techniques- and the accuracy differs from a given method. The static contact angle measurement is the most common. It consists of the sessile drop and captive bubble in liquid method, while the dynamic contact angle technique consists of the Wilhelmy plate and the inclined plane method (Figure 2-4). The sessile drop method is the focus of this thesis. Other methods are available in a number of contact angle textbooks, thesis, and literature review [61, 62].

Figure 2-4. a. Customised instrument used to measure the contact angle of drops using the traditional side illumination with a microscope camera; and b. Schematic illustration of the mean contact angle of drop on the glass surface being measured in Equation 9.
The mean contact angle, $\theta$ of both sides of the drop:

$$\theta_{\text{mean}} = \frac{\theta_1 + \theta_2}{2}$$  \hspace{1cm} (9)

### 2.1.2 Factors that affect the contact angle measurements

As mentioned earlier, Young’s formula described in equation 1 makes many assumptions, such as; the solid surface is smooth and homogeneous; the liquid droplet is static and assumes a finite geometry; and there is no gravitational effect. Also from Young’s model - equation 1, only two parameters can be determined - $\theta$ and $\gamma_{lv}$. In practise, even the smoothest surfaces have regimes of smoothness and roughness when examined by a high-powered microscope. An example is the routinely used microscope glass slides examined in this thesis work. Here, four types of microscope glass slides observed with an optical microscope indicate some slides have greater surface roughness than do others (Figure 2-5).

![Figure 2-5. Optical micrographs of the precleaned states of different substrates composed of soda lime. I: Sail Brand (Catalogue number: 7101); II: Pathology grade (Catalogue number: 7101A); III – SureFrost; and IV- SuperFrost Ultra Plus.](image)
The following reasons outlined in the literature support the use of equation 9 to calculate the contact angle of a liquid droplet on the surface of a glass. Glass surfaces have 1. Edge or surface roughness; 2. Surface pore sizes, enabling liquid to penetrate the pores and thus reduce droplet shape on the surface. For instance, when \( T > \) ambient temperature, \( \theta \) may recede at a faster rate; 3. Relative humidity may affect the shape of the droplet drastically; 4. Surface heterogeneity; and the most common, 5. “The Eye error bias measurement” at the contact point of liquid droplet on the surface [42-48].

2.1.3 Advancing and receding contact angle
Several techniques are available for measuring the dynamic contact angle of a liquid droplet. These include the inclined plane method; add and remove volume method; time-dependent dynamic studies; and the Wilhelmy plate method (Figure 2-6).

Figure 2-6. a. Digital photographs of the inclined plane apparatus in the lab. The units consist of a rotational arm for adjusting the angle of inclination from \( 0^\circ \) to \( 90^\circ \). The sample holder fixed to the pointed hole is adjustable so that the reference angle at \( 0^\circ \) coincides with the starting point of the rotational arm. The spirit level ensures a balance plane. The rotating arm can be adjusted to the desired inclination angle \( \alpha \). Adjusting the inclination \( \alpha \) makes it
possible to measure the dynamic contact angle of both the advancing and the receding angles. b. Schematic illustration of the advancing and receding contact angles by the inclined plane method.

The difference between the receding and advancing contact angles is the contact angle hysteresis. The contact angle hysteresis characterises the surface topology; especially to verify variations in contamination and chemical heterogeneity on different surfaces.

For a liquid droplet to remain on an inclined surface at a given time, the work of adhesion at the interfacial surface energies must be greater than the gravitational force that acts to oppose and make it roll down the plane on a hydrophobic surface, and spread on a hydrophilic surface.

The dynamic contact angle is not the only surface technique that measures hysteresis. Hysteresis can also occur on a flat plane that is rough. In chapter 4.2 (Figure 1), the contact angle measurements obtained by static technique for the same volume of drops produced variations in contact angle measurements on both sides of liquid droplets, with variations more pronounced on some surfaces relative to other substrate types.

2.1.4 Contact angle hysteresis: A new perspective

Fundamentally, the contact angle hysteresis \( \Delta \theta \) measures the contact angles of liquid droplet from both sides on a plane surface (Figure 2.6.b) and represents a useful parameter for comparing the contact angle of the same liquid on different surfaces. \( \Delta \theta \) is the arithmetic difference between \( \theta_a \) and \( \theta_r \), expressed as:

\[
\Delta \theta = \theta_a - \theta_r \tag{10}
\]

The contact angle hysteresis \( \Delta \theta \) occur because of the following; summarised in this literature [49] as caused by surface heterogeneity; roughness; overturning of molecular
segments at the surface (i.e., short-range orientation of molecular species at the surface); adsorption/ desorption; and surface deformation. Detailed explanations are in the subsequent chapters.

The two types of hysteresis discussed in this thesis are, contact angle hysteresis based on the surface roughness (equation 10, above), and dimensionless hysteresis factor dominated by chemical interactions and heterogeneities on the surface (equation 13, below). Extrand C. W. et al. [49, 50] derived the equation for measuring the surface heterogeneities and chemical interactions by the dimensionless hysteresis factor, H. The derivation is in the next paragraph.

The interfacial surface tension, \( \gamma_{lv} \) at the inclination plane in Figure 2-6.b for a hydrophilic surface and for hydrophobic surface (schematic illustration not shown) respectively as:

\[
\gamma_{lv} \cos \theta; \gamma_{lv} \cos(180 - \theta) \]

So that the interfacial surface tension, \( \gamma_{lv} \) at the inclination plane in equation 10 is:

\[
-(\gamma_{lv} \Delta \cos \theta) = \gamma_{lv} \cos \theta_r - \gamma_{lv} \cos \theta_a
\]

\[
\gamma_{lv} \Delta(-) \cos \theta = \gamma_{lv} \cos(\theta_r - \cos \theta_a) \]

\[
\Delta = H = \frac{\frac{\theta_a - \theta_r}{\theta_{mean}}} , \text{where} \quad \theta_{mean} = \frac{\theta_a + \theta_r}{2} \quad \text{(from equation 9)} \quad \ldots \ldots \quad (13)
\]

The dimensionless hysteresis factor \( H \) is the same as the delta symbol, \( \Delta \) in equation 13. Equation 13 gives the expression of a liquid droplet on an inclined plane for both hydrophilic and hydrophobic surfaces. Also in equation 13, the mean contact angle, \( \theta_{mean} \) rather than the advance contact angle, \( \theta_a \) reported in these references [49, 50] represent the correct
derivation. This is because the parameters affecting the change in contact angle of a liquid droplet along the inclination plane (expressed in equation 13) is \( \theta_a \) and \( \theta_r \). \( H \) is dependent more on chemical interactions and homogeneities on the surface and less on the surface roughness.

Another way of calculating the dimensionless factor is to derive the equation of the roughness that modifies wetting characteristics. According to R.N. Wenzel [43], the roughness that modifies wetting characteristics is the ratio of the actual surface to that of a smooth surface having the same geometric shape and dimensions. Since the surface area is directly proportional to the base radius that the liquid droplet contact makes with the surface, the \( H \) factor for the surface roughness that modifies wetting on both hydrophilic and hydrophobic models in Figure 2-3 is as follows;

\[
r_{\text{philic}} = \left( \frac{6V_0 \sin^3 \theta}{\pi(1 - \cos \theta)(3 \sin^2 \theta + (1 - \cos \theta)^2)} \right)^{1/3}
\]

where \( \theta = 180 - \beta \)

\[
r_{\text{phobic}} = \left( \frac{-3V_0 \sin^3 \beta}{\pi(1 - \cos \theta)^2(2 + \cos \beta) - 4} \right)^{1/3}
\]

According to this reference [44], the drop base radii of the geometric surface for hydrophilic and hydrophobic surfaces are as calculated in equations 7 and 8 respectively:

So that the dimensionless factor \( H \) for the surface roughness that modifies wetting becomes:

\[
H = \frac{r_{\text{actual}}}{r_{\text{philic}}} \quad (\text{Hydrophilic surface}), \quad H = \frac{r_{\text{actual}}}{r_{\text{phobic}}} \quad (\text{Hydrophobic surface})
\]
2.1.5 Applications of contact angle

The contact angle measurement provides one of the most versatile methods for profiling first-hand, the physics and surface chemistries of substrate surfaces [51]. It is routinely use in the lab to study surface phenomena at the microscopic and macroscopic levels. In addition, the contact angles allow droplets studies of nanoscopic dimensions [52]. Because of the diverse nature of solid surfaces and the type of liquid and drop geometries that liquid droplets assume on different surfaces, a number of techniques are used. Some of these reviews are earlier referenced [34, 42-45].

The contact angle also plays an important role in diverse industrial and commercial processes. For instance, in oil recovery processes, the contact angle evaluates the reservoir wettability and its effect in oil recovery [53]. The contact angle of compositional layer of the crude oil/brine/rock interactions in the reservoir is useful for evaluating water stability on the solid (mineral) surface. The contact angle also helps to understand the pH effect correlation with the surface charge of the oil-water interface with the solid surface, which is strongly dependent on the brine pH [54], where a higher pH facilitates oil removal and a lower pH causes crude oil to adhere to the solid surface [55-57]. Other areas where the contact angle is important is the simulation of drop profiles on fibre systems by the drop length-height method [58]. Contact angle also plays a significant role in understanding the surface phenomena of “non-stick” surface to water and stain [59-61] and in evaluating the surface property for protein adsorption [62, 63]. This thesis work presents the contact angle as the key step for controlling the self-assembly processes because when drops give consistent contact angle on the surface (as in the case with a plain surface), it is an indication that the surface is reproducible. Particularly, a smooth, reproducible surface is likely to give rise to quality self-assembled materials.
2.2 Wetting of surfaces

Wetting of surfaces is generally used to describe the shape that liquid droplets assume on different solid surfaces, either to “interact or passivate in contact” with one fluid rather than another. Exceptions are metal surfaces that tend to behave differently for uncoated and coated surface with/or without oxide layers [63, 64].

In quantitative terms, wetting by a liquid droplet is the orientation that a polar or non-polar groups make in contact with the surface in order to minimize surface energies. For liquid droplets with polar groups on hydrophilic surfaces, liquid aligns toward the polar phase in order to move away from the surface in air at the aqueous interfaces. The converse is true for hydrophobic surfaces.

Depending on the interaction forces, two types of surface energy exist. High-energy surfaces, classified under the polar interactions: ion-ion, ion-dipole and dipole-induced dipole and low-energy surfaces, classified under the non-polar (dispersive) interactions. Examples of high-energy surfaces in air include: water, ultra-clean glass surface, hydrogels and metal oxides and their high energy functional pair groups, for example, include: -OH, -COO⁻, -OSO₃⁻, -NH₄⁺, -NH₂, -OSO₃H, -COOH. The low-energy surfaces are not limited to hydrocarbon (-CₙH₂n+₁), fluorocarbons (CₙF₂n+₁), and silicone surfactants [64-69]. The schematic illustration in Figure 2-2 depicts the model shapes and contact angles of a water droplet at different surface conditions observed in practice.

2.2.1 The paradox of spreading on a solid surface

Wetting by a liquid droplet on a solid surface can transit at three different phases according to the Young equation (equation 1), as shown in Figure 2-7.
Figure 2-7. The three wetting states of a liquid droplet on solid surfaces (Young’s equation). Red arrows indicate that the wetting states are more than the three models described by Young (See Figure 2-2 for illustration of the possible states in practice).

However, in practical situations, liquid droplets dispensed on a solid surface do spread, especially for drop size that is outside the spherical cap approximation volume [70]. This is because as soon as the fluid is in contact with the surface, there is alteration of the surface caused by the imbalance of surface tension. Some of the discussions of wetting phenomena on solid surfaces are in these references [69-73].

The De Gennes et al. [69] review suggests factors such as wetting transitions, van der Waals forces, fluid dynamics and pinning of the contact line to be the key factors involved in spreading. The review concludes that dry spreading on a solid surface seems to follow a consistent pattern but moist spreading requires specification of control parameters.

The argument by Marmur [71] is that wetting is not by the static thermodynamic equilibrium model represented by Young’s equation, but by dynamic, non-equilibrium processes. For a discontinuous transition has to occur between the solid surface and the fluid-fluid interface.
Three types of spreading exist: (1) forced spreading; (2) spontaneous spreading to an equilibrium contact; and (3) spontaneous spreading where no equilibrium contact angle exists.

On the other hand, the Bussmann et al. [72] - circular droplet model seems to look at spreading of different fluids on impact (and not when gently dispensed) on a dry solid surface. Nevertheless, the model supports the notion that the contact angle is significant on impact at the surface boundary and bears a direct correlation with the contact line during spreading. The model agrees quite well with predictions of numerous applications of Rayleigh-Taylor instability theory [74, 75].

The Greenspan circular droplet model [73] looks at a rather holistic study to address key fundamental areas in: spreading or retraction of a circular droplet; motion of a droplet on a coated surface to a region of greater adhesion; distortion of droplet shape owing to surface contamination; and application to biological systems. Quantitatively, the model uses lubrication equation and dynamic contact angle to describe the forces acting on the fluid at the contact line.

To summarize the paradoxes of all these arguments on the spreading phenomena, A.M. Cazalat [76] concludes that there has to be a unifying theoretical framework that validates experimental methods; these include the macroscopic and microscopic equations of wetting at the surface.

2.2.2 The spreading law on a glass surface

Following the discussion on the motion of liquid droplet on a solid surface, spreading consists of both the macroscopic and microscopic phenomena at the surface [76]. Further, the macroscopic surface properties are: (1) volume of drop $V$; (2) radius of wetted spot, $r$; (3)
contact angle $\theta$ between the liquid and solid at the three-phase contact line; and (4) gravity effects. Generally, spreading is the relative hydrophilicity that a liquid assumes on the surface at the time of contact with the substrate. This consequently determines the shape that liquid droplets assume on the surface, as either partial (incomplete) wetting or complete wetting. Model examples are in Figure 2-7. Despite the different theories and mathematical expressions for spreading of liquid droplets, results from experimental studies and theoretical calculations are still far from being the same. Here, the thesis work looks at some of the commonly overlooked assumptions. Below is the schematic illustration and the discussion follows in chapters 4 and 5.

Figure 2-8 shows the schematic illustration of the spherical cap approximation of a thin liquid droplet of constant volume, $V = 1\mu$L dispensed on a soda lime glass surface (Supra Ultra Plus microscope glass slide).
2.3 Theory of Metal-Glass interfaces: Wetting and Adhesion

As mentioned earlier, wetting is the ability of an aqueous system to align the hydrophilic group in the aqueous system. Surfaces that the interactions are predominantly water or polar groups are hydrophilic. Hydrophilicity may also be due to surface structure and roughness [77]. Perhaps what is interesting to note is that water can also interact with non-polar (apolar) surfaces to render the surfaces hydrophilic. Theoretically, it is when Lennard Jones interactions value (L-J potential [78]) exists between water molecules and surface atoms [79, 80].

The Lennard Jones interaction is a mathematical model that uses wave mechanics to explain the phenomenon of metallic cohesion. It states that “metal cohesion is due partly to electrostatic interaction of space-charge contributions, partly to the exchange phenomenon between a pair of neutral atoms or molecules (depends on the spin of electrons), and partly
to van der Waals interactions. Particularly, when atoms spread at the surface, there is an overlap of electrons, so that the electrons which belong to one nucleus are brought under the influence of several others within the vicinity, making the metal layers to behave as a sea of electric fluid" [78].

Because of the so-called electric fluid on metal layers, surfaces are seldom inert in the true sense of it, except when in vacuum. However, outside vacuum, oxygen layer surrounds the surface, primarily held by covalent-ionic interactions or loosely held by electrostatic charges [81]. If the surface oxygen atoms are unable to bond with the metal atoms (coated metal-glass surface), what happens is that the surface oxygen will increase the screening of silicon atoms (from glass composition) to form oxides and lower the internal energy of the glass. This action leads to a strong chemical bond outcome. On the other hand, if the surface oxygen atoms form bond with the metal surface through electrostatic interactions without the exchange of electrons between the oxygen and surface metal atoms, a weak bond of van der Waals type exists. For example, in vacuum at $T = 1000 \, ^\circ$C, the interfacial energies [from solid-liquid (sl) to solid-vapor (sv)] of glass-to-metal bonding are according to oxide strength and an increase in contact angle of water on the surface follows: Pt –glass $>>$ Au-glass, Fe-glass [101].
3. Materials, methods and characterization techniques

3.1 Materials and method of analysis description

Ludox®-TM-40 colloidal silica purchased from Aldrich contains 40 wt. %. concentration suspension of silica nanoparticles (SNP) in H2O. Four microscope glass types were obtained from the following sources: Sail Brands - catalogue nos. 7101, 7101A and speciality microscope glass slides – SuperFrost Ultra Plus and SureFrost. Deionized H2O was obtained from the school chemistry laboratory. Three types of pipettes with volumes $V = 0.1-2$, $0.5-10$ and $500-100$ µL were used. Ultrasonic cleaner from Unisonics PTY Ltd Australia was used for cleaning all glass types. High performance particle sizer was used for the dynamic light scattering (DLS) experiment to measure the particle size of silica NPs at 3.2 wt. % concentration suspension in H2O. A standard disposable cuvette with volume dimensions (45 mm × 12.5 mm × 12.5 mm), chamber volume (2.5-4.5 mL), path length (10 mm) and window size (10 mm × 35 mm) covered with a fitting cap was used for the DLS experiment. A simple contact digital LCD temperature sensor of stainless tube head with detectable temperature range ($-50^\circ C \sim 110^\circ C$) and ± 0.5 °C accuracy was used in the experiment. Peltier of (60 mm × 60 mm) and (40 mm × 40 mm) dimensions with operational voltages, 12 volts and 15 volts respectively fitted with heatsinks were used to fabricate some of the microwires. Topward electric instrument, capable of taking voltage readings (0 to 30 volts) and current readings (0 to 3 amps) was used for temperature regulation of microwire fabrication except where microwires were fabricated at ambient temperature. The Optical microscope was fitted with additional components, namely: multiple nanostage directions (X, Y, Z) from Luminos industries Ltd; Nikon light source of super high pressure mercury lamp power supply; and a digital camera with ProgressRes® Capture Pro 2.6 software was used to take images of wires at various stages of the experimental work. The three scanning electron microscope (SEM)
instruments (Zeiss HD Sigma, Zeiss Ultra and Zeiss Evo) available at the Australian Microscopy and Microanalysis Research Facility of the school were used to take topographical images of the microwires. In addition, the Zeiss Ultra SEM coupled to the energy dispersive spectroscopy (EDS) detector was used to analyse the chemical composition of the microwire. The sputtering coating machine (Emitech K550X) available at the Microscopy and Microanalysis Research Facility of the school was primarily used to provide conductive metal coatings for silica microwire in preparation for SEM microscopy and also for coating some of the microscope glass slides used for control of microwire fabrication. The traditional side illumination and Top-down illumination with a microscope camera system (35X, 1.3 Mp camera, 20 s intervals) was used to image both drop size and contact angle measurements of the liquid droplets.

The statistical analysis method reported in the experimental section, chapters 4.1 to 4.6 include the absolute error and standard deviation formulae of reporting error values. Specifically, the absolute error formula was used in Chapters 4.1 and 4.2 to report the contact angle measurements of liquid drops averaged for at least ten measurements per substrate from multiple substrates while 95 % confidence limit interval was used to report the error bars indicated in the graphs.

### 3.2 Glass cleaning protocols

A physical cleaning procedure was adopted to ensure that all surfaces were reasonably clean. The untreated microscope glass slide was used as the reference, while other substrates were cleaned either under blown N$_2$ before or in combination with cleaning in a sonicated water bath at $t = 30$ mins.
A clean surface as defined by Mattox [82] is the one that contains no significant amount of undesirable materials; the threshold and the type of acceptable contamination will vary for different applications. The first reason for adopting a physical cleaning procedure devoid of either chemical or laser treatments was to ensure that the surface property of the glass is not altered in the process of removing contaminants from the surface. Routine chemical methods such as hydrogen peroxide (H$_2$O$_2$) and piranha solution (H$_2$SO$_4$ / H$_2$O$_2$ or NH$_4$OH / H$_2$O$_2$) treatments, often in combination with ultrasonic cleaning in the desired solvent and nitrogen blowing, have been reported in some papers [83-87] to improve surface cleaning. However, the use of strong chemical treatments on a hydrophilic glass surface may also increase particulate contamination on the surface which involves static attraction through charge effects with a silicate surface. This effect is most often not considered in a number of surface cleaning protocols.

Lastly, laser treatment with cheaper and lower quality glass slides (depicted in Figures 2-5 in optical micrographs I and II) with contours on the surface may increase further surface roughness through etching or ablation under some conditions [88]. Therefore, a particular cleaning protocol that is well understood and highly reproducible should, therefore, be the practice. The experimental works on contact angle of water and silica NPs on four glass types studied are in chapters 4.1 and 4.2. Figure 3-1 shows AFM measurements (in non-contact mode) of the surface morphology for (a) untreated borosilicate glass; (b) untreated quartz; (c) borosilicate glass cleaned using hot H$_2$O$_2$; (d) borosilicate glass coated with the C8 SAM, which illustrate the different contaminate sizes on a variety of microscope slides [25].
Figure 3-1. AFM measurements (in non-contact mode) of the surface morphology for (a) untreated borosilicate glass; (b) untreated quartz; (c) borosilicate glass cleaned using hot H$_2$O$_2$; (d) borosilicate glass coated with the C8 SAM. [Reprint of Figure 4 from Sumner, A. L.; Menke, E. J.; Dubowski, Y.; Newberg, J. T.; Penner, R. M.; Hemminger, J. C.; Wingen, L. M.; Brauers, T.; Finlayson-Pitts, B. J., The nature of water on surfaces of laboratory systems and implications for heterogeneous chemistry in the troposphere. Physical Chemistry Chemical Physics 2004, 6, 604-613].

3.3 Sessile drop method

The sessile drop method is one of the static techniques for evaluating the contact angle of liquid droplets on a glass surface. It is also the most routinely used method for contact angle measurements because it is fast and very easy. In the sessile drop method, the glass microscope slide is placed on a flat stage so that the edge of the drop and image are both visible on the computer screen when viewed with the microscope connected to the computer screen. Liquid drops are then dispensed and measured several times on the
different locations on the glass substrate. While it is a common practice to measure the tangent at the point of contact on one side of the drop, it has also been suggested that measuring the contact angle on both sides of the drop and taking an average contact angle gives an accuracy measurement to an error of ± 1 or better [42, 44]. Therefore, in this thesis work (Chapters 4.2 and 4.3), the contact angles of the liquid drops dispensed on the glass surface were measured at least ten times and the average value taken as the contact angle. The θ measurements of liquid drops repeatedly dispensed at different areas of the same glass surface also eliminates the “eye error bias measurement”. The schematic illustration of the sessile drop method is shown in Figure 2-4.

3.4 Dynamic light scattering (DLS) techniques

The DLS is an optical technique used for analysing dynamic properties and the spectral broadening due to Brownian motion of particles. The technique is useful for a broad range of physical, chemical or biological systems in solution [89]. The accuracy of particle size measurement may be down to 1 nm. Examples of DLS applications include emulsions, polymers, nanoparticles, proteins and colloids.

In principle, the DLS technique deals with the extraction of spectral information obtained from the particle of a sample within a spatially limited volume. The suspended particle in Brownian motion hit by a monochromatic coherent light generates scattered light and spread in all directions. The intensity of fluctuations correlates with the distances between the particles within the scattering volume, which may vary in time. For solutions that are dilute, the spectral width yields particle size information for hydrodynamic radii from nm to the µm range and particles are mostly monodispersed. However, concentrated samples are difficult to measure with the DLS technique for many reasons: 1. High particle concentration hinders
the Brownian motion, 2. multiple scattering of light occurs and leads to undesirable averaging of the hydrodynamic radii of the particle, 3. Complicated to read polydispersity samples because of the spatial and temporal dependencies [90]. However in these literatures [90, 91] a variety of dual beam, dual detector experiments have prospects for obtaining spectra data which are unaffected by multiple scattering of light or at most be suppressed. Additional features, such as colour coding, time coding or special 3-D wave vector arrangements – combination of which may allow large variations of the scattering angle and size of the scattering vector.

In this work, the monochromatic coherent source (Laser light) focused towards the cuvette contains silica NPs solution (diluted to ~ 3.2 wt. % concentration with H₂O) (Figure 3-2). As the laser light hits the sample in spherical Brownian motion, it scatters, and a photon detector at a fixed angle (scattering angle, α) then detects the imprint. The laboratory instrument used in this work only allows measurement of the mean particle size within a limited size range. The analysis of the data treatment shows a statistical plot of average intensity of scattered light (equivalent to particle size hit) versus the size distribution of particles by laser light within the spatially limited volume. An extremely dilute solution can also bring about undesired multiple scattering effects, interparticle interactions and insufficient signals [92]. The dilution concentration for the DLS measurement of Silica NPs was between 2.5 -3.2 wt. % in deionised H₂O.

Figure 3-2 shows the layout of components of a DLS instrument from a simple and an advanced instrument.
Figure 3-2. DLS components. Simple DLS component features vs extended DLS features. For the lab experiment, the default setting conditions used is a laser light source (λ = 600 nm) at a fixed scattering angle, α = 173°. The modified 3D cross-correlation spectroscopy comes with an additional modulated device. 1-Laser. 2. Beam splitter. 3. Mirror. 4, 6. Lens. 5. Sample. 7. Photon detector. 8. Cross-correlator. 9. Modulator. The schematic diagrams are modified images from the web source. As an additional note, by modulating the incident laser beams and gating the detector output, separation of scattered lights become feasible in the upgrade. In addition, the upgrade can also suppress negative effect associated with multiple scattering. The below link leads to more information about the upgrade: http://www.lsinstruments.ch/technology/dynamic_light_scattering_dls/modulated_3d_cross-correlation_technology/

3.5 Thermoelectric (Peltier) module

A Peltier module is a solid-state thermo-electric device use to rapidly cool or heat small materials intended for small application purposes. A basic Peltier module, used as either a heat pump or a thermoelectric cooler (TEC) for instance, consists of the following components: ceramic plates, n-type and p-type semi-conductor elements sandwiched between ceramic plates, two dissimilar conductors (a thermocouple, insulated by polyvinyl chloride, PVC) - incorporated at the junction of the padded Peltier element, fan and heatsink units.
In principle, the Peltier effect is the gain or loss of heat at a junction when there is an applied current. A reverse effect that relates to the Peltier effect is the Seebeck effect. By passing a current through to two dissimilar semiconducting materials, a temperature difference occurs. For example, to make the top side of the Peltier plate function as the cool side, there must be an applied current between the two electrical junctions, so that the hot side attached to the heat sink rapidly conducts heat away, and as long as the hot side is cool, the cold side gets cooler. The combination of these effects: Seebeck, Peltier, Joule, and Fourier, will determine its area of application. Generally, these effects are useful for reversing the direction of heat flow [93]. Exception is the Joule effect, which only causes the temperature of a material to increase in the direction of the heat flow upon applying a current.

Figure 3-3 below shows the improved Peltier module.

Figure 3-3. Peltier module (TEC). Left: Improved experimental set up. Right: Here, the voltmeter reading was initially set at the operational voltage (12 mV). As the appropriate current is applied, there is a passage of electrons from the n-type element. This is the compartment where electrons move toward the hot end of the ceramic plate and holes (caused by doping of the intrinsic semiconductor of the p-type compartment to move toward the cold end). The difference in thermal energy carried by both the n and p-type semiconductors is the net-flow of heat observed from the cold end to the hot end. In other words, the ceramic plate inhibits the flow of electrical current at the cold surface region but allows the heat to pass through the hot ceramic surface region. Light Aluminium heat sinks, combined with (the) fan(s) ensure that heat flow at the surface is continuously cool.
For the fabrication of microwires, the Peltier module is suitable at ambient temperature range. However, below ambient temperature, humidity condition makes the fabrication process difficult and irreproducible. Hence, the reason for using a humidity controlled chamber reported in the experimental section, Chapter 4.3.

3.6 Sputtering metal coating

Sputtering metal coating is the process of bombarding and transferring a target metal of grain size deposition (nm size) onto a sample (Figure 3.4).

![Sputtering vacuum deposition](image)

Figure 3-4. Sputtering vacuum deposition.

Typically, the target material for coating is located at the cathode and the sample to coat is at the anode. At the default setting conditions (current = 25 mA; time = 2 s; vacuum pressure: $1 \times 10^{-1}$ mbar), argon gas is passed through the cathode gas tube to saturate the chamber. Collision of electrons with gas atoms initiates the ionization process causing free electrons to accelerate by an electric field. The continuous luminous glow seen in the chamber is the
ionization process when it reaches the Townsend discharge level [94]. At this point, regeneration of electrons causes a multiple avalanche that permits electric conduction through the gas to produce a self-sustaining glow luminance observed in the chamber [95]. In addition, the glow discharge in the chamber is dependent on the work function of the target material and pressure of the gas in the chamber. The glass samples and microwires studied were sputter coated with either Au or Pt.

3.7 Optical Microscopy (OM)
The optical microscope, with attached digital camera obtains most of the preliminary images shown in this thesis work. Typical operation is that a light from the microscope lamp source passes through the condenser to the sample. The condenser ensures light reaches the sample by altering the incoming divergent light into a converging beam light that illuminates the sample (Figure 3-5). Depending on the sample, light may either be absorbed (partially) or pass through the sample/ or scattered. By adjusting the two knobs on the instrument (coarse and fine adjustments), regulating aperture size to fit the angle of the light that reaches the sample, and with an appropriate objective lens (x 5 magnification and a numerical aperture (NA) = 0.15 was used throughout), sharp image was obtained as soon as the sample was in focus. The magnified image seen on the monitor screen called the optical micrograph of the sample is dependent on the scale chosen.
Figure 3-5. The optical ray diagram for a transmitted illumination type microscope. 1. White light source. 2. Sample. 3. Sample. 4. Microscope stage. 5. Objective aperture. 6. Objective. 7. Set of eyepiece. 8. Attached camera.

3.8 Scanning electron microscopy (SEM)

SEM is a powerful technique use in the examination of materials of $10^3$ to $10^4$ magnification images than the optical microscope technique. SEM features usually have good depth of view and high resolution down to 25 nm. In this study, the SEM technique is in conjunction with the technique of the energy-dispersive x-ray microanalysis (EDX) to analyse the composition of silica microwires and Au-coated microscope glass slide. A schematic illustration of the scanning electron microscope (SEM) is as shown in Figure 3-6.
The three scanning electron microscopes used in this work operate under a high vacuum. To load a sample and remove a sample in the chamber, the SEM is vent before and after use. This is to ensure that the chamber maintains a high vacuum state. Typically, the SEM instruments use either a tungsten filament or a field emission gun. The electron beam accelerates through a specified voltage (3 to 5 kV, as used in this work) and passes through four aperture systems before it hits the sample. The anode system, along with the magnetic lens, helps to guard the moving electron beam in its course. The beam then scans the surface of the specimen on the stage by scanning coils after which suitable detectors collect the scanned electrons. Both the secondary electron (SE 2) and in-lens detectors were used in this
thesis. The SE 2 works at a long working stage distance of at least 5 nm to the beam source while the in-lens detector works at a shorter working distance, less than 5 nm but must not be lower than 3 nm (the recommended level when in-lens mode). The in-lens detector gives sharper and clearer images because electron beams are able to interact well with the surface. Therefore, a low voltage is suitable for an in-lens detector mode but a high voltage is what is required to give good images when in SE 2 mode. The magnification of the image is the ratio of the size of the screen to the size of the area scanned by the beam on the specimen.

Finally, the EDX, as mentioned above, is the additional feature of the SEM instrument. Under a high voltage, the electron beam generates X-rays within the specimen, which has characteristic property of the elements that it emits. The detector (Backscattered detector) then converts the high voltage into voltage pulses. These voltage pulses measures over a period of time (seconds) as a histogram chart. The collection of the different X-ray energies pulsed in the specimen in the process is the spectrum of the elements present.
4. Results, Discussion and Experimental section

4.1 Evaluation of glass surface cleaning methods to obtain reproducible contact angle measurements for the control of self-assembly processes using drops.

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Please note that these sections are presented as stand-alone works and, hence, are individually referenced at the end of each section.
Chapter 4.1

Evaluation of glass surface cleaning methods to obtain reproducible contact angle measurements for the control of self-assembly processes using drops

Introduction
A clean surface is the one that contains no significant amount of undesirable materials; the threshold, and type of acceptable contamination varies for different applications [1]. For instance, applications for the manufacturing of high yield semiconductors require any certain contaminants to have a size that does not exceed 125 nm, a defined level beyond which fatal device effects may have too high a frequency to be tolerated [2, 3]. On the other hand, an atomically clean surface may need a more efficient cleaning method, such as laser cleaning techniques reported in the literature [4-7]. Alternative routine chemical methods used for glass surface cleaning include hydrogen peroxide (H$_2$O$_2$) and piranha solution (H$_2$SO$_4$ / H$_2$O$_2$ or NH$_4$OH / H$_2$O$_2$) treatments, often in combination with ultrasonic cleaning in the desired solvent and nitrogen blowing. Table 2 outlines some the cleaning procedures for hydrophilic glass substrates planned for later discussion.

In a related study shown elsewhere [4, 8], untreated surfaces have different contaminant type and size across different substrate materials, particularly when characterized by scanning electron and atomic force microscopies. Moreover, a method of cleaning treatment should reduce particulate contaminant size, with laser treatment being more efficient than the chemical treatment [9,10].
While these methods may reduce particulate contamination type and size, they may also change surface roughness by etching or ablation under some conditions. Laser treatment on some substrates, for instance, has been reported to cause parametric space – charge effects when ablation thresholds exceed surface defect energies [4,11]. Besides, altering the chemical nature of the surface, favorably through laser annealing, may also lead to changes through interference between the generated plasma and the polarised optical beam. This process is the basis of the Birnbaum effect [12], which leads to useful nanograting formation—it has even been extended to work within confined volumes of glass using multiphoton effects to generate 3D nano-gratings within a solid [13, 14].

On the other hand, surfaces that have been cleaned are also prone to recontamination, either via adsorption in a dirty environment or by other contaminants that act to seed and attract further contaminants. Particulate contamination on a silicate surface often involves static attraction through charge effects. A good understanding of the surface property of the glass and the cleaning methods is clearly critical. The use of high purity glass slides that are precleaned is ideal, but often a cheaper, lower quality glass of variable composition have also been reported [8 ] to give consistent contact angle, $\theta$, with an error $\pm 2^\circ$. A particular cleaning protocol that is well understood and highly reproducible should, therefore, be the practise.

The contact angle of a liquid on a surface is a routine experimental approach for controlling and understanding fluid drops, particularly at the solid-liquid-vapour interface [15-22]. The contact angle provides information of the surface parameters that needs measurement. In addition, the contact angle is useful for characterising both microscopic and macroscopic phenomena on the surface. A surface defines properties such as contact angle as a
consequence of surface molecules, surface defects and the structures with the liquid. The contact angle contains information of the surface both at the molecular or nanoscale and on the microscale or larger level when surface variations are present. Therefore, defining the specific contact angle based on material properties alone requires the exact understanding of the changes involved with treatments.

The present thesis only looks at the physical aspect of cleaning. The reason is to understand if the simple cleaning procedure would not impact considerably variation in liquid drop on the treated surface, and on subsequent control of drops for self-assembly. Therefore, the aim is to evaluate glass slide that gives a reproducible surface by the contact angle method.

**Experimental details**

**Materials and Methods**

The four different microscope slides obtained from soda lime glass (composition: 72 % SiO₂, 14.5 % Na₂O, 0.30 % K₂O, 7.05 % CaO, 3.95 % MgO, 1.65 % Al₂O₃, 0.06 % Fe₂O₃) were from the following sources: **Sail Brands** - catalogue nos. 7101, 7101A and speciality microscope glass slides - **SuperFrost Ultra Plus** and **SureFrost**. Table 1 shows the summary of some commercially available microscope slides with their glass composition. Deionized H₂O was obtained from the school chemistry laboratory. Pipette with volume \( V = 0.5-10 \, \mu\text{L} \) was used. Ultrasonic cleaner from Unisonics PTY Ltd Australia was used for cleaning all glass types. Nitrogen gas was acquired from a tube connected to the N₂ flow gun. The customised contact angle goniometry set up in Figure 1 was used for the contact angle measurements under the following conditions: \( T = 21-22 \, ^\circ\text{C}, \, RH = 31-32 \, % \).
Glass surface treatment

Glass substrates from the different commercial sources were either blown under N$_2$ or in combination with ultrasonic cleaner. The reference glass substrates were used in their precleaned states without further treatment. For the glass substrate blown under N$_2$; continuous N$_2$ from the high-pressure flow gun was applied directly on the surface for 15 mins to dislodge and remove contaminants weakly held to the surface. Each glass slide was used immediately without storage to avoid recontamination, either by static charge or adsorption. The other glass slides were blown under N$_2$, and further cleaned in an ultrasonicating bath with deionised water for 30 mins, followed again by drying under N$_2$ flow gun.

Contact Angle Goniometry

Contact angles with deionised H$_2$O ($V = 1$ µL) were measured with the sessile drop method using a customised contact angle goniometry (Figure 1b). Each contact angle value reported here is the average of at least ten measurements per substrate from multiple substrates. The reproducibility of the contact angle measurements for different substrates treated under the same conditions was estimated using multiple repeated measurements.

Results and discussion

A clean surface is one that contains no significant amount of undesirable contaminants capable enough to render the surface irreproducible. The first glass treatment that was used involved blowing the surface under high-pressure N$_2$ flow gun for 2 mins. The reason was to remove contaminants that are loosely attached to the surface. Low quality glass slides may also have oil film traces from glass cutter tool, for example from diamond, which requires the sheet of glass to be lubricated along the cutting line with a light oil. On the other hand, the second glass treatment involved a combination of the first treatment and microscope slides
cleaning with deionised water (100 mL) in an ultrasonicating bath for 30 minutes and followed by rinsing again in deionised water (100 mL) and drying under nitrogen for over 5 minutes. The ultrasonication process involves the physical action of cavitation on water—the formation of submicroscopic voids released by ultrasonic waves when the instrument frequency is greater 20 kHz [22]. The ultrasonic wave creates agitation in the water, causing small bubbles to form and enlarge in time as successive waves pass along until implosion occurs on the surface in all directions. This physical action is what scrubs the surface of glass to remove particulate matter and oil films. The additional rinsing ensures the loose particulate contaminants are washed off.

After cleaning the glass slides, contact angle of water for four different microscope slides was measured by the sessile drop method. The glass microscope slide was placed on a flat horizontal xyz translation stage so that the edge of the drop and image are both visible on the computer screen when viewed with the microscope. Liquid drops were then placed ten times on different locations on the glass substrate to check the reproducibility of the contact angle of water droplet measured. The contact angle measurements were from both sides of the drop and the average value was considered; with the least error value, ± 3 ° used as the standard cut off point for distinguishing a surface that is consistent from the one that is not probable to give a reproducible surface. Table 2 shows the contact angle measurements of the different microscope glass slides along with their absolute error readings (θ₁, θ₂). θ₁, θ₂ are the average contact angle of liquid drops’ readings from the individual edges of the glass. The absolute error formula was used to determine the accuracy of the measured value which was obtained by finding the average of the difference from the least to maximum readings on both sides of the glass. The average contact angle value of both sides (θ_{av})
represent the corrected value for the eye error bias measurement from both sides of the glass edge.

From the measurements (Table 2), substrate IV gave the best reproducible surface, with a consistent contact angle value (39 ± 1)°. The other substrate types (I and II) had high error values for the same method of cleaning and wide variation on their surfaces. Substrate III was fairly stable as the error value was within the reproducible mark. The wide variation in contact angle values with regards to cleaning methods of substrates I and II, reveal two things about the surfaces (I and II): 1. Surface is not reproducible. 2. Method of cleaning is not suitable. Table 3 shows the literature results of some cleaning methods and contact angle of water obtained on different glass slides. Here, it can be inferred that the different methods of cleaning claimed produce variation in contact angle, admittedly, with some surface conditions better than orders. One can also conclude from the given table (Table 3) that there is no standardised protocol for cleaning glass surface but from the results in this section, a simple cleaning procedure such as ultrasonication process and blowing under N₂ gun when applied under a relatively, smooth high quality glass surface can give a reproducible surface.

Finally, the contact angle values (θ₁, θ₂ in Table 2), measured from both sides of a single drop, are depicted by the bar graph in Figure 2. This figure shows the progression in cleaning from the precleaned state to when blown under N₂ and sonicated in H₂O appreciably reduce the contact angle difference on both sides of a drop of liquid on the substrate. Overall, the cleaning method applied to the substrate with the best reproducible surface follows this order: IV > III > II > I.
Conclusion

Reproducibility is necessary in many areas of nanoparticle applications, particularly in self-assembly processes requiring controllable dimensions [22,24-25]. However, low quality microscope glass surfaces may have inherent non-uniform surface roughness [26,27]. This roughness may arise from sources such as particulate contaminant [8] or heterogeneity [28] or even from surface pore sizes [29] and contour ditches.

The results from the various cleaning methods, in the literature (Table 3) and the one in this chapter (Table 2) teaches two things when there are variations in contact angle measurements on a substrate surface; that either the surface is not reproducible or the method of cleaning is not suitable. Moreover, liquid drops of the same volume on some surfaces after cleaning have also been reported (Tables 2 and 3) to have low and high contact angle values. Therefore, the contact angle only provides the surface profile of the relationship between the liquid drop and the surface condition at the time of drop.

Given the definition of a clean surface, that is, a surface with no significant amount of undesirable contaminants capable enough to render the surface irreproducible. The conclusion that can be drawn from this study is that reproducible surface can be achieved using the physical cleaning method adopted for substrates III and IV. Thus, these substrates are good candidates to consider in the control of drop for the fabrication of silica microwire in the subsequent experimental sections.
Fig. 1. Materials and methods. a. Spirit level (top) – used to gauge that platforms are perfectly horizontal. The ruler was used to calibrate diameter (mm) of liquid drops on glass substrates when imaged with a digital microscope. Four types of glass substrates studied (precleaned and treated surfaces) and pipette. b. Customised contact angle goniometry instrument was used to measure the contact angle of drops by the lateral (Sessile drop) method using a digital microscope displayed. c. Drop shape of water at the edge of the substrate and the contact angle measurements taken on both sides of a drop of liquid. e. Optical microscope.
Fig. 2. Bar graph: Variation in contact angle difference ($\Delta\theta = \theta_2 - \theta_1$) within a measured drop of 1 µL of H$_2$O on substrate – was used to compare the variation in surface roughness: Routine glass slides: I. (Cat. No. 7101) and II. Pathology grade (Cat. No.7101A) - Group 4A. III: SureFrost (Group 6I). IV: SuperFrost Ultra plus (Group 5F). The error bars are with 95 % confidence interval.
<table>
<thead>
<tr>
<th>Material</th>
<th>Description</th>
<th>Chemical composition</th>
<th>Source</th>
<th>Group reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borosilicate glass</td>
<td>Micro cover glasses, No.1, 25 mm dia.x0.13-0.17 mm</td>
<td>64% SiO₂, 9% B₂O₃, 7% ZnO, 7% K₂O, 7% Na₂O, 3% TiO₂, 3% A₃O₅</td>
<td>VWR Scientific, Inc., Buffalo Grove, IL</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Designation E438-92: specification for Type I, Class A</td>
<td>81% SiO₂, 13% B₂O₃, 4% Na₂O, 2% Al₂O₃</td>
<td>ASTM International West Conshohocken, PA</td>
<td>2</td>
</tr>
<tr>
<td>Silica glass</td>
<td>Quartz cover slips substrate grade,</td>
<td>Corning 7980 Synthetic Fused Silica: 72% SiO₂, 14.5% Na₂O, 0.30% K₂O, 7.05% CaO</td>
<td>Quartz Plus, Inc. Brookline, NH</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>25 mm dia. X 0.16 mm (Silicate glass slide)</td>
<td>3.95% MgO, 1.65% Al₂O₃, 0.06% Fe₂O₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Yancheng Huida Med Inst Ltd., China</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soda lime glass</td>
<td>Standard microscope glass slides:</td>
<td>72% SiO₂, 14.5% Na₂O, 0.30% K₂O, 7.05% CaO</td>
<td>Yancheng Huida Med Inst Ltd., China</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>(Made from normal/super white glass):</td>
<td>3.95% MgO, 1.65% Al₂O₃, 0.06% Fe₂O₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>A. Cut (Underground Edges/90° Corner [Cat. No.: 7101, 7101A])</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B. Ground Edges/90°/45° corner [Cat. No.: 7101, 7101A]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C. Frosted end/ends/90°/45° Corner [Cat. No.: 7105A, 7107, 7107A]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>D. Beveled edges/45° corner [Cat. No.: HD4501H/HD4501A]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adhesion glass slides</td>
<td>Same chemical composition as</td>
<td></td>
<td>ThermoFischer Scientific Australia</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Group reference 4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>E. SuperFrost™ Plus: + surface and strong electrostatic attraction to surface</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>F. SuperFrost™ Ultra Plus: Same as E + best optimisation on the glass the surface where heat is involved</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G. Polyamine slide: Same as E + suitable for biochemical bonding</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>I. Sure Frost: adhesive slink coating and specifically developed for harsher applications (HD21102 1PD Plain edges)</td>
<td></td>
<td>Trajan Brand, Australia</td>
<td>6</td>
</tr>
<tr>
<td>Cleaning Method</td>
<td>I</td>
<td>II</td>
<td>III</td>
<td>IV</td>
</tr>
<tr>
<td>-----------------</td>
<td>----</td>
<td>-----</td>
<td>------</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>$\theta_1$</td>
<td>$\theta_2$</td>
<td>$\theta_{av}$</td>
<td>$\theta_1$</td>
</tr>
<tr>
<td>A</td>
<td>26 ± 4</td>
<td>33 ± 11</td>
<td>30 ± 8</td>
<td>19 ± 4</td>
</tr>
<tr>
<td>B</td>
<td>29 ± 4</td>
<td>32 ± 6</td>
<td>30 ± 6</td>
<td>37 ± 2</td>
</tr>
<tr>
<td>C</td>
<td>26 ± 4</td>
<td>28 ± 5</td>
<td>27 ± 4</td>
<td>42 ± 7</td>
</tr>
</tbody>
</table>

A = Pre-cleaned state. B = when blown under $\text{N}_2$ and C = When blown under $\text{N}_2$ and sonicated in $\text{H}_2\text{O}$ for 30 minutes. I - Sail Brand (Group reference 4A, Table 1); II – Pathology grade (Group reference 4A, Table 1); III – SureFrost (Group reference 6I, Table 1); IV = SuperFrost Ultra Plus (Group reference 5F, Table 1); All the contact angle values are in degrees. The error value readings is from absolute error formula.
TABLE 3. SOME CLEANING METHODS AND CONTACT ANGLE OF WATER OBTAINED ON DIFFERENT GLASS SLIDES

<table>
<thead>
<tr>
<th>Material</th>
<th>Cleaning methods</th>
<th>Contact angle/°(±)</th>
<th>Standard Error(°)</th>
<th>Literature reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Group no. 1 (from table 1):</strong> Boholite cover glass</td>
<td>1. Unfinished glass (1 mL droplet)</td>
<td>32</td>
<td>2</td>
<td><strong>8</strong></td>
</tr>
<tr>
<td></td>
<td>2. Unfinished glass (10 mL droplet)</td>
<td>24</td>
<td>5</td>
<td><strong>9</strong></td>
</tr>
<tr>
<td></td>
<td>3. Water-cleaned (1 mL droplet)</td>
<td>35</td>
<td>N/A</td>
<td><strong>8</strong></td>
</tr>
<tr>
<td></td>
<td>4. Plasma-cleaned (1 mL droplet)</td>
<td>&lt;10</td>
<td>N/A</td>
<td><strong>8</strong></td>
</tr>
<tr>
<td></td>
<td>5. H₂O₂-cleaned (1 mL droplet)</td>
<td>&lt;10</td>
<td>N/A</td>
<td><strong>8</strong></td>
</tr>
<tr>
<td></td>
<td>6. Unfinished glass (10 mL droplet)</td>
<td>27</td>
<td>6</td>
<td><strong>9</strong></td>
</tr>
<tr>
<td></td>
<td>7. Method 5 + base piranha: (20% H₂O₂; 28% NH₄Cl; 42% H₂O)</td>
<td>8</td>
<td>N/A</td>
<td><strong>9</strong></td>
</tr>
<tr>
<td></td>
<td>8. Method 5 + Laser treatment with 193 nm</td>
<td>8</td>
<td>1</td>
<td><strong>9</strong></td>
</tr>
<tr>
<td></td>
<td>9. Method 7 → after 17 hrs (10 mL droplet)</td>
<td>10</td>
<td>1</td>
<td><strong>9</strong></td>
</tr>
<tr>
<td><strong>Group no. 3 (from table 1):</strong> Quartz cover slip</td>
<td>1. Quartz pristine (1 mL droplet)</td>
<td>22</td>
<td>4</td>
<td><strong>8</strong></td>
</tr>
<tr>
<td></td>
<td>1. Quartz pristine (10 mL droplet)</td>
<td>20</td>
<td>1</td>
<td><strong>6</strong></td>
</tr>
<tr>
<td><strong>Group no. 4 (from table 1):</strong> Soda lime microscope slide</td>
<td>1. 30 min in 1:3 H₂SO₄: HCl, rinse in H₂O₂, dry under N₂</td>
<td>Instrument limitation (&lt;5°)</td>
<td>&lt;2.5</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>2. Method 1 → incubation (30 min.) in conc. H₂SO₄</td>
<td>Instrument limitation (&lt;5°)</td>
<td>&lt;2.5</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>3. Rinse in H₂O₂, dry under N₂</td>
<td>Instrument limitation (&lt;5°)</td>
<td>&lt;2.5</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>4. 5 min in 1:1:1 H₂O: H₂O₂: H₃PO₄</td>
<td>2</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>5. H₂O at 80°C</td>
<td>31</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>6. Method 4 → incubation (1 min.) in 1:1:1 HCl: H₂O₂: 30% H₂O</td>
<td>Instrument limitation (&lt;5°)</td>
<td>&lt;2.5</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>7. Rinse in H₂O, dry under N₂</td>
<td>9</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>8. 20 min in 1 M NaOH, rinse in H₂O, dry under N₂</td>
<td>19</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>9. Method 7 → 30 min in piranha (1:2 H₂O₂: H₃PO₄): Rinse in H₂O, dry under N₂</td>
<td>12</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>1. Pre-cleaned state**</td>
<td>30</td>
<td>8</td>
<td>(this work)**</td>
</tr>
<tr>
<td></td>
<td>2. Pre-cleaned state**</td>
<td>21</td>
<td>5</td>
<td>(this work)**</td>
</tr>
<tr>
<td></td>
<td>3. Method 1 → blown under N₂</td>
<td>30</td>
<td>6</td>
<td>(this work)**</td>
</tr>
<tr>
<td></td>
<td>4. Method 1 → sonicated in H₂O, dried under N₂</td>
<td>27</td>
<td>4</td>
<td>(this work)**</td>
</tr>
</tbody>
</table>

- N/A – Not available; **Pathology microscope glass slide in the precleaned state (Table 1: Group 4A – Catalog. No. 7101A)
- * Average contact angle taken on both sides of drop.
References


Chapter 4.2

Controlled and reproducible fabrication of self-assembled silica microwires from spherical caplet drops on glass surface sputtered with Au particles

Introduction
The surface property of a substrate is known by the interaction of the liquid with the surface, and is a measure of the contact angle of the liquid at the three-phase contact line (Young’s definition). The contact angle also contains information of the surface at the molecular or nanoscale when surface variations are present [1-5]. In self-assembly, it is imperative for the assembled products to have scalable and controllable dimensions for the material to exhibit function and carry unique properties. Moreover, for self-assembly structure to organise into a well-defined pattern, the mobile phase (colloidal suspension of silica nanoparticles) needs to be optimised and a clean, smooth surface is desirable [6,7]. Therefore, a glass substrate with good surface reproducibility is a prerequisite. This has been covered extensively in chapter 4.1.

Furthermore, there may be need to modify the surface of a glass either by surface functionalisation [8] or sputtering - illustrated in this experiment. For instance, studies have shown template to reduce surface defects and also control structures during the self-assembling process [6,8-10]. The present study explores the control of glass surface properties to produce silica microwire with more orderly structures close to ideal body centred cubic (bcc) or hexagonal close (hcp) packing. This chapter is a follow up study on the fabrication process of silica microwire [11]. Additionally, it shows an example of improving the fabrication process in moving from varied form structures made up of aggregated
particles and random networks to more orderly structures close to ideal body centred cubic (bcc) or hexagonal close (hcp) packing.

As described in the literature [11], silica microwires are produced during the evaporation of a drop of silica nanoparticles on a glass surface (uncoated surface). The evaporation process starts with a reduction in volume of solvent during convective flow. As the volume of solvent recedes, nanoparticles start to pack and bind through van der Waals interaction forces to form very thin, glass-like structures called microwires. The enormous stress of the drying of these materials causes silica nanoparticles to self-arrange via short-range intermolecular forces to periodic short packing configurations, which can either lead to ordered or disordered outcome when viewed under the scanning electron microscope (SEM). The lowest free structure being hcp/and or bcc packing arrangement.

However, fabrication of microwires from the self-assembly of silica nanoparticles may occasionally give rise to clustered (aggregated) particles and random networks, depending on the glass surface condition and a number of other implicated factors, which include but are not limited to: cleaning protocol, surface condition of glass at the time of drying, evaporative route and humidity condition, drop volumes and drop shapes. Combination of these factors may affect the quality of the wires produced and the packing arrangement of the wires.

The SEM micrographs show silica microwire structure to have a highly robust surface. The glass surface sputtered with Au particles and subsequently used in fabrication of microwires interestingly gave rise to consistent hcp/and or bcc packing, with approximate pore size diameters ~ (5-6) nm with silica nanoparticle average size distribution: ~ (20-30) nm.
This experiment demonstrates repeatable self-assembly of ordered structures with none of the variations associated with aggregation or random distribution using Au coated slides. It also shows a reliable and reproducible method of fabricating orderly structures in a controlled fashion; an essential step to enable rigorous application to filter and sieve applications that rely on precision pore fabrication.

Given the recent demonstration of practical self-assembly of silica nanoparticles through evaporation [11-19], it is clear that the fabrication of microwires offers a flexible window for enormously and potentially being used in number of application processes from lab-on-a fibre, nanophotonics platforms to precision pore fabrication process.

Experimental details

Materials and Methods
After the four glass substrates were screened in the experimental section (in Chapter 4.1), SuperFrost Ultra Plus microscope glass slide was rated to give the best reproducible surface. The substrate produced a consistent contact angle with the least error value (39 ± 1) °. As follows, the glass substrates used in this section are all from SuperFrost Ultra Plus. Deionized H₂O was obtained from the school chemistry laboratory. Pipette with volume \( V = 0.5-10 \, \mu\text{L} \) was used. Ultrasonic cleaner from Unisonics PTY Ltd Australia was used for cleaning the glass surface. Nitrogen gas was acquired from a tube connected to the \( \text{N}_2 \) flow gun. The customised contact angle goniometry set up in Chapter 4.1 (in Figure 1) was used for the contact angle measurements under the following conditions: \( (T = 21-22 \, ^\circ\text{C}, RH - 31-32 \%) \). Glass substrate was either sputtered with a coat of Au-particles or Pt-particles under vacuum using the sputter coater( EMITECH K550X) instrument with the following conditions: for Au/or Pt-sputtered glass surfaces - Current = 25 mA; \( t = 2 \, \text{s} \); vacuum pressure = \( 1 \times 10^{-1} \)
mbar; grain size deposition for Au-particles ~ 15 nm and Pt-particles ~ 9 nm. All glass surfaces were blown under high-pressure N₂ flow gun for 2 mins, which was followed with deionised water (100 mL) in an ultrasonicating bath for 30 minutes and followed by rinsing again in deionised water (100 mL) and drying under nitrogen for over 5 mins. The non-coated microscope glass slide was used as the control. All liquid drop volumes used for the contact angle measurements had a constant volume, V = 1 µL of silica nanoparticles solution. The sessile-drop technique was used for the measurement of the contact angle. The contact angle of the side image was captured after 10 s. Each contact angle value reported is the average of at least ten measurements per substrate from multiple substrates. The reproducibility of the contact angle measurements for all the substrates was estimated using multiple repeated measurements.

**Surface wettability and evaporative route**

On the glass surfaces (non-coated and sputtered coat with Au or Pt particles), 1µL drop of silica nanoparticles with diameter, ~ (20-30) nm at the following concentrations (1 wt.%, 2 wt.% and 3 wt.%; pH = 9 with NH₄⁺ counterions) was sonicated for one hour and was carefully dispensed on the substrate surfaces and allowed to evaporate under a covered styrofoam box. (Figure 2).

**Results and discussion**

The coating of glass surface with either Au/or Pt-particles was aimed primarily to control the drop shape during evaporation and subsequent production of uniform microwire with close packed structures (hcp/bcc). The glass substrate was cleaned as described by the previous method in chapter 4.1. Briefly, the glass slides were blown under N₂, and further cleaned in an ultrasonicating bath with deionised water for 30 mins, followed again by drying under N₂.
flow gun. The dried glass slides were either Au or Pt-coated prior to the determination of the contact angle of water using the sessile drop method (drop volume = 1 µL). The evaporation of 1 µL drop of silica nanoparticles at different concentrations (1, 2, and 3) wt. % were dispensed on the different surfaces. Figure 1 shows the bar graph obtained for the contact angle variation on both sides of the drop for the different surface conditions.

![Bar graph](image)

Fig. 1. Bar graph: Variation in contact angle difference ($\Delta \theta = \theta_2 - \theta_1$) within a measured drop of 1 µL of H$_2$O on substrate – was used to compare the variation in surface roughness: IV: SuperFrost Ultra Plus glass slide (non-coated surface). IV-Au. Glass sputtered coat with Au. IV-Pt. Glass sputtered coat with platinum.

The result of the bar graph shows the same cleaning protocol (in colour: blue) did not have much difference in contact angle variation for surface sputtered with Au-particles and non-coated substrate (IV). This means that the surface is relatively uniform. However, there was a high contact angle variation with respect to the same surface sputtered with Pt particles, which suggests the presence of high metal aggregation of Pt particles on the glass surface.
(non-uniform). It also suggests that the Au coated surface is reproducible. The contact angle variation on the flat plane was calculated by substracting the arithmetic difference between the two contact angle values:

\[ \Delta \theta = \theta_2 - \theta_1 \]  

Several reports attribute \( \Delta \theta \) to many factors, these are summarized in detail in this literature [20] as caused by the following: surface heterogeneity, roughness, overturning of molecular segments at the surface (i.e. short-range orientation of molecular species at the surface), adsorption/desorption and surface deformation.

Fig. 2. The set-up that was used to fabricate silica microwires at ambient temperature.
The glass surfaces were later used to fabricate microwires at different concentrations using a covered styrofoam box. The purpose of the confined evaporative route was to ensure control of convective air flow into the chamber during evaporation (Figure 2); and as the volume of water reduces, nanoparticles pack into aggregates to form the minimum energy configuration (hcp/bcc).

Figure 3 shows the optical micrographs of the circular patterns obtained from drying at different concentrations. The three substrates studied (non-coated surface, Pt-coated surface and Au-coated surface) of the same glass material composition and brand show that at 1 wt. % concentration of silica nanoparticles, there are more nanoparticles deposition in the coffee-ring region than in any other region (for 1 wt. % concentration of SiNP). So that as water gets removed at the edge during evaporation, there are no more nanoparticles to effectively sustain the ring process to the next phase. However, with increase in concentration, further rings are formed, and thin wires begin to rise up. Here, concentration effect seems to have an overall effect on the control of microwire formation during evaporation and Au-coated surface seems to result in the formation of more uniform microwires after the first coffee-ring stain region. This is interesting as circular drops on Au-coated surface can now be controlled to produce uniform microwires.

The SEM micrographs of microwires (at 3 wt. % concentration of SiNP droplet) were imaged as bulk material at four different regions along the wire dimensions (Figure 3), and as depicted in Figure 4 shows the descriptive statistics used to image the pore sizes of the different micrograph regions. Bulk characterization of microwires helped to eliminate the size limitation associated with picking and studying individual microwire. Also, bulk
characterization of microwires gave a good statistical distribution of data for the pore size measurements.
Fig. 3. Optical micrographs of silica microwire formation from small volume drops ($V=1\mu L$) of silica nanoparticles solution at different concentrations using the confined evaporative route. The coffee-ring stains are the dense ring deposits that surround the periphery of the circular patterns. The pattern is as a result of dispersion and deposition of nanoparticles along the perimeter of the drop through capillary flow to produce a dense ring (“coffee-ring stain”), also responsible for the initial pinning process [7, 11, 21]. As the evaporation process continues, water molecules lost at the perimeter of the drop must be drawn from the centre to the perimeter of the drop to keep the contact line fixed. Through convective flow, microwires are lifted up from the surface and as the volume recedes completely, microwires overcome surface tension and can rise up from the glass surface. The 3 wt. % concentration of SNP suspension represents the optimal concentration required to produce very thin microwires. The wire widths are seen to increase with higher concentrations up to 5 wt.% for the same drop volume. All scales are between 800 $\mu m$ to 1 mm in distance.

Figure 4 shows the SEM micrographs of the surface packing of these wires produced on both uncoated and Au-coated surfaces from 1 to 3 wt. concentration of silica nanoparticles. Particularly, the numberings (1 to 4) for each SEM micrograph is the order of silica nanoparticles packing, starting from the primary coffee-ring stain (region 1) and ending with the centre of the circular structure (region 4). The uncoated surface at different silica nanoparticles concentration consistently produced random networks, except at 1wt.% concentration of silica nanoparticles in region 1 that produced hcp/bcc packing configuration. On the other hand, SEM micrographs of Au-coated glass slides unprecedently produced hcp/bcc packing configuration along the four regions. In order to study pore size distributions
and demonstrate repeatable self-assembly of ordered structures with none of the variations associated with aggregation or random distributions seen for the unsputtered glass surface, the Au coated slides for three concentrations ([SiO₂] = 1, 2, and 3 wt %) had pore sizes of ~5-6 nm in diameter, all with hcp/bcc packing (Figure 4f), with the optimal pore size recorded at 5 nm in effective diameter. Expanded images of each of the micrograph in Figure 4 are shown after the whole figure to allow the reader to see the finer detail and the recorded experimental conditions and scale bar.
Fig. 4. SEM Micrographs of self-assembled silica microwire structures at various concentrations. 

a to b. 1 to 2 wt. % concentration of silica nanoparticles produced on uncoated glass surface. 

c to e. 1 to 3 wt. % concentration of silica nanoparticles produced on Au-coated surface. 

f. Bar graph shows the descriptive statistics for the pore size distributions of assembled silica microwire structures on a glass surface sputtered with Au-particles to give the lowest hcp/bcc packing configuration at different concentrations.
Expanded images with scale bars of 4a micrographs:
Expanded images with scale bars of 4b micrographs:
1↔2
Transition boundary

200 nm
WD = 6.8 mm  EHT = 5.00 kV  Mag = 28.62 K X  Signal A = SE2

3
200 nm
WD = 5.8 mm  EHT = 5.00 kV  Mag = 76.47 K X  Signal A = SE2
Expanded images with scale bars of 4c micrographs:
Expanded images with scale bars of 4d micrographs:
Expanded images with scale bars of 4e micrographs:
In order to understand the reason why the Au-coated surface produced a well-controlled nanostructured surface, the SEM micrograph of the Au-coated surface was examined. Figure 5a shows the typical microphase structures of silicate glasses that was taken from reference [22]. Studies have shown the microphase surface depicted as “c” segment on the glass surface to be produced during spinodal decomposition mechanism [22-24], caused as a result of either cooling or heating a single stable phase. The spinodal decomposition is one of the metastable structures produced by glass forming oxides during phase separation. The electron micrograph of the microphase structure of a spinodal decomposition is characterised by sponge-like interpenetrating phases, with high degree of connectivity among particles in each phase. Comparison of Figure 5a with the SEM micrograph of Au-coated glass surface (Substrate IV-Au) in Figure 5b shows that the Au-coated surface has a similar microstructure surface. While Figure 5c shows the energy dispersive x-ray spectroscopy (EDS) spectrum of Au-coated glass surface. X-ray microanalysis study (EDS) was used to confirm the prominent elemental peaks in the spectrum, (53.9% Au, 22.4% O, 19.6% Si, 2.2% Na, 1.5% Mg and 0.4% Al). By comparing with the internal glass composition of uncoated substrate (composition: 72% SiO$_2$, 14.5% Na$_2$O, 0.30% K$_2$O, 7.05% CaO, 3.95% MgO, 1.65% Al$_2$O$_3$, 0.06% Fe$_2$O$_3$), it is probable that the prominent elemental peaks that appear in the spectrum represent the surface fraction by wt. % that may be considered as one of the factors responsible for influencing the behaviour of the motion of liquid droplets on Au-coated surfaces. Figure 5d shows the optical micrograph of a macroscopic contour of another brand type of microscope glass (non-coated) (Sail brand, studied in Chapter 4.1). The surface is similar to the surface arrow direction in Fig5a (Phase B); supported by reference [22] to represent an example of discrete droplets whose origin is from homogeneous nucleation.
followed by growth. Lastly Figure 5e shows the optical micrograph of microscope glass slide (substrate IV) (non-coated surface), similar to the microphase region of the pointed arrow in Figure 5a (Phase A).

Fig. 5. Comparison of typical microphase structures in silicate glasses and microscope glass surfaces from different sources used in this experiment. (a) Microphase structure of silicate glass source. b. SEM micrograph of Au-coated glass surface (Substrate IV-Au). c. Energy dispersive x-ray spectroscopy (EDS) spectrum of Au-coated glass surface. d. Optical micrograph of a macroscopic contour of another brand type of microscope glass (Sail brand, studied in Chapter 4.1). e. Optical micrograph of microscope glass slide (substrate IV) in the non-coated surface, observed to bear resemblance with microphase region of the pointed arrow in a (Phase A).

Enlarged individual images of micrographs 5b and c are shown below:
**Conclusion**

By comparing with variance in network structures of microwires fabricated on non-sputtered surface (control), a reliable way of fabricating orderly structures close to ideal body centred
cubic (bcc) or hexagonal close (hcp) packing has been achieved. The Au-coated surface enhanced the spatial ordering of nanoparticles in a more controlled manner, with pore sizes of ~ 5-6 nm in effective diameter. The uniform pore structure may be used in sieve applications that rely on precision pore fabrication[25,26]. In addition, the scope of application of a well-controlled, spatial periodic arrangements is huge and includes many areas in biotechnology, nanotechnology, optoelectronics and potential applications in high-capacity battery banks.

References


Chapter 4.3

Analysis of the spherical cap approximation of a liquid droplet on Au coated and non-coated surfaces during evaporation

Introduction
Evaporation of liquid droplets on surfaces have been studied by various researchers [1-7]. Evaporation is useful in the area of assembling unprecedented nanostructured materials [8-11], to fabricate microwires from colloidal suspension of silica nanoparticles [12]-the follow up study on fabrication process was discussed in chapter 4.2. Other areas where evaporation plays a major role include: microfluidic flow devices [13, 14], gene mapping [15, 16], alternative and faster route to bioassay preparation [17].

The theoretical and practical considerations relating to a drop of liquid on different surfaces still remain an open and active research area. For instance, some reviews have dwelled on factors such as wetting transition and fluid dynamics to be the key factors involved in spreading during evaporation [18]. There are also who hold the view that depending on the surface conditions, a liquid droplet may experience forced spreading or spontaneous spreading [19]. On the other hand, some modelling studies on circular droplet on spreading of drops supports the notion that the contact angle is significant on impact at the surface boundary and bears a direct correlation with the contact line during spreading [20].
In the present study, the rate of evaporation of a liquid droplet (H$_2$O and 3 wt. % concentration of silica nanoparticles) on Au-coated and non-coated surfaces were investigated by the sessile drop method. The main objective was to provide clarity on the kinetics involved during evaporation on different surfaces. The understanding of the kinetics, may lead to useful information for controlling drops and fabrication of materials with precise dimensions. In the work published by another research group [1], it was shown that the evaporation rate of a sessile drop (H$_2$O) resting on a solid (glass) surface depends on the radius of the liquid-solid interface and remain constant, but that the drop volume decreases as the contact angle decreases at ambient temperature: “the study only describes the behaviour of pure liquid (H$_2$O) on the surface”.

This study on the other hand looks at macroscopic parameters that influence the motion of fluid (water and colloidal drop of SiNPs) on glass substrates that are Au-coated and non-coated. The parameters include: (1) volume of drop, \( V \) (2) radius of wetted spot, \( r \); (3) contact angle, \( \theta \), between the liquid and solid at the three phase contact line and (4) gravity effects. Also important considerations taken into account include : 1. The liquid droplet shape is hemispherical when resting on the solid surface. 2. The contact angle values are also taken from both sides of the liquid droplet during evaporation.

**Experimental details**

**Materials and Methods**

The customised contact angle goniometry set up in Chapter 4.1 (in Figure 1) was used for the contact angle measurements under the following conditions : \( T = 21-22 \, ^\circ\text{C}, \, RH = 31-32 \% \). Stopwatch was used to monitor the kinetics of evaporation of colloidal drops of silica nanoparticles and water. Glass substrate was sputtered with a coat of Au-particles under vacuum using the sputter coater( EMITECH K550X) instrument under the following
conditions: for Au-sputtered glass surfaces - Current = 25 mA; t = 2 s; vacuum pressure = 1 x 10^{-1} mbar; grain size deposition for Au-particles ~ 15 nm. Glass surfaces were blown under high-pressure N₂ flow gun for 2 mins, which was followed with deionised water (100 mL) in an ultrasonicating bath for 30 minutes and followed by rinsing again in deionised water (100 mL) and drying under nitrogen for over 5 mins. All liquid drop volumes used for the contact angle measurements had a constant volume, V = 1 µL, used either as 1 µL drop of deionized H₂O or a drop of silica nanoparticles solution. The sessile-drop technique was used for the measurement of the contact angle and also used to follow the kinetics of evaporation for all glass surfaces.

Evaporation of liquid droplet on glass surface
On the glass surfaces (non-coated and sputtered coat with Au), 1 µL drop of liquid (H₂O and and 3 wt. % concentration of silica nanoparticles) was carefully dispensed on the substrate surfaces and then allowed to evaporate under a covered styrofoam box. The image software was used to calibrate the stage with a thin ruler and the contact angle of both sides of drop was captured after every 20 s during evaporation. The data was then analysed to measure the perimeter and height of the drop.

Results
Analysis of the spherical cap approximation of a liquid droplet during evaporation on a flat plane
The four macroscopic parameters that influence the motion of fluid on a glass substrate include: (1) volume of drop, V (2) radius of wetted spot, r; (3) contact angle, θ, between the liquid and solid at the three phase contact line and (4) gravity effects as noted by this reference [21].
Geometrically, the spherical cap approximation that a liquid droplet assumes on a flat plane is hemispherical in shape, so that the height of the sphere is equal to the radius (depicted in Figure 1b).

For spherical cap approximation (h = r),

\[ h_o \rightarrow h_t \sim r_o \rightarrow r_t \]  \hspace{1cm} (2)

Here, \( h_o \), \( h_t \) are the initial height and height of drop after time \( t \) and \( r_o \), \( r_t \) are the initial radius and radius of drop after time \( t \), respectively during evaporation.

Due to surface interaction forces, roughness, evaporating flux, and concentration of colloidal particles in solution, particle deposits may behave differently from different surface conditions. So that, the spherical cap approximation during evaporation is modified to

\[ r_o \rightarrow r_t \sim \frac{h_o}{r_o} \sim \frac{h_t}{r_t} \]  \hspace{1cm} (3)

Previously shown elsewhere in the literature [1] is that the evaporation rate of a sessile drop (H\(_2\)O) resting on a solid (glass) surface is found to depend on the radius of the liquid-solid interface and was found to remain constant but that the drop volume decreases as the contact angle decreases at ambient temperature. The spherical cap approximation is the aspect ratio of the droplet shape (that is, the ratio of height to radius). Since the base radius is constant (or infinitesimal), the value of the height during evaporation can be substituted for the base radius.

Again, since the volume of a spherical cap drop is

\[ V = \frac{2}{3}\pi r^3 \]  \hspace{1cm} (4)
the volume $V$ of a drop of liquid left on the surface within the spherical cap approximation at time $t$ during evaporation is given by approximation:

$$V = \frac{2}{3} \pi \frac{h^3}{r^3} \times 1 \text{ mm}^3$$  \hspace{1cm} (5)

The graph profiles in Figure 2 show the estimated volume of liquid drop with respect to the drop’s shape (calculated as the aspect ratio of drop) that is left on the glass surface during evaporation. During evaporation, H$_2$O molecules that leave the surface may experience frequent collision with less energetic H$_2$O molecules on the surface so that the estimated volume is affected by the vapour pressure, atmospheric pressure and molecular weights of surrounding vapour and air. As illustrated by the models in Figure 1a and b, evaporation process proceed with the slow collapse of the drop’s height during which the aspect ratio ($h/r$) increases as time $t$ increases and volume of H$_2$O decreases.
Fig. 1. a. The schematic illustration of the partial wetting of a liquid droplet (spherical cap approximation). b. Geometrical shape of the liquid droplet.
Fig. 2. Time dependent plot of the volume of a liquid droplet during the confined evaporative route: 1 µL drop of H$_2$O and 3 wt. % SNP solution on: a. uncoated glass surface, b. Au-coated glass surface at ambient temperature.

The rate of volume of drop left on the surface was estimated using the differential calculus as

\[
\frac{dV}{dt} = \frac{dV}{dr} \times \frac{dr}{dt}
\]  

(6)

where \( \frac{dV}{dr} \) from equation 4 is

\[
\frac{dV}{dr} = 2\pi r^2 = S
\]  

(7)

\( S \) is the surface area of the spherical cap approximation. During the evaporation process, there was no significant change in the base diameter of water droplet applied to the
uncoated surface (the result is supported by reference [1]), but a significant change was recorded when the solvent was replaced with SNP drop, with the ocassional increase and decrease in base diameter with time. However, for the Au-coated surface, significant changes were observed for both the solvent and SNP drops, with a decrease in base diameter with time t. So that the base radius of water drop change ($\frac{dr}{dt}$) is constant on uncoated surface but is significant for a Au-coated surface. Thus, the integration of equations 6 and 7;

\[ \int_{t_i}^{t_f} dV = AS \int_{t_i}^{t_f} dt \] (8)

\[ (V_f - V_i) = AS (t_f - t_i) \]

\[ R_v = \frac{V_f - V_i}{t_f - t_i} = AS \] (9)

where $A, S$ are rate of change of base radius at the contact line and surface area of the drop respectively. Therefore, the rate of change of drop volume ($R_v$) of H2O that remains on the uncoated and coated surfaces when different liquid drops are applied within the spherical cap approximation during evaporation is summarised below:

**TABLE 1. WATER RETENTION ON THE SURFACE**

<table>
<thead>
<tr>
<th>Liquid drop</th>
<th>Substrate type</th>
<th>Rate of change in drop volume (mm$^3$ s$^{-1}$) x 10$^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>Non-coated</td>
<td>5.0</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>Au-coated</td>
<td>1.6</td>
</tr>
<tr>
<td>SNP</td>
<td>Non-coated</td>
<td>9.0</td>
</tr>
<tr>
<td>SNP</td>
<td>Au-coated</td>
<td>2.0</td>
</tr>
</tbody>
</table>
The table shows that \( \text{H}_2\text{O} \) retention on the surface remains higher on non-coated surface than the Au-coated surface during evaporation. This study provides clarity on the prediction of flow behaviour of liquid droplet on the surface, that is those due to surface chemistry and surface topology [22]. The two substrates used here are examples of high energy surfaces, which in the presence of air and under any of the following polar interactions: ion-ion, ion-dipole and dipole-induced dipole, are expected to influence the surface chemistry [23,24]. The high water retention on the non-coated surface suggests that \( \text{H}_2\text{O} \) interaction with the uncoated surface is stronger than the Au-coated surface. This may invariably influence the surface topology, which in fact may explain why nanostructured surfaces of silica microwire fabricated on non-coated surfaces have occasional structures made up of aggregated particles and random networks.

**Conclusion**

The spherical cap approximation of a liquid droplet on two types of surfaces have been analysed using the sessile drop method. The analysis shows that the base diameter of water droplet on non-coated glass surface remained constant but the Au-coated surface had significant changes for both the solvent and SNP drops during evaporation. In conclusion, the surface conditions give the direction of molecular structuring in fluid flow as previously pointed in this reference [23]. The glass surface that was not coated had high water retention, which resulted in mostly random packing arrangement on nanostructured surface of the microwire. However, the Au-coated glass that had less water on the surface produced uniform, crystal-like packing of hcp/bcc arrangement on nanostructured surface of the microwire (SEM micrographs: see Chapter 4.2). Thus, the study validates earlier experiment
in chapter 4.2 that the behaviour of fluid flow involving liquid droplet within the spherical cap on a gold-coated surface can be controlled.

References


Chapter 4.4

Fabrication of silica microwires on an Au-coated surface below the ambient temperature

Introduction
The study on evaporation of drops has received considerable interest by many researchers, examples are the few references that highlight the recent advancements [1-5]. In particular, there have been extensive discussions toward understanding the underlying physics. Deegan et al. [4] first attributed the observed phenomenon to be caused by induced capillary and convective flow within a drop fluid. It was suggested that particles are initially dispersed over the entire drop to later become concentrated around the perimeter, referred to as the coffee ring stain. In addition, the type of particle that remains adhered to the surface upon evaporation depends on the mode of evaporation.

During the evaporation of a colloidal droplet on a substrate, the solute particles in solution remain attached to the glass surface so that only water molecules are evaporated from the bulk solution. Depending on the evaporative route taken, the nature of solid surface, the rate of evaporation of H_2O, nature of interacting forces present in solution and on the solid surface, the mode of particle deposits may give rise to a variety of patterns on the surface. Some of the methods use for depositing particles on the surface have been discussed in this reference [5] and include: 1. Thermal maragoni flows, 2. Concentration maragoni flows, 3. Control of contact-line motion, 4. Patterned substrate, 5. Solute crystallization, 6. Interfacial bulking and 7. Particle shape.
This section investigates the fabrication of colloidal nanoparticles suspension into silica microwires at \( T = 0 \, ^\circ\text{C}, 5 \, ^\circ\text{C}, 10 \, ^\circ\text{C}, 15 \, ^\circ\text{C} \). The aim of this Chapter is to understand the nanostructured surfaces of different microwires fabricated at ambient temperature and cold temperature range on Au-coated surfaces.

**Experimental details**

**Materials and Methods**

The apparatus and procedure used in carrying out substrate characterisation before controlling the self-assembly processes were described in detail in Chapters 4.1 and 4.2. Glass substrate was sputtered with a coat of Au-particles under vacuum with the sputter coater (EMITECH K550X) instrument under the following conditions: for Au -sputtered glass surfaces – Current = 25 mA; \( t = 2 \, \text{s} \); vacuum pressure = \( 1 \times 10^{-1} \, \text{mbar} \); grain size deposition for Au-particles ~ 15 nm. All glass surfaces were blown under high-pressure \( \text{N}_2 \) flow gun for 2 mins, which was followed with deionised water (100 mL) in an ultrasonicating bath for 30 minutes and followed by rinsing again in deionised water (100 mL) and drying under nitrogen for over 5 mins.

**Evaporative Process**

1 \( \mu \text{L} \) drop of silica nanoparticles (SNP) with diameter, \( \sim (20-30) \, \text{nm} \) at concentration (3 wt. %; pH= 9 with \( \text{NH}_4^+ \) counter ions) previously sonicated for 1hr was carefully dispensed on the Au-coated substrate surface, and allowed to evaporate under a covered Styrofoam box. Here, the self-assembly of SNP was carried out in a controlled chamber, as depicted in Figure 1. Table 1 shows the dew point range recorded at different temperatures.

**Results and discussion**

Condensation is a serious problem during fabrication of silica microwires at the cold temperature conditions. Condensation leads to the formation of liquid droplets on the cold
surface, so that if the substrate surface, surrounding environment and humidity conditions are not controlled, the effect may lead to the image depicted in Figure 1- the formation of tiny liquid droplets on glass surface but no microwires.

To correct these anomalies, the glass surface was coated with Au particles as in the previous experiments. The reason is that Au surface has a low water retention during evaporation (see Chapter 4.3). This is ideal for production of microwires on cold surfaces. The humidity-controlled chamber (in figure 2) was used to fabricate the microwires shown in Figure 3. The humidity-controlled chamber consists of a. internal fan, kept the place dry. b. regulated temperature and dew point conditions. c. styrofoam box, minimised airflow from fan. d. flat wooden plank additionally ensured an air-dried region. There was no dew point recording for microwires fabricated at 0 °C because the chamber was dried for one hour before the SNPs drop (V = 1 µL) was placed in the chamber. Table 1 shows the dew point and varied temperatures of the microwires.

TABLE 1. DEW POINT AT VARIED TEMPERATURES

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>D.P (%)</td>
<td>0*</td>
<td>29-30</td>
<td>15-16</td>
<td>13-15</td>
</tr>
</tbody>
</table>

T- Temperature; D.P- Dew point.

The D.P ranges were the values recorded in the chamber during the fabrication of microwires. The volume of colloidal SNP was also very small (1 µL). The D.P value reflects the amount of water vapour present in the chamber.

* No D.P value recorded in the chamber when the temperature reading was set at 0 °C.
Fig. 1. Pixelated image from condensation of a drop of colloidal solution of silica nanoparticles ($V = 10 \, \mu$L) at 0 °C during evaporation process in the lab using a previous Peltier set-up. (Glass is non-coated here).

Fig. 2. The chamber for the fabrication of silica microwires at ($T = 0, 5, 10, 15$ °C). Loading and removal of each sample was carried out by opening the circular valve of the chamber (top right). This ensures that the temperature and dew point are not affected considerably.
Fig. 3. SEM images of the microwires produced in the cold temperature range. Most of the wires blown off during transfer. The regions numbered (1-3) show the regions examined for the packing configuration of the all the wires and the regions statistical data were drawn.

Enlarged images with the scale bars are shown below:
Figure 3 show microwires of varied size dimensions produced at the different temperatures. The formation of these microwires in the cold temperature conditions suggest that nanoparticles have different cooling rates, which tends to affect the motion of fluid on the surface. Consequently, the cooling rate also affects the rate at which solvent lost at the perimeter of the drop is replaced by the liquid within the drop, known as capillary action. Additionally, the delayed response of H2O taken up at the cold temperature may also affect the way microwires are produced upon drying. The results show uniform wires at (0 °, 5 °C) and tapered microwires at (10 °, 15 °C). The circled regions (in black colour) show the direction for the colloidal dispersal of nanoparticles. At 0 ° and 5 °C, colloidal dispersal of fluid seems to produce long and thinner microwires, but as the temperature increases, the circled region becomes more central so that wires eventually become tapered wires at 15 °C. The different circled region suggests the direction of fluid flow inside the drop kept changing at the different temperatures.

Figure 4 shows SEM images of microwires captured at the regions of interest (ROI): 1, 2, and 3 (indicated at the top-left hand image in Figure 3). The regions show nanoparticles arrangement on the microwire surface. The SEM micrographs of these microwires show nanoparticles cluster followed by boundary network on the entire nanostructured surface. Here, the nanostructured surface produced a different structural arrangement below ambient temperature. The nanoclusters consist mostly of bcc/hcp packing, and tetrahedral strains may be the cause for losing hcp/bcc clustered structures in certain regions than others.
Fig. 4. SEM micrographs of clustered hcp/bcc packing of self-assembled silica microwire structures having continuous boundary networks produced on Au-sputtered surface in the cold temperature range compared with the nanostructured arrangement of microwire fabricated at ambient temperature.

The bar graph represents the statistical data for twenty measurements of the diameters of the clustered particles (hcp/bcc not deformed) at the three different locations on the microwire surface. At 0 °C, the different regions showed effective mean sizes (~150 nm), indicating that the nanoparticles were uniformly distributed during the evaporative process. The same size was measured for SEM micrograph at 10 °C, but at 5 °C, the clustering sizes of hcp/bcc packing increased from regions 1 to 3 (100-130) nm. At 15 °C, there was no more symmetry, but more of random packing in all the regions. These variations in structural packing of microwires suggest that hcp/bcc packing may depend on the dew point (D.P) values (Table 1).

![Bar graph of clustered regions of hcp/bcc packing structures of silica microwire in the cold temperature range. DEG- (° C).](image-url)
Conclusion
On Au-coated surface, the trend observed is that microwires go from being thinner to taper when the temperature increases. But the clustered packing configuration into hcp/bcc depends on the D.P. Overall, the optimal conditions for fabricating microwires below ambient temperature is at 0 ° C (completely dry chamber) The study confirms that there is a structural difference difference between microwires fabricated at ambient and below ambient temperatures. These two methods of fabrication (cold and ambient temperatures) shows that the nanostructured surface can be fine-tuned to give functions to the microwires, and in general, to the nanostructured surface of a colloidal dispersal of silica nanoparticles upon drying on a substrate surface. At this stage, the origin of the boundary network is unknown. In addition, some of the condensation theories in these articles [6-9] are largely conjectural. Hence, the reason for introducing an imaging tool: 3-D-Phase Contrast Variation to trace the origin of the boundaries and the structural differences of microwires fabricated at different temperatures, discussed in the next chapter (Chapter 4.5).

References


Chapter 4.5
Understanding the structural networks in silica microwires with a 3-D-Phase Contrast Variation Tool

Introduction
The phase contrast method is a tool use for extracting information processed by optical sytems. It is produced as either a two-dimensional (2-D) or three-dimensional (3-D) object recognition [1-8]. This technique is mostly used in digital holography. The hologram is produced by capturing the image of an object as a photographic recording, then a 3-D object image is reconstructed numerically. Similarly, the SEM image obtained as a micrograph on the TV scanner can be reconstructed using an image J software [6]. The software is developed with multifunctional features to display, edit, analyse, contrast, and process digital pixels as a two-dimensional array of small integer numbers of colour palette sizes [10]: $2^3$-8 bit; $2^4$-16 bit; and $2^5$-32 to reflect the bit colour of the file formats. Unfortunately, SEM micrographs commonly come in eight bits (8-bit), which is the default setting for all the images reported, and on the colour-depth chart, is classified as an 8-bit grayscale digital image. This means that each pixel represented is a single sample image made up of intensities of shades of gray. On the gray band scale, black is represented as having the weakest intensity, and white the strongest intensity. Quantitatively, black and white regions are standardised as 0 and 1 respectively, with the possibility of any number between 0 and 1[10].

Digital Image Analysis Method
Two image analysis levels have been adopted. The first image analysis is pattern recognition using exploratory data analysis. The mathematical approach to this method is in reference to [1]. The pattern recognition divides the image data according to colour palette size (to
distinguish between black and white colour mode) (contrast stage). Here, the pattern of the original image is not affected even though the contrast has been changed. The image contrast is replaced with black-white [B (0) W(1)] intensity, also equivalent to the pixel colour mode-8 bit colour palette size.

The second level is the reconstruction of the recognised pattern. This involves a phase inverse of B(0)W(1) to W(0)B(1) and a filter mode channel converts it to variance, either as 2-D or 3-D, the colour palette size changes from 8 to 32-bit mode. The mathematics are not clearly understood, but a close mathematical expression has been discussed in references [4, 5].

The aim of this chapter is to understand the structural differences of nanostructured surfaces of microwires at different temperatures, specifically at ambient and cold temperatures. Another area of interest in this section is to propose a theory of the origin of the boundary network, which is different from crack due to stress. This chapter may be considered as a follow up study of the experimental section of chapter 4.4 : fabrication of silica microwire on an Au-coated surface below the ambient temperature. Figures 1-3 demonstrate the steps taken to obtain a 2-/3-D phase plot of a nanostructured surface of silica microwire.
Fig.1. SEM micrograph of nanostructured surface of a silica microwire produced on an Au-sputtered surface at 0 °C. The micrograph section represents the second region after the coffee-region, usually characterized by large, distinctive, patterned structures.
Fig. 2. Stages involved in digital image analysis of Figure 2 to a 2-D Phase Contrast Variation.
Fig. 3. Digital image analysis of Figure 2 to a 3-D Phase Contrast Variation. This is a three-step process. In a 3-D PCV, information of the network structures that are beneath the surface can also be recognised as well.

Evidence: A 3-D-Phase Contrast Variation tool to distinguish the nanostructured surfaces of microwires produced at different temperatures – semblance with rope / mesh images

Figure 4 shows different nanostructured surfaces of microwire produced from evaporation of colloidal dispersal of liquid droplets of silica nanoparticles on glass surfaces. The illustrative pictures shown beneath are similar architectures (rope/mesh) taken from the Shutterstock web site, reference [9].

Figure 4a shows the micrograph section of a nanostructured surface of a microwire produced at ambient temperature on an Au-coated surface. The phase contrast (2-D) of the boundary
network shows a highly compact nanostructured surface and the illustrative picture is similar to a dense mesh surface (DENSE-MESH PATTERN).

Fig. 4 (i). Nanostructured surface of microwire with a DENSE-MESH PATTERN.

Figure 4c shows the micrograph section of a nanostructured surface of a microwire produced on an Au-coated surface below ambient temperature. The phase contrast (2-D) shows an open-cross boundary surface (OPEN-CROSS-ROPE PATTERN). This open-cross rope
pattern surface was the boundary network found on all nanostructured surfaces of microwires fabricated below ambient temperatures in chapter 4.5.

Fig. 4(ii). Nanostructured surface of a microwire with an **OPEN-CROSS-ROPE PATTERN**.

Figure 4e is the micrograph section of the nanostructured surface of microwire occasionally produced at ambient temperature on a non-coated glass surface (Sail Brand). The phase contrast (2-D) shows a boundary network of a dense interwoven basket surface (**DENSE-INTERWOVEN BASKET PATTERN**). Unlike the other two surfaces above, the dense-interwoven pattern surface is not reproducible but comes up occasionally during transition.
re-arrangements of nanoparticles at slightly elevated temperature above the ambient temperature. This is also possible at ambient temperature on sail brand glass surface.

![Fig.4 (iii). Nanostructured surface of a microwire with a, DENSE- INTERWOVEN, BASKET PATTERN.](image)

**Conclusion**

The main objective of this section was to use an additional analysing imaging tool to recognise the phase patterns of nanostructured surfaces. The basic principle is using the tool to reconstruct a recognised pattern.

For microwires fabricated on Au-coated surfaces below ambient and ambient temperatures, two recognised patterns have been identified. 1. Nanostructured surfaces that have dense-
mesh boundary patterns at ambient temperature. 2. Nanostructured surfaces that have open-cross-rope boundary patterns. These two patterns are reproducible.

Based on the current findings from these studies (chapters 4.3 to 4.5), the following arguments are summarised: 1. metastable states may exist in silica nanoparticles rearrangements upon evaporation from the glass surface; 2. the particles of these metastable states may be smaller than the average nanoparticle size (<< $\phi \sim 20-30$ nm). 3. below ambient temperature, capillary lines may split into dendritic microchannel pots, used for maintaining the new confined domains- metastable configuration; 4. Also below ambient temperature, surface tension increases, causing the moving fluid to decrease and the force of adhesion between the drying droplet and Au-coated surface increases. The capillary process involves the transport of water to the edge of the droplet, so that the delay forces the fluid to permeate into the spongelike boundary network at the Au-coated surface to create microchannel pots; and through intermolecular forces, nanoparticles within the confinements come together to form the metastable configuration state. Conversely, above ambient temperature, surface tension decreases, so that there is a decrease in the adhesive interaction of the liquid at the Au-coated interface, causing moving liquid to move rapidly from inside of the fluid drop to be replaced at the edge of the drying drop.

References


Chapter 4.6

Preliminary studies of protein integration into mesostructured glass, fabricated by controlled self-assembly of silica nanoparticles

Introduction

Most biological molecules such as lyophilized monoclonal antibodies are unable to stay outside their non-native environment over a period of time because they get denatured to the non-native structure of a lyophilized cake [1]. It has been shown in the literature [2-6] that sugar solution helps the protein to be stored in the glass matrix state. An alternative approach reported in the literature is the spray-drying method which involves a tedious process where the optimal storage for protein stability was recorded at 40°C within the glassy matrix state [1]. Other possible methods involve the sol gel method. The disadvantage with this method is that the organic precursors use in the formulation may adversely affect protein stability.

Here, it is proposed that the integration of silica nanoparticles with protein upon evaporation may provide an insoluble host in water, and the problems with charging of the surface is also avoided at the same time. In addition, the glassy-matrix structure of silica microwires may potentially insulate the environment and makes it possible to extend the thermal performance well beyond what was previously reported.

The aim of this experimental section was to optimise the favourable condition that allows for protein integration into uniform and stable mesostructured glass. The materials that were used include: Protease protein (PRO) from Bacillus licheniformis was obtained as type VIII, lyophilized powder; D-(+)-trehalose dihydrate (TRE); anhydrous D-(+)-glucose and colloidal suspension of silica nanoparticles (SNP).
Experimental details
Materials and Methods
The apparatus and procedure used in carrying out the substrate characterisation before controlling the self-assembly processes have been described in previous experimental sections. Briefly, glass substrate was sputtered with a coat of Au-particles under vacuum using the sputter coater (EMITECH K550X) instrument under the following conditions: for Au-sputtered glass surfaces – Current = 25 mA; t = 2 s; vacuum pressure = 1x $10^{-1}$ mbar; grain size deposition for Au-particles ~ 15 nm. All glass surfaces were then blown under N$_2$ continuously for 2 mins to ensure that surfaces were thoroughly clean. The drop volume was kept at a constant volume, $V = 1 \mu$L of silica nanoparticles (SNP) colloidal solution ([SiO$_2$] = ~ 3 wt. %, diameter, ~ 20-30 nm). Additional materials used are described. The enzyme, Protease (PRO) from Bacillus licheniformis was a gift from Dr Shane Wilkerson in the School of Chemistry, University of Sydney. The Protease protein is from Sigma-Aldrich, obtained as type VIII, lyophilized powder. D-(+)-trehalose dihydrate (TRE) was obtained from the service department in the School of Chemistry, University of Sydney. The sugar (TRE) also obtained from Sigma-Aldrich. Anhydrous D-(+)-glucose was obtained in Professor Maxwell Crossley laboratory in the School of Chemistry, University of Sydney. The glucose was obtained from Sigma-Aldrich. All sample solutions used as stock were dispersed in deionised water at the following concentrations by weight fraction : PRO (~ 0.1 wt. %) and TRE (~ 95 wt. %). The stock solutions were further diluted with deionised H$_2$O, so that the final concentrations used for liquid droplet in the self-assembly process were : PRO (~ 0.05 wt. % ) and TRE (3.3 wt. %). Again, the volume of liquid droplets added onto each layer was, $V = 1\mu$L for each sample drop (Figure 1). The initial stock concentrations of D-(+)-glucose and SNP by weight fractions were
99.7 wt.% and 3.3 wt. % respectively (Figure 1). The final concentration that was mixed by
glucose and SNP.

![Diagram of multicomponent additions](image)

Fig.1. The schematic illustration of the multicomponent additions of different solutions added on top of each other. The glass substrate has an Au-coated surface (BLUE = SNP, Green = PRO, Orange = TRE).

After adding the different drops onto each other on an Au-coated glass slide, each batch was then covered with styrofoam boxes as in previous experiments reported in chapters 4.2 to 4.4, and then allowed to evaporate at ambient temperature. The styrofoam was covered almost completely, with only a small opening that was ~ 2 cm x 2 cm in dimensions.

**Results and discussion**

Various strategies for optimising glassy-matrix structure (either 2 or 3-component systems that contain drop of colloidal suspension of silica nanoparticles as one of the components) have been considered in this section. At the beginning of the experiment, D-(+)-glucose was added into the colloidal suspension of silica nanoparticles so as to study the possible outcome of the drying droplet upon evaporation. For $V = 10 \mu$L droplet containing D-glucose/SNP additions (33 : 1) by wt. % fraction that was left to evaporate on the surface at the laboratory temperature (22 °C) produced tapered microwires. The nanostructured surface of the microwire was similar to the open-cross rope pattern described in chapter 4.5.
(also see appendix 4C for the nanostructured surface). When some of the microwires were dissolved in deionised water (200 µL) for 24 hrs, the wires remained insoluble. The water that remained after the wire was removed was tested for the presence of glucose using osazone test, which is the reaction of D-glucose solution with excess phenyl hydrazine to give glucose phenyl hydrazone. It is expected that the crystallization of the product should produce bright intense crystals. But the solution that was left on the shelf for more than a week showed no observable change to confirm the presence of glucose. However, when the same droplet volume, \( V = 10 \) µL containing D-glucose/SNP additions (33 : 1) by wt. % fraction was covered, multiple nucleation growths inside the drying drop emerged. Several weeks later, the nucleation growth produced a hierarchical assembly structure of glucose-silica nanoparticle material (see figure 2) known as the Ostwald ripening process [7-9]. The process is based on the effect of a finite volume fraction of coarsening behaviour of two-phase systems. This coarsening behaviour involves spontaneous particle ordering: dependent on size distribution function and cluster expansion. As a result, the effect causes competition and distribution among droplets to broaden and to increase the coarsening rate. In addition, the mechanism describes a thermodynamically-driven spontaneous process that energetically favours the nucleation growth of larger ones on the surface over smaller ones that are embedded in the coarsening phase. So that thermodynamically, larger particles on the surface are less stable than the smaller ones that are embedded. This experiment is appropriate for future studies.
Fig. 2. Optical micrographs. Stages in the self-assembly of D-glucose/SNP mixture (33: 1) by wt. % fraction. Droplet volume, $V = 10 \mu$L was covered. Stages: 1 = development of a thick coffee-ring pattern; 2 to 3: multiple nucleation growths within the coffee-ring border; 4 = matured nucleation growth (Ostwald ripening process) surrounded by smaller nucleation growths; 5 to 7 = multiple coffee-ring borders; 8, 11 and 12: ripening of coffee-ring structures; 9, 10 = emergence of new coffee-ring growth within the old coffee-ring structures.

Enlarged images with the scale bars in Figure 2 are shown below:
Trehalose, a dissacharide and a non-reducing sugar on the other hand has been documented for use as cryoprotectant[10-12], freeze-drying reagent [13-15], used to limit phase transition [16, 17] and as protein and lipid stabilizer [18-20]. The subsequent experiments therefore involved multicomponent additions of silica nanoparticles suspension (SNP), trehalose (TRE) solution and protease enzyme (PRO), except one, where all 3 components were added onto each other. Further, SNP droplet was dispensed as the first component on the Au-coated glass slide.

The dynamic light scattering (DLS) instrument was used to measure the effective average size distribution (Z) and polydispersity index (PDI) of the multicomponent mixtures of silica nanoparticle and trehalose specified as SNP_TRE; trehalose and protease enzyme as TRE_PRO and silica nanoparticles, protease enzyme and trehalose additions as SNP_PRO_TRE. The DLS parameters used for the measurements include, a laser light source; wavelength, $\lambda = 600$ nm at a fixed scattering angle, $\alpha = 173^\circ$.

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### Z-AVERAGE vs PDI OF VARIOUS SAMPLES

<table>
<thead>
<tr>
<th>Samples</th>
<th>Z-Average (nm)</th>
<th>Polydispersity index value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNP_TRE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SNP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TRE_PRO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SNP_PRO_TRE</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Fig. 3. The schematic illustration of the multicomponent additions of different solutions. The glass substrate has an Au-coated surface (BLUE = SNP, Green = PRO, Orange = TRE).

Figure 3 shows the bar chart of the PDI of the multicomponent mixtures versus their average particle sizes. All measurements were performed in a temperature-controlled chamber at 25 °C. The PDI values show that the component mixtures have moderate association in the mixture, but are neither monodispersed (homogeneous) nor have broad distributions. The Zeta Average size in this respect measures the apparent size adopted by the solvated component mixtures and for SNP, is the mean size distribution of silica nanoparticle.

Figures 4 to 6 show that the SEM images of the drying drops and micrographs of their nanostructured surfaces differed considerably. Also, the SEM images show interaction regions, that indicate possible active sites on those spots (circled regions).

Fig.4. The SEM image and micrographs obtained from the self-assembled addition of colloidal suspension of silica nanoparticles and protease enzyme at (60: 1) by wt. % ratio.
Enlarged images with the scale bars for the SEM micrographs shown below:
Figure 4 shows the probable interaction regions, depicted as 1 and 2 in the enlarged images shown above. The SEM micrograph of region 2 shows uniform doped microwires with well-ordered hcp/bcc packing configuration, also shown are interstitial volumes that spread across the surface. A similar nanostructured surface was obtained in region 1 for the same figure (not shown). In addition, the protease enzyme interaction with silica nanoparticles may have more than one matrix form: “crystalline or glassy-matrix states”. In the crystalline matrix form, the self-assembled structure is expected to break easily in deionised water with ultrasonication method while the glassy amorphous (ordered) structure is expected to be insoluble. The reversible phase of the doped nanostructured material in water using ultrasonication method is part of the future studies.
Fig. 5. The SEM image and micrographs obtained from the self-assembled addition of colloidal suspension of silica nanoparticles and trehalose at (1: 1) by wt. % ratio. Enlarged images with the scale bars for the SEM micrographs shown below:
Figure 5 also shows the probable interaction regions, depicted as 1 and 2 in the enlarged images shown above. Here, the presence of trehalose interaction with silica nanoparticles without the protease enzyme resulted in “flaky” surface depicted in region 1. Furthermore, the spinodal arrangement of nanoparticles depicted in region 2 has been the consistent nanostructured feature observed for all silica microwires assembled with sugar mixtures, either as glucose or as trehalose. Spinodal arrangement has been dealt with in Chapter 4.2 and well-illustrated in the results contained in Chapter 4.4.

![Figure 5](image)

**SNP_PRO_TRE**

*(60 : 1 : 60) by wt.%*

Fig. 6. The SEM image and micrographs obtained from the self-assembled addition of colloidal suspension of silica nanoparticles, protease enzyme and trehalose at (60: 1: 1) by wt. % ratio.
Enlarged images with the scale bars for the SEM micrographs shown below:
Figure 6 consist of all the three components in the addition, that is, colloidal suspension of silica nanoparticles, protease enzyme and trehalose. The microphase separation of the drying droplet mixture (regions 1 and 2) differed in microphase from Figures 4 and 5 and the SEM micrograph of the nanostructured surface of the material shows the same spinodal arrangement as in Figure 5.

Table 1 shows the summary of the parameters used to evaluate the regions circled. The table shows interaction level of different additions. SNP_PRO (Figure 4) used the most interaction volume space. The addition produced microphase separation that was symmetrically positioned and SNP_PRO_TRE used the least interaction space that produced microphase separation that was asymmetrically positioned (Figure 6), and the same goes for SNP_TRE (asymmetrically positioned) (Figure 5).
Furthermore, SNP_PRO produced uniform mesostructured glass of lowest close packing configuration of hcp/bcc with average pore sizes - 5-6 nm, while the other mixtures at this stage could be regarded as having packing configurations that are metastable going by the N values, which represents the number of particles involved in the close packing arrangements. Here, it is proposed that the packing might be a collection of hcp and bcc close packing oriented in different directions in the matrix structure.

**TABLE 1. SUMMARY OF THE PARAMETERS USED TO EVALUATE SELF-ASSEMBLED ADDITIONS OF DIFFERENT SOLUTIONS**

<table>
<thead>
<tr>
<th>Drop mixture</th>
<th>$d_1$ (μm)</th>
<th>$d_2$ (μm)</th>
<th>$d_\text{pr}$, $d_\text{pr}$ (μm)</th>
<th>$S_\text{eff}$ (%)</th>
<th>$\phi_\text{pr}$ (nm)</th>
<th>$\phi_\text{cls}$ (nm)</th>
<th>N</th>
<th>Packing type</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNP_PRO</td>
<td>78</td>
<td>370</td>
<td>534,(86)*</td>
<td>83</td>
<td>16 ± 4</td>
<td>127 ± 6</td>
<td>8</td>
<td>hcp/bcc</td>
</tr>
<tr>
<td>SNP_PRO_TRE</td>
<td>69</td>
<td>192</td>
<td>785,(524)b</td>
<td>33</td>
<td>9 ± 3</td>
<td>133 ± 6</td>
<td>15</td>
<td>§Random</td>
</tr>
<tr>
<td>SNP_TRE</td>
<td>145</td>
<td>245</td>
<td>570,(180)c</td>
<td>68</td>
<td>13 ± 6</td>
<td>127 ± 9</td>
<td>10</td>
<td>§Random</td>
</tr>
</tbody>
</table>

$d_1$, $d_2$ Diameter of small and Large interaction regions respectively; $d_\text{pr}$, $d_\text{pr}$ Total diameter of included region possible for interaction and diameter of the region excluded for interaction, respectively.

$a,b,c$ The values in brackets show the excluded space not used.

$S_\text{eff}$ (%) Interaction space between the different liquid droplets; $\phi_\text{pr}$ Particle size; $\phi_\text{cls}$ clustered particle size used for close packing.

* The error values show the variation of the different particle sizes. Absolute error formula was used for $\phi_\text{pr}$ and $\phi_\text{cls}$.

N Number of particles used for close packing.

§ Metastable glass transition states

**Conclusion**

The addition of multicomponents systems of liquid drops using edge-to-edge contact upon drying on a glass surface can be used to generate microphase structures. The three multicomponents systems produced two microphase regions indicated by the circled regions
(regions 1 and 2). These regions have been suggested as the probable site for protease enzyme (as depicted in Figures 4 and 6). Table 1 was used to evaluate the best protein storage condition. Introduction of trehalose in the binary addition or multicomponent addition has also been observed in this work to limit microphase separation.

However, the objective of this work was to explore an alternative approach for protein storage using colloidal suspension of silica nanoparticles as the principal component in the mixture. From the different additions used, SNP_PRO produced a highly uniform structure, which as suggested may be in the crystalline matrix form or the glassy (ordered) matrix forms. The next question to address is wether the matrix form can be seperated using ultrasonication method. If it is reversible, it means that protein can be regenerated from the assembled structure. And if it irreversible upon sonicating the microhase structure in water then it means that it is in the glassy matrix state. Other studies include, the relative stability of the protease enzyme at elevated temperature either in the crystalline-matrix or glassy matrix form.

The ultimate application of this composite matrix structure of protein and silica nanoparticles is the transportation of vaccines to and within countries with high climate temperatures that exceed temperature $T > 45 \, ^\circ\text{C}$. Protease enzyme has been used in this chapter but other protein molecules could also be explored.

References


5. Concluding Remarks and Future Direction

The formation of silica microwires by self-assembly of silica nanoparticles was discovered at the University of Sydney by Naqshbandi, Canning and Crossley et al. Preliminary aspects of this work were published in Nature communications in 2012 [1] and since then, in a number of other papers by the same group.

This thesis work focused on understanding the fundamental issues involved in the self-assembly process - controlling and manipulating drop shapes of colloidal suspension of silica nanoparticles on surfaces to produce uniform self-assembled structures. The surface conditions dictate the direction of molecular structuring during fluid flow. It was therefore imperative at the beginning of the thesis project to understand glass substrate that was likely to give a reproducible surface. The reproducibility of glass surfaces was gauged with the contact angle of water by the sessile drop method. Also in a broader context, the experiments in this thesis, in addition explores studies on the following: evaporation kinetics of a drop of liquid and control on the surface using Au-coated slides to produce uniform silica microwires. Other studies include nanostructured characterization of microwires at different temperatures and integration of protein into silica nanoparticles. Chapters 4.2 to 4.6 include some areas identified for future studies.

The experimental works show that colloidal dispersion of silica nanoparticles for a given drop volume \( V \approx 1 \sim \mu L \) of liquid can be controlled to provide an effective route into uniform mesostructured glass (silica microwires). The success of this approach depends on a number of factors, such as the cleaning method, choice of a glass slide (Au-coated surface), optimal drop volume to add to the surface per unit area, optimal concentration, reducing the amount of air flow and covering the work area in the most efficient way. In the beginning, there was a
follow-up study on room temperature fabrication of silica microwires [1]. Therefore, the first experimental study (chapter 4.1) focused on selecting the microscope glass slide that was likely to give a reproducible surface. The method of cleaning applied on the different surfaces included the physical process of ultrasonication and blowing under high-pressure nitrogen flow gun to remove contaminants from the surface. A “standard cut-off” was used to evaluate a reproducible surface with the least contact angle error obtained by the sessile drop method (shown in figure 2 and table 2 of chapter 4.1).

The second experimental section (Chapter 4.2) looked at nanostructured variance of microwires fabricated from different surfaces. The result shows a reliable way of demonstrating surface control: where Au-coated surface enhanced the spatial ordering of nanoparticles in a more controlled manner, with pore sizes of ~5-6 nm in effective diameter. The scope of application of a well-controlled surface and periodic arrangements of nanoparticles is huge and that includes many areas in biotechnology, nanotechnology, optoelectronics and high-capacity battery banks. Furthermore, in the experimental section (Chapter 4.3), the kinetics of evaporation of a drop of liquid on Au-coated and uncoated glass surfaces show uncoated surface have the tendency to retain water more than the Au-coated surface. However, with less water on the surface during evaporation, there will be faster evaporative process, less time for nanoparticles to form aggregate clumps, uniform dispersion, and less time to interact with the surface; configuration into hcp/bcc arrangement becomes uniform and leads to production of thinner wires or spatially ordered nanostructured surface. The superior flow behaviour of Au-coated surface during the evaporative process and combination of doped electrolytes into \(X\)--(nanoparticles) \((X = Au, Ag, graphite and graphene)\) may have future application as super-capacitors.
Condensation is a serious problem during fabrication of silica microwires at cold temperature conditions, especially when the surface of the microscope glass slide is uncoated. The fabrication of microwires at cold temperature (Chapter 4.4) led to the introduction of a new imaging tool (3-D-Phase Contrast Variation) to characterize the nanostructured surfaces of these wires. The classification includes 1. Nanostructured surface with dense-mesh boundary pattern produced at ambient temperature. 2. Nanostructured surface with open-cross-rope boundary pattern produced below ambient temperature. The two patterns are reproducible. A potential area where the 3-D- phase contrast can be applied is a digitally reconfigurable surface. The 3-D-Phase contrast coverts the SEM micrograph to the reconfigured surface and then uploaded on a compatible digital design. Example is reprogrammable hierarchical designs. Digitally reconfigurable surface may answer the conjectural view on condensation theories, including the arguments raised in Chapter 4.5.

The last experimental section (Chapter 4.6) shows that despite the remarkable nanophase separation from drop solutions added together, it was interesting to observe a highly organised nanostructured surface with SNP_PRO (silica nanoparticles: Protease) ratio addition. At this stage, the crystalline or glassy state of the material still needs confirmation. In addition, it would be interesting to investigate the surface kinetics, especially the activity of Protease in relation to temperature variation.

As technology moves to miniaturization, there is the need to develop smart materials with densely functionalised surface per volume, fast transient time on the surface, highly sensitive surface that can detect and provide surface discriminatory functions with the emission of a characteristic colour for different proteins that comes on contact with the surface device. The paradigm shift will include drastic reduction in sizes of materials, nanostructured
surfaces with high catalytic, ferroelectric, mechanical, optical and magnetic properties. The development of novel materials with such capabilities will definitely usher in unprecedented breakthroughs. Imagine using a microscope glass slide to build a super-charge capacitor or use as temporary energy storage. Imagine turning-off a malignant tumour or proffering safer alternative routes to life-threatening diseases with highly functionalised, nanostructured materials. This research area holds a promising outlook and I am delighted to further new investigations along the following areas explained below:

**I. DEVELOPMENT OF A HIGHLY FUNCTIONALISED, NANOSTRUCTURE STACKED SURFACE TO PRODUCE A SUPER-CHARGE CAPACITOR**

Super-capacitors are polarised devices that process and store a high amount of energy (converted to electrical potential energy) per unit volume than a normal capacitor. For super-capacitors to work efficiently, they must have a high-powered density surface to retain energy per unit (small) volume and very fast transient time to conduct the energy to the next panel. Examples where super-capacitors are useful include to power computers, smartphones and other electronic devices. Currently, the challenges with super-capacitors include a low-terminal voltage (Max. Voltage is best at 2.7 volts), stacking arrangement of cells in series or the need to step up the device with other devices and the very high cost involved at the moment when compared to conventional capacitors.

Proposed in this thesis (Future work) is the use of nanostructured surface to generate stacked panels that have compact surfaces to accommodate a high-powered density surface per unit volume, fast transient response to the next panel, low energy loss and very low cost in terms of design. Structurally, the self-assembly of silica nanoparticles upon evaporation have compact, robust surfaces (hcp/bcc) and low-loss structures. Also demonstrated in the
following studies, chapters 4.2 to 4.4 – that an Au-coated surface can give a highly organized arrangement of silica nanoparticles. By changing the surface coatings of microscope glass slides with Au, Ag, graphite and graphene, and using the bottom-up approach to fabricate mixed nanoparticles into nanostructured surface, my goal would be to build a super-capacitor that has optimal terminal voltage above 2.7 volts. Already, graphene is currently receiving a considering attention as one of the panels component in super-capacitor devices. Graphene reports an operation efficiency of three-order in magnitude than conventional super-capacitors. The efficiency of the different panels is going to be characterized by the calculations obtained from the terminal voltage, power dissipation, current and resistance. The focus of this research is on characterizing the different nanostructured surfaces produced and optimizing the different panels. This area of research is highly interdisciplinary and multidisciplinary approach is essential for its success. My plan in the near future is to collaborate with like minds with requisite skills that are highly creative, energetic and hungry for success in this line of research.

II. MANIPULATION OF NANOSTRUCTURED SURFACE TO ENHANCE PROTEIN DETECTION ON A MICROFLUIDIC OPTICAL CHIP

The aim of this proposed work is to fabricate a glass-enabled chip device as a platform for protein discrimination on the surface. Molecular integration of biological probes into nanoparticles is increasingly receiving much attention as a powerful and sensitive tool for characterizing surface protein. While there have been coming up increasing fabrication methods for protein detection in recent years, quite a few studies have come up with incorporating incompatible materials into optical chips as a possible tool for surface characterization kit. A possible reason is because most fabrication methods require the use of
high temperature, or solubility issue may sometimes be a major hindrance, and consequently limits their use as a detection tool for protein molecules at the surface. With slabs fabricated from silica nanoparticles, not only do they offer an alternative nanostructured surface platform, but also provide robust surface pathways for protein detection on the nanoscale. Therefore, a biocompatible-doped slab with biologically relevant moieties would enable better understanding of such processes.

The surface chemistry of silica is particularly tractable as substrate platform and can be transferred as analysis surface techniques on a microscale. The fabrication of glass or integration with chemical, biological or semiconductor probes (quantum dot) at the macroscale is disadvantageous in many ways; one it requires an unusually high temperature to preform speciality glass (doped) or the process of cutting patterned glass could be very expensive for the top-down patterning process as chips. However, with the self-assembly bottom-up method, which is the process of building a self-assembled block from small units, it would be possible to correct the inherent fabrication problems with glass. Silica slabs can be produced from silica nanoparticles. The slab is then transferred as an analysis tool for microfluidic optical device. This concept therefore provides one of the platforms for the emerging application of integrated microfluidic optical devices.

This project will build on my existing knowledge of fluorescent probes, photochemistry, SEM imaging, and slab fabrication from silica nanoparticles, optical and confocal microscopies. The relevance of this study is that complex protein mechanisms can be potentially studied. The project will therefore involve fabrication, integration, surface characterization of nanostructured surfaces obtained from the self-assembly of silica nanoparticles.
APPENDIX I: STRUCTURAL DEFECTS ON ROUTINELY USED MICROSCOPE GLASS SLIDES: IMPLICATION TO CONTACT ANGLE MEASUREMENTS AND ASSEMBLED SILICA MICROWIRE STRUCTURES

This appendix presents the ancillary images to account for the structural defects that are present on a variety of glass types. The glass slides have been evaluated and compiled as part of the research report in Chapter 4.1.

INTRODUCTION

Routinely used microscope glass slides have defects regions. Investigation of the optical micrographs of glass slides (Figure 3) (SECTION 4.1) revealed two striking features about the surface topography - 1. Substrates I and II had rough edges. 2. Substrates I and II, in particular substrate I, had multiple contour ditches that may plausibly justify the reason behind the large error values. It also explains the reason for the wide variations in contact angle and error values. The summary is in Table 2 (Chapter 4.1).
Figure 1. Micrographs of glass type: 7101 A (Pathology grade) – Substrate II (Group 4A) in section 4.1 of the thesis work. The highlighted regions shows the edge and contour spots on the glass surface.
Figure 2. Micrographs of glass type: 7101-substrate 1 (Group 4A)
Figure 3. Micrographs of glass type: Sure Frost-substrate III (Group 6l)
Figure 4. Micrographs of glass type: Superfrost Ultra Plus –substrate IV (Group 5F)
Given the optical micrographs obtained from the edge of the various substrates, it is clear that the difference between the contact angle values ($\theta_1$, $\theta_2$ in Table 3 of section 4.1 in the thesis, and detailed data in Table 2 in the appendix) exhibited variations in contact angle values of drops form the glass edge with the sessile-drop method. Particularly, substrates I and II showed greater tendencies to have drops that are not reproducible.

While cleaning of the glass slides is critically important, the rough edges cannot be smoothened by chemical methods, consequently results obtained from such glass substrates are not reliable and reproducible. It is for this reason why glass surfaces were screened to get the best glass slide for the self-assembly process in this work. For instance, when surfaces have contours, assembling on such surfaces usually lead to irregular structures and wire variables, which is one of the main challenges of using poor glass slides. For example, below were the SEM micrographs from a pathology grade glass slide (7101 A-Group 4A).
Figure 5. SEM micrographs of glass type: 7101 A (Pathology grade) - substrate II (Group 4A)
Figure 6. SEM micrographs of glass type: 7101 A (Pathology grade) - substrate II (Group 4A)

(a)

Method I: Substrate (I) + sonicated, N2 blown (R = 25 ± 4°)
GLASS TYPE: 7101 - SUBSTRATE I (GROUP 4A)

Substrate I + hot plate dry + acid Piranha solution, sonicated, N2 dry (R = 12°)

Substrate IV (Durar Flint Ultra Pink)
+ Blown under N2 only (R = 40 ± 3°)
GLASS TYPE: 7101 - SUBSTRATE I (GROUP 4A)

Substrate IV + ultra sonicated in H2O, N2 dry (R = 2 ± 3°)

Substrate IV+ heat in a hot water bath, hot plate dry (R = 42 ± 3°)

Substrate III - Blown under N2 only (R = 2°)
Figure 7: (a) Contact angle of H$_2$O ($V= 1$ µL) droplet with different cleaning procedures by the sessile-drop method. (Only the contact angle of one side of the drop was measured here). (b) Digital images of silica microwires fabricated on different glass substrates as circular drops ($V= 10$ µL drop of 3.2 wt. % concentration of silica nanoparticles and left to evaporate at ambient temperature on a flat plane. The drops on the different substrates were not covered.
TABLE 1. CONTACT ANGLE OF 1 µL DROP OF WATER BY THE SESSILE-DROP METHOD

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<th>Max. Error (±)</th>
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<tr>
<td>III C (2)</td>
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<td>27</td>
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(The contact angle was only measured from one end of the drop)

A = Precleaned state; B = N₂ blown only; C = N₂ blown, ultra-sonicated [C (1) = 30 mins. C (2) = 60 mins.] in H₂O and dried under N₂

* Pathology microscope glass slide in the precleaned state (Table 1: Group 4A – Catalogue No. 7101A)

I = Sail Brand (Group reference 4A, Table 1)

II = SuperFrost Ultra Plus (Group 5F, Table 1)

III = SureFrost (Group 6I, Table 1)
Figure 8. Graph plot of contact angle (°) versus time (seconds). 1 µL drop of water droplet was dispensed on the different glass substrates. The sessile-drop method was then used to monitor the rate of change of contact on one side of the drop as the water evaporates from the surface. The drops were covered except for the opening where drops are imaged by the microscope. It was inferred here that there was no significant change between when the light source from the microscope was turned on and off.
TABLE 2. AVERAGE CONTACT ANGLE RESULTS OBTAINED FOR 1µL DROP OF WATER BY A SESSILE-DROP METHOD ON A FLATE PLANE (THE SUMMARIZED TABLE IS IN CHAPTER 4.1 OF THE THESIS AS TABLE 3).

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<th>θ1 (°)</th>
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<th>θav (°)</th>
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GLASS SUBSTRATE II

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I - Sail Brand (Group reference 4A, Table 1); II – Pathology grade (Group reference 4A, Table 1); III - SureFrost (Group reference 6I, Table 1); IV = SuperFrost Ultra Plus (Group reference 5F, Table 1); All the contact angle values are in degrees.
Figure 9. Drop’s circularity test. 1 µL drop of water droplet was dispensed on the different glass substrates. The sessile-drop method was then used to monitor the rate of change of contact on one side of the drop as the water evaporates from the surface. The drops were covered except for the opening where microscope was directed. The optical micrographs from the coffee-ring effect after evaporative process (uncovered work area) further demonstrate the glass slide marked in red as the one that produces the best adhesion with the surface, despite the fact that it has the largest contact angle out of the 3 substrates.
APPENDIX 2: COMPARATIVE STUDIES BETWEEN UNCOATED AND COATED GLASS SUBSTRATES: EVAPORATION OF 1 µL DROP OF H₂O AND COLLOIDAL SUSPENSION OF (3 wt. % CONCENTRATION) SILICA NANOPARTICLES (SNP)

This appendix presents the tables of the evaporation studies that was carried out in chapter 4.3 of this thesis work.

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SNP DROPLET ON A GOLD-COATED GLASS SUBSTRATE

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Another macroscopic parameter considered during evaporation is the contact angle of liquid droplets at the three-phase contact line. The charts in Figure 5 show the variation in contact angle on both sides of the evaporating drop at time t. The signature patterns followed during evaporation is used to correlate the fingering instability within the coffee-ring boundaries. Theoretically and proven experimentally, coffee-ring stains are experienced by a drying colloidal droplet on a glass substrate.
(a) Variation in contact angle of a drop of H\textsubscript{2}O (degrees) (uncoated glass surface)

(b) Variation in contact angle of a drop of H\textsubscript{2}O (degrees) (Au-coated glass surface)

B = side of drop 1
C = side of drop 2
Fig. 1. Time dependent chart of the variation in contact angle of a liquid droplet during confined evaporation: 1 µL drop of H₂O and 3 wt. % SNP solution on a. A drop of H₂O on uncoated surface. b. A drop of H₂O on Au-coated surface. c. A drop of SNP solution on uncoated glass substrate. d. A drop of SNP on Au-coated glass surface. All at ambient temperature.
APPENDIX 3: APPLICATION OF A 3-D PHASE CONTRAST VARIATION TOOL TO DIFFERENTIATE THE STRUCTURAL NETWORKS OF SILICA NANOPARTICLE STRUCTURES

This appendix presents supplementary images presented in chapter 4.4 of this thesis.

INTRODUCTION

The introduction of a 3-D Phase contrast variation tool to self-assembly process has been explained in section 4.3 of this thesis work. The main objective here was to use it as an additional analysing imaging tool, particularly to recognise the phase patterns of the different packing arrangements for silica nanoparticle structures. The basic principle here is using the tool to reconstruct a recognised pattern. This involves a phase inverse of Black-White patterns present on an SEM micrograph to a 3-D Phase contrast. By using a filtering mode channel present in the software tool (Image J), the variance between BW can either be converted to a 2-D or 3-D. A 2-D image simply gives back the 8-bit gray scale image colour in SEM micrograph. However, with a 3-D-phase contrast, the image quality is converted from 8 to 32-bit mode. The mathematics is not clearly understood here but a close mathematical expression have been referenced in the thesis. Finally, apart from using this tool as an image analysis method, it is proposed that the 3-Phase contrast image has the potential of being used in a 3-D modelling, where one can actually use it to generate precise mathematical equation that describes the packing arrangement within the self-assembly process. This has been identified in this thesis work as a potential thesis project for another work.
Figure 9. SEM micrographs and their phase contrast images. (a-b),(c-d),(e-f). The illustrative pictures showing similar architectures on macroscopic objects shown beneath the micrographs are taken from the Shutterstock web-site, reference [113]
Figure 10. 3-D Phase contrast of the self-assembly of silica nanostructured wires in the cold temperature range (0-15 °C) studied.
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APPENDIX 4: COFFEE-RING EFFECT AFTER D-GLUCOSE WAS MIXED WITH COLLOIDAL SUSPENSION OF SILICA NANOPARTICLES (IMAGES: WHEN COMPLETELY DRY) (Chapter 4.6)

A : D-glucose-SNP after droplet has dried
B: D-glucose-silica microwire surfaces
C: Nanostructured surface of D-glucose-silica microwire
D: Various stages in D-glucose-silica nanoparticles mixture via nucleation in multiple regions to give multiple coffee-ring structures (not completely dry state)
Various stages in D-glucose-silica nanoparticles mixture via nucleation in multiple regions to give multiple coffee-ring structures (completely dry state)

Figure 11: Different stages of self-assembly of silica nanoparticles – D-glucose mixture.

Bibliography


70. See reference 65.


83. See reference 36.


92. www.lsinstruments.ch/technology/dynamic_light_scattering_dls/dynamic_light_scattering_theory/
