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Forms of Mesoporous Silica: Fibers, Films, Curved Shapes and Patterns

by

Hong Yang

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Department of Chemistry
University of Toronto

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Abstract

Oriented mesoporous silica films have been synthesized at air-water and solid-water interfaces by a surfactant-based supramolecular templating technique under quiescent aqueous acidic conditions. Solid substrates include freshly cleaved Muscovite mica, pyrolytic graphite, and sputter-deposited gold. Convergent evidence from PXRD, SEM, TEM, AFM, POM and gas adsorption isotherms have shown that the silica films are mesoporous and in closely packed hexagonal phase. Registry of silicate-surfactant assemblies on atomically flat substrates, mica and graphite, has been established by AFM, SEM and POM studies. Control of film properties such as the degree of polymerization of silica, film thickness, and hexagonal packing order has been demonstrated by adjusting acidity, temperature, and post-treatment conditions.

Mesoporous silica has also been synthesized with a range of spectacular curved shapes. Optical birefringence has been observed for some of the shapes and the origin has been traced to the hexagonally close packed arrangement of silica channels. The mesostructure-morphology relationship of gyroid, discoid and fiber shapes have been established by TEM, SEM, AFM and POM studies. The channel structure of mesoporous silica films and some curved shapes are thought to be initiated by defects in the growth liquid crystalline seed. A distinct mode of formation has been found for micron size mesoporous silica spheres. Low acidity and high temperatures favor sphere formation and the growth process is based on colloidal flocculation. The main factors that contribute to the nucleation, growth and form of mesoporous silica morphologies have been identified.

Proof-of-concept for building hierarchical mesoporous structures has been illustrated through the use of patterned self-assembled monolayers (SAM) on gold. Mesoporous silica is found to preferentially grow on SAM patterned regions of the film.
Acknowledgments

I would like to express my sincere thanks to my supervisor, Professor Geoffrey A. Ozin who has spent enormous time on this project. His dedication to materials chemistry and the love of education have greatly affected me and changed my career perspectives. During the years of my stay in his group, he gave me both research freedom and excellent guidance, and allowed me to play with “soap bubbles” blithely like a sand boy. For all these reasons and many beyond, I am deeply indebted to him.

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The kind offer from Mr. Robert Scott to proofread my thesis and his friendship are greatly appreciated.

Finally, I wish to thank my parents for their unconditional love. My wife, Xinhong’s support and sacrifices have been most valuable in allowing me to conduct my research wholeheartedly.
To my parents, my wife and my daughter
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Chapter One
Shape of Surfactant Templated Mesoporous Silica

1.0 Preamble

Shape has interested scientists throughout the ages. Classical examples include studies initiated century’s ago in biology on the origin of life, the appearance of living form and evolution. Josephy Needham, in 1936, claimed “the central problem of biology is the form problem.” Shapes are also traditional themes in crystallography and mineralogy. In modern materials science, the application requirements of particular forms are enormous. Materials need to adopt a particular form such as a wire, film, membrane, or monolith, and have sizes ranging from nanometers to meters to perform a required function. In this context, the field of organic liquid crystals is beginning to impact on materials inorganic chemistry.

The discovery of surfactant-templated mesoporous inorganic materials is one of the recent milestones in the journey. This area quickly evolved from bordering fields, such as sol-gel chemistry, colloidal chemistry, nanostructured materials, and biomineralization. The form problem for inorganic mesostructures emerges as an important research area because of the many perceived applications of the materials. It is the search for solutions down this avenue of investigation that led to the take-off of this project four years ago.

1.1 Liquid crystals

The discovery of liquid crystals is interesting and seemingly ambiguous. As early as the 1850s, the first liquid crystal molecule, Myelin, had been made and its birefringence observed. In the late 1880s, the intense pursuit for understanding the “two melting points” phenomenon of several cholesterol esters by botanist Otto Lehmann and physicist Friedrich Reinitzer lead to the creation and establishment of the field of liquid crystals.
1.1.1 Introduction to liquid crystals

Liquid crystals represent a delicate phase of matter which has lost the long range positional order of ordinary crystals but retains orientational order of anisotropic structural units. The mesophase possesses both the fluidity of a liquid and certain order of a solid. There are two major liquid crystals, namely, thermotropic (Greek ἄρματος = heat) and lyotropic (Greek λυτός = solve) depending on how their mesomorphism changes with external conditions. Thermotropics emerge on melting an appropriate crystalline precursor, while lyotropics form by dissolving the precursor in a suitable solvent at a particular concentration. Since the phenomenon is associated with structure sizes ranging from about 1 nm to 1 μm, it belongs to the province of colloids. Surfactant (the so-called “surface-active” molecule) assemblies and lyotropic liquid crystals have traditionally been the subjects of colloidal chemistry.

Surfactant molecules, also called amphiphiles, typically consist of two parts, namely a polar head group and a long hydrophobic chain. A cationic surfactant with a sixteen hydrocarbon chain, cetyltrimethylammonium, is illustrated in Figure 1.1 (the counter-anion is not shown). When dissolved in a solvent, typically water, the hydrophobic alkane chains of the surfactants tend to aggregate to form a core structure, leaving the head groups exposed to the solvent molecules.

![Figure 1.1](image)

Figure 1.1. Cerius® illustration of cetyltrimethylammonium surfactant.
From surfactants to liquid crystals, there exist intermediate structures, which can be micelles with spherical or cylindrical shapes, inverse micelles, and vesicles, hollow bilayer assemblies which typically form spheres. The lyotropic liquid crystal can exist as lamellar, hexagonal, cubic and other phases. Supramolecules may refer to any one of these surfactant assemblies. Representative supramolecular structures are shown in Figure 1.2.

In solution these assemblies have defined curvatures and normally position themselves in one of the phases for a given set of conditions and concentrations. The optimal aggregates are governed by inherent surfactant properties such as hydrophobicity, surface interaction with solvent and "favorable geometric" packing. There are two different sets of data that have been used as packing parameters. The one developed by Israelachvili is based on the imaginary shape of an individual surfactant, which can range from a cone to truncated cone, cylinder, or wedge, along with the best geometric packing of such shaped units. In this model, the surfactant number of an amphiphilic molecule determines the shape or phase of the aggregates. This number $N_s$, is defined by the volume of the hydrophobic portion $V$, effective head group area $a_o$ which includes the counterion, and chain length of the amphiphiles $l$, according to the equation:

$$N_s = \frac{V}{l \cdot a_o}$$  \hspace{1cm} \text{Eq. 1.1}

Clearly all three parameters are heavily dependent on the conditions of the micro-environment such as electrolyte and surfactant concentration. Despite these uncertainties and the fact that "dynamic shape" does not exist in reality, this model is still widely used because it can predict the structural trends of the assemblies in terms of the phase changes within the solution environment.

The other approach to classify the structure is by the mean curvature $H$, given by equation 1.2:

$$H = \frac{1}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$  \hspace{1cm} \text{Eq. 1.2}

where $R_1$ and $R_2$ are the principle radii of curvature normal to one another, Figure 1.3. By convention, the sign of the radius of curvature is positive if its direction is towards the head group.
Figure 1.2. Illustration of different surfactant assemblies: (a) spherical micelle, (b) inverted micelle, (c) cylindrical micelle, (d) cubic, (e) lamellar, and (f) vesicle.
Figure 1.3. Illustration of perpendicular radii of curvature for an assembly.

The criteria for optimally packed structures based on these two numbers is summarized in Table 1.1.

Table 1.1. Criteria for optimally packed structures for surfactant assemblies.

<table>
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<tr>
<th>Packing shape</th>
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<th>mean curvature ( (H) )</th>
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<td>Definition</td>
<td>( N_s = \frac{V}{l \cdot a_o} )</td>
<td>( H = \frac{1}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) )</td>
</tr>
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<td>spherical micelles</td>
<td>cubic ( (Pm3n, \ldots) )</td>
<td>1/3</td>
<td>1/R ( (R_1=R_2=R) )</td>
</tr>
<tr>
<td>infinite cylinders</td>
<td>hexagonal ( (P6m) )</td>
<td>1/2</td>
<td>1/2R ( (R_1 = R, R_2 = \infty) )</td>
</tr>
<tr>
<td>bicontinuous cylinders</td>
<td>cubic ( (Ia3d, \ldots) )</td>
<td>1/2–1/3</td>
<td>1/2R ( R_1 = R \sim \infty, R_2 = \infty )</td>
</tr>
<tr>
<td>planar bilayers</td>
<td>lamellar ( (L) )</td>
<td>1</td>
<td>0 ( (R_1 = R_2 = \infty) )</td>
</tr>
<tr>
<td>inverted micelles</td>
<td>cubic ( (Pm3n, \ldots) )</td>
<td>&gt; 1</td>
<td>&lt; 0</td>
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</table>
1.1.2 Liquid crystal defects

**Defects in general** All matter is built of atoms and molecules. According to a recent theory developed from studies on semiconductor nanocrystals, scaling laws govern the size dependence of the structures and properties of solid materials. The bulk properties of a solid are quite different from the properties of nanocrystalline materials consisting of around ten or less unit cells. For instance, a nanocrystal has a much lower melting point than its bulk form, dropping inversely with respect to its radius. A direct consequence is that an inorganic crystal, typically with a size larger than 10 or 20 nm, can possess defects which may for example, act as active sites for the nucleation of a phase transition or continued growth. Defects are common for regular solids and profoundly affect the properties of a material. They are pivotal for example, to crystal nucleation, growth and form, bulk and surface reactivity, phase transitions, ionic mobility, electrical charge transport, optical characteristics, magnetic and mechanical behavior.

A defect in a crystal commonly exists in thermal equilibrium with the system. There are two major types of crystal defects: point defects such as lattice vacancies and interstitial atoms, and extended linear and planar defects. Points, lines, and walls can be considered as zero-, one-, and two-dimensional defects, respectively. A dislocation is an example of a typical linear defect while grain boundaries and shear planes are the most common planar defects.

**Defects in liquid crystals** Defects also exist in liquid crystals and can be points, lines and planes. The rotational dislocation in a liquid crystal is often called a disclination or disinclination. Planar defects in liquid crystals often form "walls". Vacancy and interstitial impurity defects which exist in crystalline solids may also exist in liquid crystals. However in contrast with the sub-microscopic dimensions of defects found in crystalline solids, those of liquid crystals can be microns in size. The energy required for creating defects in liquid crystals is far less than that for crystalline solids, thereby enabling the formation of defects with large dimensions and strong distortions of the director fields. They are responsible for birefringence textures made visible between cross polarizers in an optical microscope where
distinct patterns are diagnostic of particular liquid crystal structure types.

Surface interactions are of special importance in liquid crystals as they can lead to the formation and stabilization of particular types of defects, and control of homeotropic or planar anchoring of anisotropic units with respect to the director field. In addition field effects, for instance, gravitation, electric, magnetic, shear and stress, can also affect nucleation and growth processes of liquid crystals and patterns of director fields. Several types of point, linear (dislocation and disclination) defects, and two-dimensional walls are found to exist in liquid crystals.\textsuperscript{16}

Liquid crystals usually act as elastic media and its various deformations can be treated by elastic continuum theory, an analogue of the classical theory of elasticity for solids. This is the approach most often used to calculate director field patterns in a range of liquid crystal morphologies.\textsuperscript{17} The continuum theory is largely developed for the thermotropic nematic phase which may be considered as a medium with a local uni-axis and a variable optical axis. The director profile is obtained by minimizing the free-energy function of elastic (i.e., splay, bend, twist distortions), surface and field forces in the liquid crystal for different morphologies.

In morphogenesis of mesoporous silica, the line defect is of particular importance and the Volterra method which is used to classify the linear singularity (or dislocation) of liquid crystals is applicable. Creating a line singularity in a medium with only translation and rotation dislocations is the Volterra process.\textsuperscript{14,18} To generate a defect or a line discontinuity in such a medium, a cut is applied along a surface $S$, confined by a wedge line $L$, the lips ($S_1$ and $S_2$) of the surface are then allowed to relax, and the space in-between is filled with either perfect liquid crystal units or void space, \textbf{Figure 1.4}. Therefore, all displacements can be described by a quantity $d(r)$, the displacement vector, following the equation

$$d(r) = b + \Omega (vr)$$

Eq. 1.3

where $b$ is the translational component for the displacement, called the Burgers vector, and $\Omega (vr)$ is related to the rotational component (a rotation of distance $r$ from the axis $v$ at a angle $\Omega$). Thus, for a purely translational defect, also known as an edge dislocation, or simply a dislocation, the Burgers vector $b$ is a non zero quantity and angle $\Omega$ is zero. Conversely, in a
screw dislocation, also known as a rotational dislocation or disclination, \( \mathbf{b} \) is zero and \( \Omega \) is a non zero quantity. An illustration of edge and screw dislocations is shown in Figure 1.5. The former can be viewed as a plane sandwiched half way into a cluster of ordered stacking planes and causing the distortion from perfect packing. The disclination class, can often be detected by polarized optical microscopy. Disclinations and dislocations are the most frequently encountered defect types for liquid crystalline materials.

![Figure 1.4. Illustration of the Volterra process for the generation of a line discontinuity.](image)

It may be instructive to further explore the disclination as it helps to understand the morphogenesis of mesoporous silica materials. A given disclination defect can be quantified by its rotation angle in the Volterra process. For example, \( \pm \pi \) defects are generated if the lips of the surface rotates by 180° with respect to one another followed by relaxation, Figure 1.6. The sign of the angle can be defined by examining a hodograph of a wedge line confined in an imaginary directional circle around the line, Figure 1.6d. The sign is positive if the direction of the circle at all points and the corresponding overlapped points of the hodograph are in the same direction. The two most commonly observed disclinations, \( \pm \pi \) and \( \pm 2\pi \), are illustrated in Figure 1.7.
Figure 1.5. Illustration of (a) an edge dislocation and (b) a screw dislocation.
Figure 1.6. Generation of a defect line in a directional medium following the Volterra process: (a) wedge line, (b) lip rotation of 180°, (c) relaxation of medium to form a $-\pi$ defect, and (d) hodograph.

Figure 1.7. Some common wedge lines for (a) $+2\pi$, (b) $-2\pi$, (c) $+\pi$ and (d) $-\pi$ defects.
Anisotropy and liquid crystal defects All liquid crystals possess long range directional order and a material can be classified as being an isotropic or anisotropic medium according to the refractive indices along its three principal directions. If the refractive indices are equal along all three directions \((n = n_1 = n_2 = n_3)\), then the medium is isotropic. The micellar and bicontinuous cubic phases belong to this category. If at least one refractive index differs from the others, the materials are anisotropic and birefringence patterns can be seen. Thermotropic and lyotropic liquid crystals in lamellar or hexagonal phases will both possess optical anisotropy. Furthermore, if the indices along two directions are equal but not the same as the third direction \((n_1 = n_2 \neq n_3)\), such as in a hexagonal phase, the materials are called uniaxial and \(n_1, n_3\) are named the ordinary and extraordinary indexes, respectively. The molecular explanation for birefringence is based on the fact that the electric vector of an incident electromagnetic wave polarizes the medium differently along those directions.

When an optically anisotropic medium is placed between cross polarizers in convergent white light, an interference pattern can be seen through the microscope. For a hexagonal symmetry system a cross can be seen if the direction of the light is aligned with the optical axis. The two arms of the black cross are called the isogyres, the center of the cross is the melatope, and the rings are the isochromes which arise from differential retardation and interference effects due to variable angles of inclination of the light path through the medium.

This technique has been used since the beginning of liquid crystal research and is still an efficient way to identify director fields, defects, and structure types of liquid crystalline phases. It is anticipated that a hexagonal mesoporous silica with two dimensional \(P6m\) symmetry and a pure \(+2\pi\) defect channel structure would show a birefringence texture like the one illustrated in Figure 1.7a when the optical axis and director field are normal to each other. For a \(+\pi\) disclination type defect, only two arms of the black cross normal to one another should be seen between crossed polarizers.
1.2 Inorganic mesostructures through supramolecular templating

1.2.1 Introduction to inorganic mesostructured materials

Definition of Meso  
*Meso* is a term that has been used in several fields and each one has its own distinct meaning. Physicists define meso according to the observed phenomenon. In the case of electronic properties, a mesostructure will be in the size range of 10 to 30 nm which is related to the wavelength of electrons at the Fermi level, whereas for photonic properties sizes between 200 to 1000 nm are considered to be mesostructured. In biochemistry and cell science, mesostructures are in the range of 1 to 50 μm. Mesophase, an alternative name for liquid crystals, has probably been coined because of such a classification.

Materials chemists, on the other hand, define porous systems according to the average width of the pores or the diameter of a cylindrical pore. The standard technique for the measurement of porosity is the gas adsorption isotherm, normally using nitrogen or argon at liquid nitrogen temperature. The pore system is classified into micropores (< 20 Å), mesopores (20 to 500 Å) and macropores (>500 Å). The hysteresis loop of an isotherm may have different characteristics depending on the pore sizes and shapes, and six major types of loop exist. The “so-called” type IV isotherm arises from capillary condensation and is characteristic of mesopores, as shown in Figure 1.8. It is this definition of a mesopore that will be used throughout this thesis.

![Figure 1.8. Illustration of a type IV isotherm.](image)
General synthesis strategy for mesoporous inorganic materials  Inorganic mesoporous materials with different compositions but without ordered pore structures have been made by a number of methods. Currently, the major approaches are the sol-gel hydrolysis of alkoxide metal precursors, pyrolysis of organics, and chemical or electrochemical etching. A large number of metal oxide mesoporous ceramics can be synthesized in different forms such as thin films, monoliths and spheres. The most widely commercialized material in this category may be Vicor glass. Typically the mean pore size can be controlled through choice of solvents, and control of hydrolysis rates by using acid or base catalysts. Pyrolysis of organics in an inert gas environment leads to the formation of microporous and mesoporous forms of carbon. Another class of non-ordered mesoporous structures is obtained by chemical or electrochemical etching. Using anodization, porous aluminum oxide can be obtained with pore sizes above ~ 10 nm. One of the important aspects of aluminum oxide porous materials is that the orientation of the pores is normal to the surface, which makes it a good candidate as a membrane or a host structure for making nanosized semiconductors and other nanostructured materials. The most recent member of the family of mesoporous materials is the carbon nanotube.

Ordered mesoporous materials were first discovered in 1992 by Kresge and co-workers at Mobil Oil Corporation in an effort to find large pore molecular sieves, although such mesostructured materials may have been accidentally made as low density silica some two decades earlier. In their first publication, the Mobil group laid out the general procedure for making ordered mesoporous materials by using surfactant supramolecular assemblies as templates. Silica-based powdered materials having mesopores with diameters of 2-10 nm were made as hexagonal and cubic phases by organizing silica around surfactant templates under basic conditions. Since this breakthrough intense research activity has been directed to the field and the first publication of the Mobil invention has now been referenced over 600 times in only five years. There are several important aspects that make the method stand out, not the least of which is that it allows one to make ordered mesoporous inorganic materials with controlled diameter pores and channels. The approach also shows how inorganic-surfactant interfacial interactions can facilitate the formation a range of mesostructured materials.
1.2.2 Supramolecular templating

As mentioned in the first section, surfactant based supramolecular assemblies such as micelles and liquid crystals have been known for over a century. The idea of using these assemblies as templates seemed to come naturally for organic and polymer chemists as a rich literature on supramolecular templated polymers and organics existed before the nineties. In retrospect, non-templating applications of surfactants in structure modification of inorganic solids, especially inorganic surfaces, have also been studied. With all of this accumulated knowledge, the discovery of a synthetic route to mesoporous materials by using liquid crystal templates was truly a timely breakthrough which filled a gap in the self-assembly field and caused a paradigm shift in solid state synthesis.

Dozens of reviews on mesoporous materials have appeared during the past several years. The general consensus on the formation mechanism is similar to the original hypothesis, namely either through the interaction between inorganic species and surfactant micelles at interfacial regions or through the “diffusion” of polymerizable inorganic precursors into the polar regions of a liquid crystal, the so-called “true liquid crystal" templating mechanism. There are a number of variants of the former mechanism and they represent the major pathways for making mesoporous materials. There are also several routes in which the inorganic species play pivotal roles in the formation of the final phase of the mesostructure. Such routes include the “cooperative templating mechanism", “ligand-assisted mechanism", and “neutral templating mechanism". Indeed, certain organic species which template mesoporous materials, such as neutral long chain alkylamines, do not micellize or form lyotropic liquid crystal phases in aqueous solution alone. Cetyltrimethylammonium chloride is a common cationic surfactant used for the synthesis of mesoporous materials and is extensively used in this study. Only spherical micelles can be synthesized at ambient temperature in its dilute aqueous solutions, while cylindrical or threadlike assemblies can be formed by changing the counter-anion to salicylate. In the neutral templating mechanism or ligand-assisted mechanism a metal alkoxide species respectively hydrogen-bonds or covalently bonds to a long chain amine. The approach used in this project makes use of the cooperative templating mechanism.
1.3 Shape of mesoporous silica

Shape comes naturally when materials are formed, and surfactant templated inorganic materials are not an exception. So far, mesoporous silica morphologies that have been obtained using the supramolecular templating approach\textsuperscript{23} include: (i) fibers with the channels running parallel to the long axis either through aqueous solution growth (with facets),\textsuperscript{37} spinning fabrication (without facets)\textsuperscript{38} and fiber growth at the oil-water interface,\textsuperscript{39,40} (ii) toroids, discoids and gyroids with channels whirling around the unique rotation axis,\textsuperscript{37} (iii) millimeter and micron size solid\textsuperscript{41,42} and hollow spheres,\textsuperscript{43,44} (iv) supported films by solution phase deposition onto mica,\textsuperscript{45,46} graphite,\textsuperscript{46,47} gold\textsuperscript{48} and glass\textsuperscript{49} including materials grown in capillary tubes which have the channels running concentrically around the long axis of the cylinder,\textsuperscript{50} (v) supported films by sol-gel dip-coating or spin-coating on silicon and silica,\textsuperscript{51,52} or by casting a viscous gel-type mesoporous silica,\textsuperscript{53} (vi) free-standing films with a liquid crystalline channel texture grown at air-water\textsuperscript{54,55} and oil-water interfaces,\textsuperscript{44} (vii) tubular constructs through post synthesis pH-titration,\textsuperscript{56} (viii) monoliths,\textsuperscript{29,57} (ix) self-assembled monolayer (SAM) patterned micron scale designs on gold by microcontact printing (\(\mu\)-CP),\textsuperscript{48} and (x) patterned micron scale designs by micromolding in capillaries (MIMIC).\textsuperscript{58}

It may be worthwhile mentioning that most of the well characterized mesoporous shapes were found to be hexagonal packed cylindrical structures, presumably in two-dimensional \(P6m\) space group. Exceptions include free-standing and supported films, synthesized at air-water and solid-water interfaces, which have three-dimensional hexagonal \(P6_3/mmc\) symmetry,\textsuperscript{59} as well as truncated octahedral mesoporous silica particles from the cubic \(Ia3d\) phase of MCM-48.\textsuperscript{60,61} It is safe to say that a large range of mesoporous silica shapes can be directly synthesized, however most reports to date are still confined to silica based materials. An exception is the synthesis of mesoporous platinum films in which the specific surface area is between 17 and 23 m\(^2\)/g, about 50 times less than conventional mesoporous silica made through this approach.\textsuperscript{62}
1.3.1 2D mesoporous silica: film formation

1.3.1.1 Interfacial control

**Functional interfaces.** There are five main distinct interfaces existing in nature, namely the vapor-liquid, vapor-solid, liquid-liquid, liquid-solid and solid-solid interfaces. The formation of micellar assemblies and lyotropic liquid crystals from surfactants requires a solvent, often water, present in the system in order to create the supramolecular structure. Thus, it is not surprising that all the strategies of growing thin films of mesoporous silica involves the vapor-liquid, solid-liquid and liquid-liquid interfaces.

It is well known that amphiphilic molecules such as long-chain carboxylic acids can organize into monolayers at the air-water interface, an example being Langmuir films. Such ordered surfactant overstructures have been used as templates for epitaxial and non-epitaxial aqueous phase crystal growth of inorganic nanoparticulate films. The adsorption of a surfactant onto a solid substrate is also a common phenomenon and over the years there have been many studies on the subject. Adsorbed monolayers and bilayers have all been used to describe aggregates on surfaces. Recently, visualization of some of the surfactant assemblies on solid substrates, such as mica and graphite, by atomic force microscopy has revealed that the adsorbed monolayers can in fact be ordered cylindrical micellar arrays.

Unlike the vapor-liquid and solid-liquid interfaces, the liquid-liquid interface involves two immiscible liquids, such as water and oil. When a surfactant is added to the solution, the system can form an emulsion. In fact, surfactants have always be used in the formation of microemulsions, thermodynamically stable structured mixtures consisting of oil, surfactant, and water. The surfactants are typically located at the oil-water interface with their polar head groups in the aqueous phase and hydrophobic alkane chains in the oil phase. The fluidity of these interfaces coupled with the general stability of emulsions make the system a good candidate for the synthesis of films and shapes.

**Supported films formed at water-solid interfaces.** The first example of a mesoporous silica film grown at a water-solid interface was on mica under quiescent acidic
By using cetyltrimethylammonium chloride (CTACl) as the surfactant and hydrolyzing tetraethylorthosilicate (TEOS) at high acidity, continuous films could be reproducibly grown on atomically flat Muscovite mica substrates. Powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM) revealed that hexagonal mesoporous silica films formed with the channels running parallel to and registered with the substrate. Such films on mica have also been independently studied by Aksay's group at Princeton. The same strategy for film formation was also used for the synthesis of mesoporous silica film with a $P6_3/mmc$ structure.

The supramolecular templating process for growing mesoporous silica films is not limited to aluminosilicate substrates like mica. Preferred alignment and registered growth are actually more pronounced for mesoporous silica film grown on a high quality pyrolytic graphite substrate under similar reaction conditions.

For a non-atomically flat or glassy surface, preferred orientation of the mesoporous silica film with the channels running parallel to the substrate is retained, although there is no clear evidence for "meso-epitaxy". This is the case for all such substrates used so far, including gold, SAM-modified gold, high-density polypropylene, silica, glass slides, and glass capillary tubes. This is to be expected for these substrates as no obvious surface crystallinity exists to pre-organize templating micellar cylinders at the solid-water interface. The film morphology appears to consist of coalesced discoid and ribbon shapes. Interestingly, even under flow conditions the discoid film morphology was still observed.

**Free-standing films formed at air-water interfaces.** It is perhaps "planned" serendipity that oriented free-standing mesoporous silica films were synthesized shortly after making supported films in our lab. The key to the formation of free-standing films is quiescent synthesis conditions which favors minimal disturbance of the surfactant overstructure at the air-water interface.

Free-standing films formed under a surfactant overstructure have been shown to have surface roughness in the angstrom range. A hexagonal mesostructure was observed on the air-water side of the surface of the as-synthesized mesoporous silica films by using contact mode AFM. These observations suggest that ordered surfactant overstructures may serve as the templating layer for growth of the mesoporous silica film.
The thickness of the films can be tuned from tens of nanometers to over 5 \( \mu m \) allowing the channel structure and optical birefringence to be analyzed by TEM and polarized optical microscopy (POM) which help to understand the mode of formation.\(^{55}\) Besides single chain cationic surfactants, cationic gemini surfactants have also be used for making free-standing films with a three-dimensional hexagonal structure.\(^{59}\)

**Free-standing films formed at the oil-water interface.** The growth of mesoporous silica films at liquid-liquid interfaces has been developed in the laboratories of Schüth and Stucky. Preparations were conducted under static acidic conditions with a gemini surfactant and TEOS as reactants. Films were grown at a decane-water interface. Cross-sectional TEM images of films with a thickness of less then 0.5 \( \mu m \) showed a hexagonal arrangement of pores. SEM images of thicker films reveal that they are comprised of agglomerated particles.\(^{44}\)

### 1.3.1.2 Fabrication method

Because of the intrinsic sol-gel characteristics of the reaction systems, fabrication methods such as spin-coating, dip coating and casting were also found to be applicable to the fabrication of mesoporous silica thin films. Ogawa *et al.* made the first sol-gel spin-coated mesoporous thin film on a substrate.\(^{51a}\) He used a sol-gel mixture of the cationic surfactant \( C_{18} TACl \) with tetramethoxysilane (TMOS) and a minimal amount of water as the hydrolysis reagent. To achieve high viscosity gels that are suitable for spin coating, sub-stoichiometric amounts of water were employed. Ogawa’s spin-coating technique, originally developed to make films of lamellar mesophase silicates,\(^{51b}\) was later successfully applied to the fabrication of hexagonal mesoporous silica films on glass substrates. The films were optically transparent and about 2 \( \mu m \) thick.

The casting method had been modified and applied to make transparent oriented mesoporous silica films.\(^{53}\) Ryoo *et al.* to this end, used cetylpyridinium chloride and TEOS under acidic conditions. Unlike most conventional methods, an azeotropic mixture of ethanol and n-heptane was added to the system and refluxed during the slow hydrolysis of TEOS (low acidity conditions). The water to TEOS mole ratio was less than 4 in order to keep the sub-stoichiometric requirement. Through control of the amount of water present and the refluxing
time during synthesis both ordered and disordered mesoporous silica gels can be made\textsuperscript{71} and used for film casting.

Another sol-gel processing technique, dip-coating, has also been applied to thin film fabrication.\textsuperscript{52} The bulk synthesis is essentially identical to the others, that is, an alcohol-water-silica sol and surfactant system was used. All three common mesophases, lamellar, hexagonal and cubic can be made on crystalline silicon (100) surface through control of the concentrations of components. The micellar-sol assembles due to the concentration increase that takes place as the sol-gel layer dries; thus the growth process is on the substrate. It is intriguing that the hexagonal mesoporous silica films have a sandwich structure. Oriented films having channels parallel to the surface formed at the silicon-solution and air-solution interfaces have been attributed to interfacial control of the structure of the assemblies,\textsuperscript{45,37} with randomly organized structures filling the gap between ordered regions. It is also interesting that the cubic film was formed through a lamellar-to-cubic phase transformation and is the first example of a mesoporous film with a cubic structure.

1.3.1.3 Patterning of films

To build a higher level of order into the mesoporous materials, microcontact printing (\(\mu\)CP) and micromolding in capillaries (MIMIC) techniques\textsuperscript{72} have been applied in conjunction with supramolecular templating to produce micron dimension patterns.\textsuperscript{48,58} An illustration of the MIMIC technique is shown in Figure 1.9 (\(\mu\)CP will be introduced in Chapter 2).

The most widely used \(\mu\)CP technique is based on the strong chemical bond formed between sulfur and gold, thus allowing long chain alkanethiols to form assembled monolayers on a gold surface. Micron-sized features can be created by pressing a polydimethylsiloxane (PDMS) stamp pasted with a thiol solution onto a gold substrate. Mesoporous silica predominantly grows on the SAM patterned regions when such patterned substrates were immersed in the CTACl-TEOS-HCl-H\(_2\)O reaction mixture.\textsuperscript{45,48} The mesoporous silica films have the close-packed hexagonal structure with the channels preferentially oriented along the surface. Although the growth mechanism is not yet fully understood, a heterobilayer
consisting of long chain thiols and surfactants at the SAM patterned regions has been proposed to facilitate such a growth process.

Microscopic pattern formation though MIMIC involves fluid migration driven by capillary forces along a micron size mold made of PDMS. The application of MIMIC to a CTACl-TEOS-HCl-H₂O reaction mixture in a concentration range suitable for the formation of a hexagonal phase yields a patterned mesoporous silica film.³⁸ An attractive benefit of the MIMIC strategy is control of channel orientation. It was reported that electric fields applied during the fabrication of the film could cause the channels of the hexagonal phase to align parallel to the field.

Figure 1.9. Illustration of micromolding in capillaries: (MIMIC) technique.⁷²
1.3.2 3D mesoporous silica: shape

**Chemical methods.** SEM images of mesoporous silica materials with hexagonal plate-like morphologies and non-descript powder form have routinely appeared in publications as part of the standard characterization since the very first paper on the subject.\(^{23}\) A hexagonal form has also been reported for mesoporous niobium oxide.\(^{73}\) Surfactant-based biomimetic approaches to the synthesis of inorganic materials with complex form and surface patterns represent a paradigm shift in materials chemistry.\(^ {74}\)

A large number of spectacularly curved shapes of hexagonal mesoporous silica have been discovered in one of the simplest aqueous acidic synthetic systems, CTACI-TEOS-HCl.\(^ {37}\) Despite the variation of form such as fibers, toroids, and gyroids, these shapes tend to have sharp edges presumably arising from facets of the \(ab\)-plane of a hexagonal phase. The form of the mesoporous silica can be changed in both size and shape by varying the reactant concentration, especially the amount of acid, as well as the type of surfactants and temperatures. Lowering the acidity of the synthetic mixture causes a gyroid-to-sphere shape-transformation with accompanying changes in mesostructure.\(^ {42}\)

Since the surfactant templating method relies on micellar and liquid crystal assemblies, it is conceivable that mesoporous materials could form as morphological and mesostructured replicas of their organic parents. More specifically, the observed curved shapes could be associated with defects in liquid crystalline growth nuclei and the appearance of certain facets with the symmetry of the hexagonal phase.\(^ {75}\)

Acidity control of morphology is seen in the formation of tubular mesoporous silica through pH titration.\(^ {56}\) By adjusting the synthetic conditions from highly alkaline towards neutral pH in the original synthesis solution, a pre-formed layer of silicate mesophase can evolve into a tubular mesoporous silica construct.

The liquid-liquid interface can stabilize either a stable homogenous microemulsion or a metastable macroemulsion. Such entities often organize in spherical or tubular shapes with surfactants separating the two phases at the interface.\(^ {40,41,43,44}\) Interfacial control of morphology through emulsions allows formation of spherical forms of mesoporous silica with controlled size.
Another very useful form of materials is the monolith, a uniform continuous often machinable ceramic. The first mesoporous silica structure to be made in monolithic form came from Attard’s laboratory by using a nonionic surfactant at a concentration which favors a liquid crystalline phase, thus representing the so-called “true liquid crystal templating” pathway. Monolithic mesoporous silica can be achieved through hydrolysis of TetramethTMOS at pH ~ 2. An alternative method also operates at low acidity conditions but uses a very high concentration of silica precursors, typically with co-solvents added. Monolithic mesoporous silica fibers and hollow spheres have been made by spinning and spray-drying viscous synthetic mixtures. The materials created by such methods may be useful for the mass production of low-cost shaped mesoporous materials.

Fabrication methods. Mesoporous silica fibers and hollow spheres have been made by spinning and spray-drying viscous synthetic mixtures. The materials created by such methods may be useful for the mass production of low-cost shaped mesoporous materials.

1.4 Outline of thesis

The synthesis and characterization of supported mesoporous silica films in the P6m space group using a cationic surfactant, CTACI, and TEOS in dilute quiescent aqueous acidic solutions are presented in Chapter 2. Efforts have been made to illustrate the synthesis and characterization of oriented films on substrates with atomically flat surfaces, such as hydrophilic mica and hydrophobic pyrolytic graphite to illustrate registered growth. The nucleation and growth of ordered hexagonal mesoporous silica films is then discussed. The experimental evidence for selective deposition of mesoporous silica on SAM-patterned gold is useful for understanding the mechanism of film growth on other substrates.

Oriented free-standing hexagonal mesoporous silica films are the focus of Chapter 3. Details of structure, channel orientation and other properties are addressed. Control of thickness of the mesoporous silica film can be achieved by tuning the pH of the synthesis mixture. Birefringence textures associated with the oriented hexagonal channel structure of the mesoporous silica film have been observed. It is proposed that the birefringence is associated with the optical anisotropy of the uniaxial glassy silica channel structure. Knowledge of the relations between channel structure and birefringence provide information on the mode of formation of free-standing films.

Chapter 4 deals with morphogenesis of curved mesoporous silica morphologies.
Diverse kinds of curved faceted shapes and spheres are explored as well as acidity dependent shape transitions. Investigations of the early growth stage and the effect of added alcohol and electrolytes provide a deeper insight into the formation mechanism. Liquid crystalline defects and colloidal forces inherent in surfactant-based self assembly systems are considered to play important roles in the emergence of curved mesoporous silica morphologies.

The final chapter briefly summarizes what has been learned in this thesis about the growth and form of mesoporous silica morphologies and how this knowledge might be utilized in the future.
1.5 References


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Chapter Two

Low Dimensional Form I: Supported Mesoporous Silica Films

2.1 Mica supported film

2.1.1 Introduction

One approach to the chemical synthesis of complex patterns in inorganic materials involves cooperative interactions between a supramolecular organic template and inorganic precursors to create a replica.1 This process has some common features with those involved in biomineralization. In this context, a biomimetic paradigm utilizing single organic molecules, micelles and vesicles as templates has led to the synthesis of inorganic materials with morphologies and patterns that traverse microscopic, mesoscopic and macroscopic length scales.23 An extension of this materials synthesis strategy utilizes the transcription of chemical and structural information contained within a preorganized 2D template to create an inorganic film.

It is demonstrated in this chapter that a supramolecular templating approach can yield mesoporous silica films on Muscovite mica.45 In essence, silicate-surfactant-mica interfacial effects facilitate the co-assembly of silica-surfactant micelles onto the freshly cleaved atomically flat hexagonal symmetry surface of mica. Well ordered mesoporous silica islands are observed to nucleate and grow vectorially with the channels oriented parallel to the mica surface. They ultimately coalesce into a continuous and oriented mesoporous silica film.

2.1.2 Synthesis and characterization

2.1.2.1 Synthesis

Synthesis The mesoporous silica films presented in this chapter were prepared under quiescent acid conditions6 using the following reactant mole ratio:
100 H₂O : 7.4 HCl : 0.11 CTACl : 0.13-0.24 TEOS

where CTACl refers to the cationic surfactant cetyltrimethylammonium chloride, \( \text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Cl} \), and the silica source reagent, TEOS, is tetraethylorthosilicate, \( (\text{C}_2\text{H}_5\text{O})_4\text{Si} \). CTACl (29 wt\% aqueous solution, Pflatz & Bauer) and hydrochloric acid (36.5-38 wt\% aqueous solution, BDH or Fisher) were used as received.

The synthesis of mesoporous silica films at the mica-water interface is conducted under quiescent acidic conditions. The aqueous-acid-surfactant synthesis mixture is first prepared, to which TEOS is added. The resultant mixture is stirred for 2-3 minutes at room temperature and then transferred into a polypropylene bottle containing the substrate. The substrate is arranged to lie horizontally in the synthesis vessel. Substrates can also be introduced onto the surface of the bulk synthetic solution after achieving a stable air-water interface. The film formation process commenced within minutes under static conditions in an oven at 80 °C. The growth was allowed to proceed for a period varying from one day to a week. Film formation also takes place at room temperature. Films were transferred from the vessel using tweezers and washed with de-ionized water.

The calcination and removal of the surfactants in supported films was typically conducted in air within a furnace attached to an Omega CN-2010 programmable temperature controller. The temperature was ramped at less than 1 °C/min. and the sample was held at either 450 °C or 540 °C for at least four hours. The substrate used was Muscovite mica from J. B. EM. Services Inc., Dorval, Quebec. The mica was used either directly after cleavage or with further treatment involving cleavage in de-ionized water and transferred to a 4M HCl aqueous solution at ca. 80°C for 30 minutes. No major differences were observed in the film formation for the HCl treated-mica.

2.1.2.2 Characterization

Powder X-Ray Diffraction (PXRD) data were obtained on a Siemens D5000 diffractometer using Ni-filtered Cu-Kα radiation with \( \lambda = 1.54178 \) Å. Samples of the supported films were mounted on top of a home-made low background quartz cell for
recording PXRD data. *In situ* variable temperature PXRD data was acquired by using a heating unit with a platinum strip as the support in a moisture-saturated environment. Supported films were typically attached onto this platinum surface with the thermal couple directly underneath. The temperature was ramped at 1°C/minute up to approximately 700 °C.

**Scanning Electron Microscopy** (SEM) images were obtained either on a Hitachi S-570 microscope using a operating voltage of 20 kV or on a Hitachi S-4500 field emission microscope using a low acceleration voltage of 2-5 kV to avoid charging of the film surfaces. The images shown in this thesis using high acceleration voltages were obtained on the Hitachi S-570 microscope. A thin layer of gold was generally applied to the samples when the high voltage machine was used, while images were taken on the field emission microscope without any metal coating. Whenever applicable, liquid nitrogen was used to avoid sample contamination.

**Transmission Electron Microscopy** (TEM) images of the films were recorded on a Philips 430 microscope operating at an accelerating voltage of 100 kV with a typical recording magnification in the range of 80,000 to 160,000 times. The microscope has a working resolution of 3.5 Å. Bright field TEM, in which regions with low electron density give bright contrast, was used throughout the studies. In order to get ultrathin sections (100-300 Å) of the mesoporous silica film grown on a substrate, a film was embedded in Spurr's epoxy resin (TAAB laboratories equipment, Aldermaston, U.K.), heated to form a block and cut at different angles using a RMC MT6000 ultramicrotome in combination with a Drukker diamond knife following standard procedures.

### 2.1.3 Results

**Films grown on mica** Mesoporous silica grows on mica over a relatively broad range of reactant ratios. The SEM images of the early stages of film formation with a reactant ratio of 100 H₂O : 7.4 HCl : 0.11 CTACl : 0.13 TEOS, a high acidity preparation at 80 °C, reveal geometric arrays of elongated micron dimension mesoporous silica islands with a preferred growth direction, **Figure 2.1a.** TEM images for the cross section of the islands reveal hexagonal mesostructures. Island growth can be observed to emerge at angles of 60° or 120°,
Figure 2.1b. This suggests that there is preferential co-alignment of the hexagonal unit cell axes on the $ab$-plane of mica.

A continuous mesoporous silica film eventually forms at these conditions, Figure 2.2a. The film is optically transparent. It is intriguing to observe that domains of these continuous films meet at preferred angles which may reflect registration of silicate-micelles with the underlying surface symmetry of mica. Mica-supported films have a typical thickness of about 0.6 $\mu$m as seen in a cross sectional SEM image, Figure 2.2b. The SEM image of a calcined thin film demonstrates that the macroscopic integrity of the film is maintained.

TEM lattice images of the as-synthesized and calcined films are shown in Figure 2.3. The hexagonal cylindrical channel structure of an as-synthesized film can be clearly seen in the cross sectional TEM image, Figure 2.3a. Mesoscale steps on the external surface of the mesoporous silica film can be seen in this image. This observation suggests that film forms through layer deposition in conjunction with island growth of the silica-surfactant micellar building-blocks. TEM studies also confirm that the typical thickness of the films was 5000-6000 Å and mesoporous cylinders are close packed in a hexagonal symmetry array across the entire thickness of the film. The particular film shown in Figure 2.3a has a thickness of 5300 Å.

The surfactant templates were removed by calcination at 540 °C in air. TEM lattice images of these calcined films demonstrate that the ordered hexagonal array is maintained. Furthermore, channel formation commences at the mica-solution interface and runs predominantly parallel to the mica surface, Figure 2.3b. TEM images of the calcined film also show evidence of "brick-like" lateral distortions of the mesopores after the removal of surfactants. The deformation could arise from interfacial binding and compressive forces acting on the film over extensive areas of the mica surface. The ability to preserve the film on the mica substrate during the microtoming process implies some degree of adhesion at the interface.
Figure 2.1. SEM images of the evolution of an as-synthesized mesoporous silica thin film grown on mica showing (a) preferred alignment and (b) island terminated at 60° or 120°.
Figure 2.2. SEM images of mesoporous silica films showing (a) top surface and (b) cross-section.
Figure 2.3. TEM images of mesoporous silica film on mica: (a) as-synthesized and (b) calcined.
The PXRD patterns for as-synthesized and calcined mesoporous silica film samples are shown in Figure 2.4. They both reveal at least two diffraction peaks at about 37.5 Å and 18.8 Å corresponding to the (100) and (200) reflections of a two dimensional hexagonal phase although the positions of the peaks may vary slightly for individual preparations. The diffraction pattern from a randomly oriented mesoporous silica powder sample displays the expected (100), (110), (200) and (210) reflections. The absence of the (110) and (210) reflections in the PXRD of the film samples, indicates that the c-axis of the hexagonal unit cell is oriented parallel to the mica surface (see Chapter 3). These results are consistent with TEM observations which show that the channels run parallel to the mica surface. Upon calcination of the films contraction (Δd_{100} = 2-5 Å) of the hexagonal unit cell is observed due to the removal of the surfactant template and the accompanying condensation of residual SiOH groups.

The thermal stability of the film under ambient atmosphere conditions has been studied by in-situ variable temperature PXRD, Figure 2.5. The temperatures starting from the front-side of the traces are 20, 150, 200, 240, 280, 320, 350, 410, 450, 515, 550, 550 (1 hour), 600, 620, 620 (0.5 hour), and 620°C (1 hour), respectively for a temperature ramp of 1 °C/min. up to 620 °C (the number in the bracket is the time that the sample was held at that temperature). The hexagonal PXRD pattern shows line shifts and intensity enhancements diagnostic of surfactant removal from the channels and condensation of residual hydroxyl groups in the silica walls. The high thermal stability is characteristic of a hexagonal mesoporous silica because the mesolamellar phase tends to collapse when the surfactant is removed from the structure at around 250-300 °C.
Figure 2.4. PXRD patterns for a mesoporous silica film grown on mica (a) as-synthesized, (b) calcined. (c) mesoporous silica powder. The inset shows the PXRD reflections between 3-8° 2θ with an expansion of the intensity scale.

Figure 2.5. *In situ* PXRD of mica supported mesoporous silica films. The temperatures starting from the front-side of the traces are 20, 150, 200, 240, 280, 320, 350, 410, 450, 515, 550, 550 (1 hour), 600, 620, 620 (0.5 hour), and 620°C (1 hour), respectively.
2.1.4 Discussion

Muscovite mica belongs to a large family of crystalline materials with hexagonal symmetry layer structures. The structure was first described by Pauling.\(^8\) It has empirical formula \(\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2\), and consists of double-layers of tetrahedral silicon-oxygen or aluminium-oxygen building-blocks sandwiching a single layer of octahedral \(\text{AlO}_6\) units, **Figure 2.6a.** When freshly cleaved, the exposed \(ab\) mica surface is comprised of aluminosilicate six-ring sites, **Figure 2.6b,** whose structure and reactivity can be tailored by chemical procedures. The tetrahedra in cleaved mica are in a configuration that gives an atomically flat surface with hexagonal symmetry. Under acidic conditions charge-balancing potassium ions are exchanged by protons, thereby providing reactive \(\text{SiOH}\) anchoring sites on the surface of the mica substrate for binding to silica-surfactant micellar precursor species.

The initial stage in the formation of mesoporous silica film is thought to involve silica-surfactant assemblies at the water-mica interface, **Figure 2.7.** Direct imaging of cationic surfactant assemblies with quaternary ammonium head groups on atomically flat mica has recently been achieved by electrical double layer AFM. The observations suggest that the concept of a flat bilayer structure on the surface of mica does not apply, instead micellar rods aggregate into parallel arrays of cylinders, presumably driven by hydrophobic effects, interfacial interactions and charge balance with the anionic mica substrate.\(^9\)\(^10\) The cylindrical micelle layers assemble in an ordered close-packed fashion. Therefore, the observation that oriented mesoporous silica films grow from the surface suggests that the silicate-surfactant assembly can also form an ordered layer at the boundary between mica and water where the growth process is regulated by interfacial charge and structure matching. On the basal plane of the mica substrate, the exposed hexagonal aluminosilicate rings serve as the anchoring sites. Matching of charge and structure between substrate and building-units could then cause mesoporous silica to grow with a preferred orientation along the 2-D hexagonal unit cell axes of mica to give elongated island growth and domain structures. The expansion and coalescence of these structural features on the mica surface and the continuous assembly of
Figure 2.6. Structure of Muscovite mica: (a) unit cell, and (b) $ab$-plane.
Figure 2.7. Illustration of mode of formation of a mesoporous silica film at the boundary between water and mica.

The proposed mechanism for the formation of mesoporous silica film on mica has much in common with biological design principles for biomineralization. Both work in a low temperature aqueous environment and utilize a supramolecular template to direct the co-assembly of organic and inorganic building-blocks to form a composite material. This purely synthetic approach to new materials provides unique opportunities for the creation of advanced technologies.\textsuperscript{11}
2.2 Graphite supported films

2.2.1 Introduction

As demonstrated in the previous section, hexagonal mesoporous silica films can be grown on mica surfaces. It is interesting to study whether atomically flat graphite surfaces can also be used as a substrate for film growth. Hence films were synthesized on cleaved pyrolytic graphite. A combination of PXRD, high resolution SEM, AFM and TEM, provide converging evidence that the channels of the film are aligned with the hexagonal symmetry axes of the graphite surface. The registry of the mesoporous silica film with the underlying substrate is facilitated by an organized hemicylindrical surfactant monolayer assembly at the boundary between graphite and water. This has a parallel with the aforementioned formation of mesostructured silica films on mica in which the channels are co-aligned with the surface.

To understand the formation process, an in situ pre-contact tapping-mode AFM study of the time evolution of CTACl aggregates at the graphite-water interface has been conducted. Studies of the structure of the surfactant aggregates adsorbed at the solid-water interface using this gentle imaging technique have unveiled the presence of surfactant hemicylindrical micellar assemblies that are oriented in the same way that the channels in mesoporous silica films are registered with mica or graphite surfaces. The spatial extent of the structure, the organization of interfacial surfactant aggregates and their role in directing the growth of mesostructured silica films on graphite will be illustrated.

2.2.2 Experimental details

2.2.2.1 Synthesis

The graphite used in this work is taken from a 12 mm × 12 mm × 2 mm pyrolytic graphite monochromator (Grade ZYB) from the Advanced Ceramics Corporation, Lakewood, Ohio, US. Thin sheets of graphite substrate were obtained by peeling a uniform section from the graphite block with Scotch tape and then cutting it into the desired size. A ca. 10 × 10
mm freshly cleaved pyrolytic graphite substrate was then positioned at the surface of the synthesis solution and allowed to float in a horizontal position.

The preparation and calcination of the films are similar to the procedures described in section 2.1.2.1 for the mica-supported film. 4 mM, 9 mM, and 18 mM CTACl (29 wt% aqueous solution, Pflatz & Bauer) aqueous solutions in the absence of acid and TEOS were used for the in situ AFM study.

2.2.2.2 Characterization

**Powder X-Ray Diffraction** See details in 2.1.2.2.

**Scanning Electron Microscopy:** SEM images were obtained on a Hitachi S-4500 field emission microscope using a low acceleration voltage of 2 kV to avoid the charging of film surfaces. Samples were imaged without a metal coating.

**Transmission Electron Microscopy:** See details in 2.1.2.2. Thin layers of sputtered gold coatings on the top surface of the mesoporous silica films were occasionally used to identify the film position in the epoxy-block and the sides of the film, since the adhesion forces between the film and the graphite substrate were not always strong enough to withstand the microtome cutting forces.

**Atomic Force Microscopy:** AFM experiments of mesoporous silica films were conducted on a NanoScope® III microscope (Digital Instruments, CA) using silicon integrated tip cantilevers (Park Scientific Instruments, CA) for height mode scanning of the films, and special silicon cantilevers (Digital Instruments, CA, FESP type, 227 mm cantilever, resonance frequency 70-100 KHz) for tapping mode scanning in fluids. The cantilevers were used as received. Images of the film surface topology were obtained by using direct contact (dc) scanning mode.

All images of soft multilayer assemblies on graphite were obtained with a phase extended module, operating in tapping-mode in a commercial fluid cell. The $A+B$ feedback signal was about 3 V while the RMS signal was set at around 0.3 V. Feedback gain parameters were set between 1 and 2 for both integral and proportional gains. The drive amplitude was set between 300 - 400 mV (not more than 2 nm) while the working frequency
in the surfactant was chosen to be between 20 to 30 KHz. Use of such a small amplitude to minimize the tip-sample interaction has been reported in the literature.\textsuperscript{15} The D scan head (maximum scan area is 12.5 x 12.5 μm\(^2\), z-sensitivity is 9 nm/V) was employed throughout the study. Scan rates were chosen from 1-4 Hz. To minimize the perturbing influence of scanning, tapping-mode imaging was conducted as follows. After engagement of the tip, the scan setpoint was increased (i.e., sample was lowered) until the image disappeared. The setpoint was then gradually decreased until the image was acquired. This procedure results in a gentler form of scanning. The driving amplitude in this scanning is slightly smaller than the free amplitude, as one can see from amplitude-Z-position curves. The use of pre-contact tapping-mode scanning in this study makes it possible to image the surface structure of surfactant aggregates beyond the first hemicylindrical micellar monolayer as previously reported using pre-contact mode.\textsuperscript{9,13,16}

Images were collected in both height and phase modes. The possible presence of artifacts was evaluated by varying scan direction, rate, size and gain parameters. All images are unprocessed apart from built-in real-time plane fit filters that were set for frame-by-frame subtraction. A representative tapping amplitude \textit{versus} Z-distance curve used to image surfactant assemblies adsorbed at the water-graphite interface is shown in Figure 2.8. The curve was taken for a graphite surface exposed to a 18 mM surfactant solution for 2 hours. Scanning amplitude is shown by the arrow.

Images of CTACl assemblies on graphite were obtained using two different methods. The first employed a pre-contact electrical double layer (EDL) height imaging mode. The second utilized a combined EDL pre-contact and tapping imaging mode. This method is a new way to image soft structures with minimal disturbance of the sample integrity. The frequency of the cantilever tapping in the surfactant solution was about 33 KHz. To achieve pre-contact mode during tapping, the following procedure was adopted. After the tapping mode was engaged, the tip was elevated manually by the motor for the vertical displacement. Normally the elevation needed was about 100-200 nm. The jump into pre-contact mode was evident every time.
Graphite was mounted on magnetized stainless steel AFM substrates by means of either double-sticky tape or epoxy. After addition of surfactant aqueous solution, the fluid cell was left standing for at least 2-3 minutes prior to engaging the tip.

![Graphite AFM Substrates](image)

**Figure 2.8.** Tapping amplitude versus distance curve.

### 2.2.3 Results

**Mesoporous silica on graphite.** The PXRD pattern of a film grown on graphite shows only two low angle peaks assigned to the (100) and (200) reflections of mesoporous silica with hexagonal symmetry, **Figure 2.9.** The absence of the (110) reflection for the film, compared to that of a randomly oriented powdered sample, confirms that the channel axis is aligned parallel to the graphite surface. Calcination of the film was performed at 450 °C in air for 4 hours. This high temperature treatment causes the PXRD d_{100}-spacing to contract by 1-3 Å with concomitant changes in the intensity of the PXRD pattern. The integrity of the film and its mesostructure are well maintained throughout this thermal post-synthetic treatment process.
Figure 2.9. A representative PXRD pattern for a mesoporous silica film grown on freshly cleaved pyrolytic graphite.

SEM images of the films grown on the graphite substrate are shown in Figure 2.10. The low magnification images reveal that the films are essentially continuous, Figure 2.10a. Intriguing equilateral triangle-shaped pits are observed in the films, Figure 2.10b. Also, the growth front of the films typically have parallel filamentous extensions, terminated with edges inclined at 60° or 120°, and which sometimes display sharp 60° or 120° bends. The triangle-shaped pits display both straight and convex edges. It is noteworthy that the edges of the triangles are exclusively aligned with respect to each other as well as in alignment with the edges of the filaments at the growing front of the film. A close examination of the inner walls of the triangular pits by SEM reveals a multi-layer topology with step-like features aligned with the sides of the triangles, Figure 2.10c.

TEM images of the mesoporous silica films grown on graphite show that the channels are hexagonally close-packed with a centre-to-centre distance of about 40-45 Å and run parallel to the graphite-water growth boundary, Figure 2.11a. The estimated unit cell dimensions from TEM agree well with the PXRD dimensions of 37-39 Å. A TEM image of a cross section of the film cut along the channel axis is shown in Figure 2.11b. The observed parallel lines with a repeat distance of 40-45 Å corresponds well with the separation of the
walls of the mesopores and confirms that the channels grow parallel to the graphite surface. The smooth bottom surface of the films shown in Figure 2.11, implies that the mesoporous silica film has grown from the graphite surface. This has been confirmed by examining an SEM image of a film with a thin layer gold coating which facilitates the identification of the outer surface of the film because of the very high contrast of elemental gold under the electron beam. The mesoporous silica films can be grown on graphite to a similar thickness to that of mica, approximately 0.6 µm. The graphite does not remain attached to the body of the mesoporous silica film during microtoming, even though the film can withstand strong washing by water.

In recent years, AFM has emerged as an effective probe for the topology of surfaces. Contact mode AFM images of the as-synthesized mesoporous silica film on graphite reveal a step-like layer structure. This structure exists in the central regions of the films within the walls of the triangular pits, and on the filamentous growth fronts of the films, Figure 2.12. These observations coupled with the SEM results suggest that the growth may be governed by the underlying symmetry of the graphite surface.

As in the case for mica supported mesoporous silica film, the thermal stability under ambient atmosphere condition has been studied by in-situ PXRD. During a typical temperature ramp up to 700 °C, the hexagonal PXRD pattern shows line shifts and intensity changes expected for contraction and ordering of the mesoporous silica due to removal of the surfactant from the channels and condensation of residual SiOH groups in the silica walls.

**Surfactant assemblies on graphite** There are several experimental difficulties which prevent direct study of silica-surfactant film growth by AFM, not the least of which is the polymerization and condensation of silicate on the tip. Thus aqueous CTACl solutions were used instead to study the assembly of surfactants on graphite.

The organization of adsorbed surfactants at the boundary between water and solid substrates has recently been observed using the pre-contact mode AFM (with EDL) soft imaging technique. The perturbation of the surfactant assembly by the scanning tip can be further reduced and the quality of the AFM images enhanced by using the tapping-mode in conjunction with the pre-contact EDL technique.
Figure 2.10. SEM images of a mesoporous silica film grown on freshly cleaved pyrolytic graphite (a) a large area and a growth front of the film; (b) a growth front showing the filaments and triangular pillar; (c) close up views of the triangular pillar.
Figure 2.11. TEM images of an as-synthesized mesoporous silica film showing (a) the hexagonally closed-packed structure and (b) the thickness and channel direction.
Figure 2.12. AFM images of the surface of the mesoporous silica film grown on graphite: (a) steps on the edges of the triangular pits and (b) terraces on the filaments at a growth front.
Pre-contact (EDL) tapping mode AFM images of an aqueous solution of CTACl adsorbed on graphite have been obtained over the concentration range of 4-18 mM. One can discern well-defined parallel stripes with a periodicity of 5.1 ± 0.1 nm for the 4 mM and 9 mM samples in the first few minutes after adding the solution to the cell, Figure 2.13a. Thickness measurement of the surfactant assembly shows that the aggregation is most likely a hemimicellar monolayer. Within a similar period, the 18 mM surfactant solution produced a similar periodic mesostructure but with evidence of vectorial growth of the aggregates, having an average body width of about 20 ± 3 nm and extensive regions of body length, Figure 2.13b. These objects appear to be co-aligned with the underlying hemicylindrical micellar monolayer. The AFM images also reveal the presence of domains where arrays of cylindrical micelles meet at boundaries with either 60° or 120° angles. This further suggests that the aggregated overlayer is aligned with the hexagonal unit cell axis of the graphite.

The AFM images of surfactant assemblies on graphite, at low and high concentrations, show differences with time. For example, AFM images for 4 mM surfactant solutions remain about the same during the 30 minute period after addition of the surfactant. However, for the 9 mM and 18 mM concentrations, the distances between the co-aligned micellar cylinders increases to around 9.5 ± 0.5 nm. The tip can disrupt the soft layer and burrow through the bulk of the surfactant film until it reaches either the hemicylindrical micellar monolayer adsorbed at the graphite-water interface or the graphite substrate itself. The thickness of the surfactant assembly between the structured and unstructured zone is about 40-50 nm as measured in height mode. The periodic mesostructure tends to be blurred for films thicker than about 100 nm.

After about 30-40 minutes, the 4 mM surfactant solution shows an interesting morphology with mesoscale periodicity in the range of 10 to 30 nm. The “final” stage of surfactant aggregation for concentrations of 9 mM and 18 mM is shown in Figure 2.13. New structures can be seen to emerge in the external region of the surfactant assembly. They tend to fall into classes having length scales of either 30-50 nm or 100 nm and larger. No large scale structures were observed under similar circumstances for the 4 mM concentration solutions.
Figure 2.13. Tapping mode AFM images (phase detection) of CTACl assemblies on graphite: (a) 4 mM, (b) 9 mM, (c) (height mode) 18 mM, and (d) the “final” stage, 18 mM (phase mode).
2.2.4 Discussion

The above results provide a basis for beginning to understand the origin of the preferred orientation and apparent registry of the channels of the mesoporous silica film with the hexagonal symmetry axis of the graphite surface.

Pyrolytic graphite is a layer form of carbon consisting of graphene sheets showing anisotropy in conductivity and other properties, Figure 2.14. High quality pyrolytic graphite can be easily cleaved along the c-axis. The exposed surface, or $ab$-plane, is hydrophobic and has a hexagonal structure with center-to-center spacing of 2.46 Å. Such an extended ordered structure can be expected to serve as a template for mesoporous silica film growth.

Figure 2.14. Graphite surface $ab$-plane.
The assembly process in the absence of TEOS likely begins with adsorption of CTACl on the graphite surface. The hydrophobic interaction between the alkane chain and the graphite is believed to be the driving force behind the surfactants lying flat on the graphite surface. Geometrical matching of the methylene groups in the all-trans alkane chain with the aromatic carbon six-rings in the planar graphite surface, favors a head-to-head and tail-to-tail packing arrangement of the surfactant along the hexagonal symmetry axes of graphite. This geometry is favored by hydrophobic, ion-pair and image dipole forces between the surfactants and the electrically conducting graphite surface. The result is parallel stripes of surfactants running orthogonal to the graphite hexagonal symmetry axis. The model has been evaluated by other groups using AFM and calorimetric techniques. The stripes serve as a template for the further adsorption of CTACl from solution and the formation of a monolayer of 50 Å diameter hemicylindrical micelles with a thickness of ca. 25 Å.

The pre-contact tapping mode AFM images of aqueous solutions of CTACl adsorbed on graphite over the concentration range of 4-18 mM show well-defined parallel stripes with a periodicity of 5.1 ± 0.1 nm and a thickness of at least 40-50 nm. The estimated thickness of this surfactant assembly implies the existence of about 10 layers of 5 nm diameter cylindrical micelles most likely organized as a liquid crystal film at the boundary between water and graphite.

The origin of the preferred orientation and apparent registry of the channels of mesoporous silica films with the graphite surface structure can therefore be understood in terms of the “mesoepitaxial” assembly of surfactant overstructures. In the absence of TEOS, the assembly process likely begins with adsorption of CTACl on the graphite surface. The worm-shaped mesostructures emerge at a surfactant concentration above roughly 9 mM which show vectorial growth along the direction of the long axis of the hemicylindrical micelles. These structures evolve to produce a mesostructured surfactant film. This implies that continued accretion of CTACl from solution by the hemicylindrical micelle layer on graphite leads to the development of a close-packed cylindrical micelle multilayer assembly which is probably best described as a hexagonal lyotropic liquid crystal film registered with the graphite surface. Such a surface confined liquid crystal appears to be the precursor to the
oriented hexagonal mesoporous silica film that forms on graphite in the presence of TEOS under acidic conditions, Figure 2.15.

In the presence of TEOS, nucleation of the mesoporous silica film can be initiated by polymerization of charge-balancing silicate anions in the head group region of a liquid crystal layer that has its director axis registered with the hexagonal symmetry axes of the underlying graphite substrate. Further growth of the mesoporous silica film is determined by charge and structure requirements at the surfactant-silicate/graphite interface. This process produces a mesoporous silica film in which the channels are aligned with respect to the hexagonal symmetry axes of the graphite surface. Subsequent deposition and polymerization of surfactant-silicate micellar assemblies results in the continuous growth and thickening of the mesoporous silica film until the reactants are exhausted, Figure 2.16. This templating model for the polymerization of a surfactant-silicate liquid crystal film on graphite is consistent with the observation of mutually aligned triangular-shaped pits in the body of the resulting mesoporous silica film, which are themselves in alignment with the edges of the filaments that comprise the growth fronts of the film. Growth fronts are expected to meet at 60° in the body of the mesoporous silica film to form triangular features and to terminate at the extremities of the film to create filaments displaying 60° and 120° angular features.
Figure 2.15. Graphical illustration of the stages involved in the evolution of a liquid crystal film on graphite: (a) surfactant monolayer, (b) hemicylindrical micellar monolayer, (c) vectorial nucleation of worm-shaped mesostructures, and (d) liquid crystal film.
Figure 2.16. Graphical illustration of proposed model for the formation of mesoporous silica film on graphite.
2.3 SAM patterned films: mesoporous silica with micron scale designs

The decoration of surfaces through techniques such as ultraviolet and X-ray radiation, ion and electron beams,\textsuperscript{18} microcontact printing, micromachining and lithographic molding technologies,\textsuperscript{19} provides patterned structures of sub-micrometer dimensions for a variety of device applications. Self-assembly of alkane thiols on gold surfaces allows a convenient route to selected area deposition of materials as diverse as polymers, proteins, ceramic oxides, metal colloids and semiconductors, and with potential applications ranging from cell biology to electronics.\textsuperscript{19,20} Extension of self-assembling monolayers (SAMs) to three dimensions by etching, plating, condensation and polymerization methods, may lead to new functional architectures.\textsuperscript{21} Synthesis of patterned mesoporous silica is presented, demonstrating surface anchoring of surfactant templated mesostructures.\textsuperscript{22} A hetero-bilayer synthetic pathway that facilitates the growth of patterned mesoporous silica through co-assembly of alkane thiol-coated gold surfaces, surfactant-alkanethiol bilayers, and surfactant-silicate assemblies is proposed.

2.3.1 Synthesis and characterization

**Substrate Preparation.** Muscovite mica was used as the underlying planar support for a sputtered Cr adhesion layer followed by a gold layer. The deposition was done with a Perkin-Elmer 2400 sputtering system operating at $10^{-6}$ torr background pressure. The sputtering was conducted in a bell jar at 12 milli-Torr pressure of argon gas at 800 volts. The deposition rate was estimated from a quartz crystal microbalance to be 2.275 Å/second for gold. The time duration for deposition of the adhesion layer and gold layer were typically 60 seconds and 300 seconds, respectively. The gold films so formed had a thickness of ca. 700 Å.

**PDMS stamp preparation.** In order to make polydimethylsiloxane (PDMS) patterned stamps, 10 parts of Sylgard® 184 silicone elastomer (Dow Corning Corporation, Midland, Michigan) and 1 part of Sylgard® 184 silicone curing agent (Dow Corning Corporation, Midland, Michigan) were mixed well and poured onto the surface of a patterned
silicon wafer. The mixture was then set at room temperature for several hours to let air release from the viscous liquid and cured at enhanced temperatures. The PDMS block was then removed from the silicon wafer and cut into the desired shape. PDMS stamps with a range of 3 to 10 micron size lines were used to pattern the gold.

Methanol was employed to clean the gold surface for subsequent growth of the mesoporous silica. A 1-10 mM methanol solution of hexadecanethiol (98+, Aldrich) was applied to the stamp which was immediately dried in a flow of nitrogen. The hexadecanethiol-coated stamp was used to deposit a self-assembled monolayer onto the gold substrate, Figure 2.17, which was used for the growth of the mesoporous silica overlayer. It should be pointed out that the quality of the SAM patterns can vary depending upon the procedures and stamps used.23

![Figure 2.17. Illustration of a patterned SAM prepared on gold by soft-lithography.](image)

The film synthesis was similar to that used for supported films in section 2.1.2.1, except the deposition time was normally shortened to a period ranging from two hours to one day. The reaction time is limited by the rate of diffusion of HCl into the adhesive Cr layer
which leads to the destruction of this intermediate layer and the peeling of the gold layer from mica surface. The hexadecanethiol SAM patterned gold substrate was floated at the air-water interface during film synthesis.

**Characterization** Energy dispersive X-ray (EDX) microanalysis was obtained on a Hitachi S-4500 field emission microscope with an acceleration voltage of 20 kV. PXRD, SEM, TEM and microtoming procedures were similar to those described in previous sections.

2.3.2 Result and discussion

SEM images of mesoporous silica deposited on gold and hexadecanethiol SAM-coated gold depict mainly disc- and ribbon-shaped morphologies which grow in size and show coalescence with increasing coverage. Representative SEM images for the deposited silica material are shown in Figure 2.18. The disc- and ribbon-shaped morphologies of the mesoporous silica on SAM coated gold, appear to be predominantly deposited on the SAM patterned lines of the gold surface and they located predominantly along the patterned line regions. Use of a hybrid unpatterned-patterned SAM establishes that the mesoporous silica preferentially deposits on the alkanethiol covered regions of the gold, Figure 2.18c.

Powder X-ray diffraction (PXRD) patterns for the deposited material on gold and on the hexadecanethiol SAM-coated gold typically display one intense (100) low angle reflection corresponding to a \( d_{100} \)-spacing in the range of 35-38 Å, together with a much weaker and broad (200) reflection, both of which are attributed to the hexagonal form of mesoporous silica, Figure 2.19. The absence of the (110) reflection suggests preferred growth of the hexagonal form of mesoporous silica in which the channel c-axis runs predominantly parallel to the surface of the gold substrate.
Figure 2.18. SEM images of mesoporous silica grown on a SAM patterned gold substrate: (a) low, (b) high magnifications, and (c) on a hybrid patterned-unpatterned gold substrate.
Secondary electron (SE) and EDX microanalysis is shown in Figure 2.20. The light regions in SE correspond to heavier elements and those regions in EDX maps are the areas with detected elements. Since the base for the gold layer was mica, the aluminum rich sections relate to those places with less deposition of mesoporous silica. This analysis serves to establish the distribution of the element silicon in the mica-gold and mica-gold-SAM regions of the substrate. Quantification of the selectivity of the deposition process takes into account the different penetration depths of the electron beam in these two regions. It is important to note that the thickness of the gold overlayer on the mica is \textit{ca.} 700 Å while the penetration of the electron beam under the conditions used can be at least 5000 Å. The EDX results obtained from individual spots on both patterned and unpatterned regions show that deposited mesoporous silica is primarily located on the SAM delineated regions of the mica-gold substrate (\textit{ca.} 80 \%). This selectivity implies that the rate of adhesion of silicate-micellar solute species on the SAM defined areas of the gold is much greater than that on the bare gold itself.

TEM images of an epoxy embedded, microtomed section of mesoporous silica grown on a hexadecanethiol SAM patterned on a gold substrate are shown in Figure 2.21. The larger light area at the top is the epoxy matrix, smaller dark areas at the bottom are the line patterns of the deposited mesoporous silica, and the gold substrate has been removed in the microtoming. The mesoporous silica can be identified by its hexagonal symmetry structure and is preferentially deposited on the regions of the gold substrate containing hexadecanethiol SAM, Figure 2.21. The average $d_{100}$-spacing estimated from the TEM images agrees with that determined by PXRD. On surveying the TEM images, there is evidence that the channels of the deposited hexagonal mesoporous silica run substantially parallel to the gold surface, consistent with the PXRD observation of preferred orientation of the channels. This implies that there exists a certain type of organization of an alkanethiol SAM and a surfactant overstructure in the boundary region between the gold and water.

The collected results establish the preferred growth of mesoporous silica on the SAM patterned regions. The observation of spatial selectivity likely relates to fact that lipids as well as ionic surfactants such as sodium dodecyl sulfate can be transferred to, or formed as a
bilayer on a thiol-terminated gold substrate. The hydrophobicity of the alkanethiol monolayer is believed to be the driving force for the organization of the phospholipids.\textsuperscript{24,25}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{pxrd_trace.png}
\caption{A PXRD trace for mesoporous silica grown on hexadecanethiol SAM patterns on a gold substrate.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{se_edx_mapping.png}
\caption{SE and EDX mapping of Al, Si, and Au elements for the mesoporous silica films on SAM patterned gold.}
\end{figure}
Figure 2.21. TEM images of an microtomed section of mesoporous silica grown on hexadecanethiol SAM coated parallel lines on a gold substrate (a) selected area growth (scale bar 4000 nm), and (b) the hexagonal mesostructure (scale bar 50 nm).
The proposed model for selected area growth of mesoporous silica on SAM patterned gold is highlighted in Figure 2.22. The process for creating mesoporous silica with micron scale designs likely involves "three-way-templating", in which hydrophobic interactions between the alkane tails of an alkanethiol SAM on gold and those of cationic surfactants in aqueous solution are the main driving force behind the co-assembly of an alkanethiol-surfactant hetero-bilayer. The externally arranged polar trimethylammonium head groups of this hetero-bilayer that are exposed to the aqueous solution phase act as hydrophilic landing-sites for silicate-surfactant assemblies. Since mesoporous silica can be deposited on both a pure SAM layer on gold as well as a pure Au substrate, preferential accretion and organization of silicate-surfactant micellar solute species at the bilayer region facilitates the formation of mesoporous silica predominantly in the SAM coated gold regions of the substrate.

Figure 2.22. Illustration of the selective accretion of mesoporous silica on hexadecanethiol SAM patterned regions of a gold substrate.
2.4 References


Chapter Three
Low Dimensional Form II: Free-Standing and Oriented Mesoporous Silica Films Growth at the Air-Water Interface

3.1 Introduction

Free-standing porous inorganic films or membranes are commonly made through sol-gel techniques. In a typical synthesis, alkoxides, hydroxides or metallic salts are used and through controlled hydrolysis, a sol can be achieved. The sol is then transferred onto a surface, typically solid substrates, and cast into a layer. Supported and unsupported membranes with a pore size ranging from nanometer to well above micron and a surface area of several hundreds m²/g, can be obtained after further drying and thermal treatment. Because of the intrinsic properties of sol-gel, the air-liquid interface has hardly been used for the synthesis of porous inorganic films. In one of the few examples, Klein and Gallagher have shown that the air-water interface can be used for making a silica film. By pouring a TEOS-water-ethanol solution onto a dense non-polar organic liquid, such as tetrabromoethane (CHBr₂CHBr₂), a silica gel sheet with a dried thickness of 100-200 μm with an average pore size of 25 μm can be made. The driving force for silica porous film formation comes from the difference in surface tension between the sol-gel solution and the organic liquid. A high surface tension for the organic phase and a small interfacial tension between the two phases are required for film formation.

The synthetic strategy for growing oriented mesoporous silica films on solid substrates can be extended to the interface between air and water under quiescent, dilute acidic aqueous conditions, since organized surfactant structures such as a Langmuir film may serve as a “soft” substrate for the initiation of mesoporous film growth. In this chapter, synthesis of hexagonal mesoporous silica film in which the channels are oriented parallel to the film surface will be presented. The free-standing mesoporous silica films are continuous and have a smooth surface with an angstrom scale root mean square (RMS) surface roughness based on TEM cross-sectional images. TEM studies of early growth stage films provide rich
information on channel architecture. Microscopic defects are found to pervade the channel structure and resemble those found in lyotropic liquid crystals. This suggests that free-standing mesoporous silica film evolves from the acid catalyzed polymerization of a lyotropic silicate mesophase located at the air-water interface.

A model for free-standing mesoporous silica film formation is proposed that involves a dual-templating role for the surfactant. It is based on collective interactions between a surfactant overstructure at the air-water interface, polymerizable silicate building-blocks, and micellar aggregates in solution.

3.2. Synthesis and characterization

3.2.1. Synthesis

The synthesis of mesoporous silica films at the air-water interface under acidic conditions is achieved using the following optimized reactant mole ratio:

\[ 100 \text{H}_2\text{O} : 7.4 \text{HCl} : 0.11 \text{CTACl} : 0.13 \text{TEOS} \]

using the same procedure as described in Chapter 2. Well-formed films with thickness ranging from tens of nanometers up to approximately a micron have been grown at the air-water interface. The films have been lifted onto aluminum, glass, Teflon-covered glass, copper grids with/without carbon coating, and other substrates according to characterization requirements.

Raising the pH of the bulk synthetic mixture can lead to an increase in the thickness of the film. For example, ca. 5-10 μm thick films can be obtained from the reactant ratio of 100 H₂O : 1 HCl : 0.11 CTACl : 0.13 TEOS at room temperature. In a standard preparation, 2.9 g of an aqueous solution of CTACl (wt. 29%) is added with stirring to 2.5 g of HCl (36.5-38%) and 40.8 g of deionized water by using a magnetic stirrer (Corning PC-351 hot plate stirrer) with a 0.375 inch × 1.5 inch stir bar in a polypropylene beaker, followed by the addition of 0.65 g of TEOS. The mixture was then stirred for 3 to 10 minutes at room temperature. The final mixture was transferred into either a round or square polypropylene (PP) or low density polyethylene (LDPE) bottle with different diameters and length of edge (Nalgene®, LABCOR, Inc.), and allowed to achieve a quiescent state. The mesoporous silica growth process was
typically allowed to proceed for a period of one week under static conditions at room
temperature. Depending on the initial synthesis time and the stirring rate for the mixing,
different optical birefringence textures were observed.

The calcination of the film was achieved using two different procedures. Direct
calcination was done in air in a furnace attached to an Omega CN-2010 programmable
temperature controller. The temperature ramp was less than 1 °C/min. and typically the
sample was held at 450 °C for 4-10 hours. The other calcination method involved two steps:
the sample was first dehydrated at 150 °C for over 10 hours under \( \leq 10^{-5} \) torr dynamic vacuum
and then was heated in air at 450 °C for \( ca. \) 10 hours. Most of the characterization work for
the calcined film samples was done using the direct calcination procedure unless mentioned
otherwise.

3.2.2. Characterization

**PXRD** data was obtained on a Siemens D5000 diffractometer using Ni-filtered Cu-\( K_\alpha \)
radiation with \( \lambda = 1.54178 \) Å. A home-made plexiglass sample holder was used for recording
the PXRD patterns. Samples for *in-situ* VT-PXRD were prepared by lifting the free-standing
mesoporous silica film onto a Pt strip. The strip was then assembled on the sample stage with
the thermocouple located directly underneath. The temperature ramp used was 4 °C/min.
During the recording of PXRD patterns, the temperature was constant.

**TEM** and **Selected Area Electron Diffraction** (SAED) images were recorded on a
Philips 430 microscope operating at an accelerating voltage of 100 kV. Ultrathin uncut
specimens for TEM were prepared by carefully lifting the film in a horizontal fashion from
the aqueous side of the interface, onto either a pristine or a carbon-coated 400 mesh copper
TEM grid. The films were thin enough for direct TEM imaging without any further
treatment. SAED patterns were recorded from the thin film samples on the same microscope.
Different apertures were used to observe domain effects. Microtoming was also used for the
film characterization as detailed in the second chapter. Spurr's epoxy resin (TAAB
laboratories equipment, Aldermaston, U.K.) was used for specimen preparation, including
most of the as-synthesized films and all the calcined film samples. A cyanoacrylate resin
Superglue® was used for as-synthesized thicker versions of the film samples synthesized at higher pH. Additional hardening of the matrix was induced by heating at 60 °C for 12 hours. The choice of the imbedding media was based on the intrinsic properties of the films such as the degree of polymerization.

AFM experiments were conducted on a NanoScope® III microscope (Digital Instruments, CA) using silicon integrated tip cantilevers (Park Scientific Instruments, CA) for height mode scanning of the shapes. The cantilevers were used as received. Images of the surfaces of the mesoporous silica shapes were obtained by using direct contact (dc) scanning mode.

Optical Microscopy images were recorded in transmission mode on an Olympus BH-2 microscope, using convergent white light with a Kodak Gold Ultra 400 film. Polarizers and analyzers were applied for the study of birefringence phenomena.

Laser Scanning Confocal Microscopy (LSCM) images of the films supported on a glass plate were recorded using a Bio-Rad 600 instrument in the reflectance mode, with a 100x objective using an Ar+/Kr+ 488 nm laser light source; the confocal arrangement rejects light from areas that are not in the focal plane and produces a true surface image.

Proton-decoupled $^{29}$Si solid state magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded on a Bruker DSX 200 MHz spectrometer at 40 MHz using a 90° pulse with a delay time of 600 seconds. A long delay time was used because previous studies have shown that the relaxation time of silicon in mesoporous materials can be as long as 120 seconds. A Bruker deconvolution program was used for simulation of the NMR spectra.

Thermal analyses (differential scanning calorimeter, DSC and thermal gravimetric analysis, TGA) were recorded on Perkin-Elmer Thermal Analysis Series 7 instrumentation under N₂. The temperature ramp used was 5 °C/min. Aluminum pans were used as DSC sample holders and as a reference. A platinum basket was used as a TGA sample holder.

Adsorption isotherms were collected by a gravimetric technique using a McBain balance interfaced to a computer. To prepare a sample for the measurement of adsorption isotherms, a sufficient quantity of the as-synthesized films was ground to a fine powder and
then calcined following one of the calcination procedures mentioned above. The sample (ca. 20 -30 mg) was placed in a small quartz basket which was suspended from a quartz spring and outgassed at 150 °C for 15 hours. The entire sample tube was immersed into liquid nitrogen before data collection began. Incremental amounts of gas were slowly introduced into the system by a computer-controlled piezo-electric valve. Each point of uptake versus pressure was recorded once the pressure of the system remained constant, at which point the system was in a state of equilibrium. Pressures were measured with two Baratron® pressure transducers having ranges that covered 0-100 Torr and 0-1000 Torr. The uptake of N₂ was measured by a Schaevitz linear displacement transducer, which measured the vertical displacement of an iron core suspended from the quartz spring and attached to the sample basket by a long quartz hook. The pore size distributions and the pore volumes were obtained using the Dollimore-Heal method⁹ while the surface area was obtained using the BET method.¹⁰,¹¹

3.3. Results

3.3.1. Free-standing film formed at air-water interface

A low magnification TEM image of a film grown at the air-water interface for 3-5 minutes from a mixture with the reactant mole ratio of 100 H₂O : 7 HCl : 0.11 CTACl : 0.13 TEOS shows a morphology comprised of domains with boundary walls and void spaces separating them, Figure 3.1. The inter-domain voids appear to be consolidated after approximately 10 minutes of film growth to a continuous film.

A typical powder X-ray diffraction pattern of the film showed only (h00) related reflections with at least two peaks, the (100) and (200) reflections, without any k and l related reflections, characteristic of hexagonal symmetry mesoporous silica exhibiting preferred alignment of the channels with respect to the surface of the film.
Figure 3.1. TEM image showing the void spaces between domains in the mesoporous silica film grown at the air-water interface at an early stage of growth.

Early-stage free-standing films were lifted onto TEM grids and viewed directly, they were sufficiently thin to be imaged at an accelerating voltage of 50 kV, Figure 3.2. Under these conditions, a highly ordered periodic structure with a spacing of approximately 25 Å is observed. The figure clearly shows that the channels are oriented parallel to the surface of the film. The observed periodicity is consistent with a hexagonal close-packed arrangement of 1-D channels viewed orthogonally to the film surface along the [210] or [120] direction of the hexagonal unit cell, Figure 3.3. Well-defined parallel lines with a spacing of half that of the center-to-center distance between the channels are seen.\textsuperscript{12} This observation is consistent with the PXRD data which strongly suggests preferred orientation of the channel structure within the mesoporous silica film. Although these TEM images reveal that the channels are oriented with respect to the film surface, the channels do not exist in a uniform co-linear arrangement.
within the domains. The channels in fact form a continuum of swirling and curling patterns including concentric circle, herringbone, fingerprint, and hairpin structures. The patterns resemble those observed in purely organic liquid crystals.

A SAED study of the same thin samples used for the TEM imaging provides additional insight into the channel architecture of the film. It is found that when the diameter of the incident electron beam exposed to the film is gradually increased from 0.5 to 6 microns, the SAED pattern is transformed from the (210) and (210) diffraction spots, corresponding to the ca. 25 Å center-to-center channel spacing, to an SAED pattern that displays increased streaking and arcing of the original two diffraction spots, eventually forming a discontinuous circle, Figure 3.4. The SAED patterns maintain two-fold symmetry and are consistent with a poly-domain film morphology, in which an increasingly large number of curved channels are placed within the area of the diffracted electron beam.

The as-synthesized mesoporous silica film formed at the air-water is found to maintain its macroscopic integrity after drying but can develop stress induced cracks. SEM images of films that have been transferred onto a copper grid reveal that they are essentially continuous, Figure 3.5a. Under an accelerating voltage of 20 kV, the films are electronically "transparent". Such films are also flexible, as seen in Figure 3.5b. These properties reflect the organic-inorganic composite nature of the films. Together with complementary PXRD studies, the results demonstrate macroscopic integrity and mesoporous order of the attached films.

TEM images of microtomed sections of as-synthesized and calcined free-standing film are shown in Figure 3.6. The film surface shown in Figure 3.6a is the one formed at the air-water interface. The image reveals that the channels are hexagonally close-packed with a centre-to-centre distance of about 50 Å and run parallel to the air-water interface. The difference in surface roughness between the side grown at the air interface and that grown in the solution can be seen in Figure 3.6b. Smooth film surfaces with a RMS roughness of ca. 3 Å are obtained, implying that the growth process occurs via deposition of the silicate-surfactant micelles at a surfactant overstructure localized at this interface. The film surface growing into the solution shows roughness on the mesoscopic scale, representing a replica of the silicate-micellar deposition and polymerization process. A TEM image of a sectioned
calcined film is shown Figure 3.6c. The mesoporous structure and order of the film can be seen to remain intact.

**Figure 3.2.** Representative TEM images of the channel patterns of free-standing mesoporous silica films: (a) straight herringbone, and (b) curved channel plan.
Figure 3.3. Symmetry planes and directions in oriented mesoporous silica with $P6_m$ phase.

Figure 3.4. SAED patterns of a free-standing mesoporous silica film. Effective aperture diameters, left to right: 0.5 μm (spot), 1.5 μm (streaked), and 6 μm (arcs).
Figure 3.5. SEM image of a free-standing film on a copper grid showing (a) the transparent nature under the imaging conditions (accelerating voltage of 20 kV), and (b) the flexibility of the films.
Figure 3.6 TEM image of an as-synthesized free-standing film showing (a) the roughness between the two surfaces and thickness, (b) hexagonal array, and (c) calcined film.
AFM is an effective probe of the overall topological landscape and structural detail of the surface of the mesoporous silica films, Figure 3.7. The as-synthesized mesoporous free-standing films were lifted onto either mica or glass for imaging purposes. AFM scans provide an estimate of the RMS roughness of the surface to be ca. 2 Å. This value represents the local roughness of the top surface of the film and is in good agreement with TEM results, Figure 3.6b. With two-dimensional fast Fourier transformation (FFT) filtration and the high frequency noise removed, AFM images of the films reveal patches with parallel surface features with a periodicity of ca. 50 Å, which appear to have a spheroid texture, Figure 3.7b. The AFM images were reproducible over different scan directions, load forces, tips and samples and are not considered to portray artifacts. It is possible that some of the irregularities observed in the surface of the film could arise from inhomogeneous silicate condensation processes as well as contributions from residual surfactant. The image can be viewed as a silica replica of the distribution of head groups of the surfactant overstructure existing at the air-water interface.

The macroscopic topology of the films can be revealed in detail by AFM and LSCM. The AFM images portray the overall topological landscape of the film, while the LSCM images display the contrast and optical interference patterns that emphasize the spatial variation in curvature across the film. From the AFM images, intriguing micron scale mounds that exclusively protrude away from the air-water interface can be seen. These protrusions point to the surface exposed to air, Figure 3.8. This topology is further established by LSCM, Figure 3.9.

The picture of the internal channel architecture of the mesoporous silica film that emerges from PXRD, TEM, SAED and LSCM studies, is that of swirling and curling channel patterns that meander throughout the film, but with the channel axis strictly constrained to the plane parallel to the air-water interface.
Figure 3.7. AFM image for the top surface of a mesoporous silica film: (a) raw image, (b) two-dimensional FFT filtered image of (a) with just the high frequency noise removed.
Figure 3.8. AFM image showing the (a) top, and (b) bottom surface microtopography of a mesoporous silica film synthesized at the air-water interface.

Figure 3.9. LSCM image of a mesoporous silica film synthesized at the air-water interface.
The PXRD patterns for the as-synthesized and calcined free-standing films are shown in Figure 3.10. They reveal \((100)\) and \((200)\) reflections consistent with the TEM observations that the channels run parallel to the surfactant overlayer at the air-water interface. It is possible to partially randomize the oriented samples by grinding up the films.\(^{14}\) Such a sample on a low background quartz cell shows the expected \((100)\), \((110)\), and \((200)\) PXRD reflections. The absence of the \((110)\) reflection for the as-synthesized film samples and the reappearance of this reflection for ground up samples confirms that the channel axis is oriented parallel to the templating liquid surface. On template removal by calcination of the films, the anticipated \((100)\) reflection shifts to slightly higher angles because of thermally induced shrinkage of the hexagonal unit cell arising from the condensation of residual SiOH groups in the silica channels, similar to that seen for supported films.

The thermal stability of the mesoporous films has been examined by an \textit{in situ} variable temperature PXRD experiment in air. The high temperature results are shown in Figure 3.11. The temperatures starting from the left-side of the traces are 450 (1.75 hours), 500, 650, 700, 750 (25 minutes), 750 (50 minutes), 750 (2 hours), 750 (3.5 hours) and 800 °C, respectively, where the number in parenthesis represents the time that the sample was held at each temperature. The results demonstrate that the oriented channel structure of the hexagonal arrays was retained to at least 650 °C and only began to collapse in the range 850-900 °C.

### 3.3.2. Synthesis of thick films in higher pH conditions at room temperature

The film discussed in the previous section has a thickness of about half a micron, and it is possible to make a thicker film by changing the reaction temperature and reactant ratios particularly important being the amount of acid. It is expected that the structure and properties of the film could change with reaction conditions. Free-standing films formed by using reactant ratios of 100 H<sub>2</sub>O : 1.0 HCl : 0.11 CTACl : 0.13 TEOS at room temperature synthetic conditions are discussed below.
Figure 3.10. The PXRD patterns for free-standing (a) as-synthesized and (b) calcined mesoporous silica films.

Figure 3.11. In-situ VT-PXRD patterns of a mesoporous silica film grown at the air-water interface. The temperatures starting from the left-side of the traces are 450 (1.75 hours), 500, 650, 700, 750 (25 minutes), 750 (50 minutes), 750 (2 hours), 750 (3.5 hours) and 800 °C, respectively.
SEM images of a free-standing film obtained using these synthetic conditions and agitated for 10 minutes are shown in Figure 3.12. The film is continuous and the surface of the film that grows adjacent to the air interface has a smoother surface than that of the growing front at the water interface, Figure 3.12a. The observed bending of the film presumably arises from drying effects. A cross-sectional view of the film shows the thickness to be ca. 5-10 microns, Figure 3.12b.

An optical microscopy image shows that the film can be optically transparent or opaque. Representative POM images obtained between crossed polarizers, for mesoporous silica films formed under slightly different conditions are shown in Figure 3.13. In contrast to previously reported images for ≤ ca. 0.5 μm mesoporous silica thin films, the obtained thick films display classic liquid crystal textures. The transformation of the films from those displaying discrete birefringence patterns to those with fan-type textures can be controlled by simply choosing the stirring time or rate of addition of the synthesis mixture before it is allowed to sit in a quiescent growth state. Films with a fan-type texture were obtained for mixtures stirred for ca. 10 minutes at a low stirring rate, Figure 3.13b, or ca. 5 minutes at a high stirring rate while films showing discrete birefringence patterns emerged after stirring for 3 to 5 minutes at low rate, Figure 3.13a. The observed fan-type texture is typical of a normal hexagonal lyotropic liquid crystal, H₇ phase having its optical axis in the plane of the film, which suggests that the film so-formed maintained its preferred orientation. The fan-type texture is retained upon removing the surfactant and after annealing the film at 450°C, Figure 3.13c. This implies that the optical birefringence of the film does not require the surfactant to be present in the channels and that strain anisotropy in the film is not the source of the fan-type texture.

PXRD traces of these mesoporous silica films are shown in Figure 3.14. The PXRD pattern of as-synthesized and calcined films confirms them to be hexagonal mesoporous silica and not the silicate liquid crystal mesophase for which the d₁₀₀ appears at much lower angles. The presence of only (100) and (200) low angle reflections implies that the channels preferentially run parallel to the surface of the film as in the previous cases.
Figure 3.12. Representative SEM images of as-synthesized “thick” mesoporous silica film showing (a) a typical surface with bending, and (b) cross section.
Figure 3.13. POM images of mesoporous silica films: (a) discrete texture of an as-synthesized film; fan-type texture of (b) an as-synthesized film and (c) a calcined film (scale bar: 50 μm).
Although the structure is retained after surfactant removal by calcination in air, it appears to deviate somewhat from the ordered hexagonal phase. A contraction of the hexagonal mesostructure occurred due to the condensation-polymerization of residual hydroxyls in the silica channel walls. However, the contraction of the d_{100} spacing for calcined films was quite large which implies a much lower degree of polymerization of the silica in the surfactant-containing precursor film (see below). The structure of the oriented mesoporous film was also investigated by examining the effect of grinding in a mortar and pestle. The ground-up film samples are white powders and the PXRD trace showed the expected four peaks (100), (110), (200) and (210) from diffraction planes that are typically seen in randomly oriented powder preparations of hexagonal mesoporous silica. The calcined and annealed ground-up samples also show a large contraction of the d_{100}-spacing similar to that for the calcined oriented film. The final pore sizes for calcined films were practically the same for as-synthesized and the ground samples.

It was possible to maintain an ordered channel structure by controlled calcination or pretreatment of a as-synthesized free-standing film. After the vacuum dehydration treatment (10^{-6} torr) at 150 °C, the d_{100} diffraction peak contracts ca. 2 Å. A further calcination of the dehydrated sample leads to an improved ordering of the mesoporous silica structure compared to that obtained without pre-treatment. This is evidenced by a higher diffraction intensity and a greater number of reflections in the PXRD patterns of the pretreated samples. A comparison of the PXRD patterns for calcined ground films with and without dehydration treatment is shown in Figure 3.15. Clearly the moisture content of an as-synthesized incompletely-polymerized mesoporous film can affect the stability of the structure.\textsuperscript{18}

The orientation of the channels for the as-synthesized and calcined hexagonal mesoporous films is confirmed by TEM images of microtomed thin sections, Figure 3.16. The expected hexagonal honeycomb structure is seen in both as-synthesized and calcined mesoporous silica films. Careful inspection of the TEM images shows that the hexagonally packed pores are not as well organized as those in the thinner version of the free-standing films made at low pH and 80 °C. A lower degree of condensation-polymerization of silica (see below) may lead to a less stable channel wall structure. Microtomed specimens for the thick versions of the films often show tearing artifacts which are not a problem for thinner version of the films. Vacuum
dehydration prior to calcination seems to be an essential step for stabilizing a well-ordered hexagonal mesoporous structure. Calcination without vacuum dehydration appears to cause a greater distortion of the hexagonal mesoporous structure, Figure 3.16b.

Thermogravimetric analysis of the as-synthesized film shows the expected weight changes corresponding to loss of physisorbed water below 100 °C, surfactant template around 270 °C, and water formed during the condensation of framework hydroxyls around 360 °C and 600 °C, Figure 3.17. The total weight decrease is ca. 60-70% which represents a high weight loss for the mesoporous silica preparation which typically shows weight losses in 40-50% range. This occurs because of the much lower degree of polymerization, higher silicate charge and hence larger amount of charge-balancing surfactant template imbibed within the channels.

The thermal properties of the film were also studied by differential scanning calorimetry (DSC). No evidence of an endotherm during the heating cycle from 20 °C to 250 °C could be observed, Figure 3.18. This contrasts from organic liquid crystals which typically show at least two endothermic events caused by the solid and liquid crystal melting transitions. The combined results of the TGA and DSC show that the thermal properties of these mesoporous silica films resemble those of the powdered solid. Moreover, the imbibed surfactant within the channels is not behaving like a liquid crystalline mesophase.

The proton-decoupled 29Si MAS NMR spectrum and computer deconvolution of the spectrum for the as-synthesized mesoporous silica film is shown in Figure 3.19. Three silicon sites are observed with a $Q_2 : Q_3 : Q_4$ ratio of 8 : 42 : 48. $Q_2$, $Q_3$ and $Q_4$ refer to $\text{SiO}_2(\text{OH})_2$, $\text{SiO}_3(\text{OH})$, and $\text{SiO}_4$, respectively. The observation of $Q_2$ silicon species and the high value of $Q_3 + Q_4$ relative to $Q_4$ are consistent with the large contraction of the hexagonal mesostructure observed in the PXRD pattern upon calcination. This implies a lower degree of silicate polymerization in the as-synthesized thick films as compared to thinner ones.
Figure 3.14. PXRD traces of (a) as-synthesized, (b) calcined mesoporous silica films; (c) as-synthesized, and (d) calcined ground mesoporous silica films.

Figure 3.15. PXRD traces of (a) calcined ground film without dehydration and (b) calcined ground mesoporous silica films after dehydration treatment.
Figure 3.16. Representative TEM images of mesoporous silica films: (a) as-synthesized, (b) calcined (no dehydration treatment), (c) calcined (with dehydration treatment).
Figure 3.17. A representative TGA trace of a mesoporous silica film.

Figure 3.18. A representative DSC trace of an as-synthesized mesoporous silica film.
Figure 3.19. The proton-decoupled $^{29}$Si MAS NMR spectrum and computer deconvolution of the spectrum for the as-synthesized mesoporous silica film.

Quantification of the mesoporosity and surface area of the film was conducted on a McBain balance. $N_2$ isotherms at liquid nitrogen temperature with ground-up film samples are shown in Figure 3.20. The as-synthesized silica films show negligible $N_2$ adsorption after dehydration at 150 °C in vacuum. The isotherm for the vacuum dehydrated-calcined sample is typical of that expected for mesoporous materials, showing a Type IV isotherm. The surface area calculated from Brunauer-Emmett-Teller (BET) equation is ca. 1000 m$^2$/g, Figure 3.21.$^{21}$ The mean pore diameter estimated by the Dollimore-Heal method from the adsorption branch of the isotherm is ca. 2.8 nm. The value obtained is consistent with the
center-to-center distance of *ca.* 3.7 nm obtained from PXRD of calcined mesoporous film samples. The desorption branch of the isotherm shows both low and high pressure hysteresis. It is well documented that particular shapes of hysteresis loops can be associated with specific pore structures. Low pressure hysteresis in this case may be associated with the swelling of the walls of a partially condensed mesoporous silica during adsorption.\(^{10}\)

The isotherm for the directly calcined sample shows less uptake of nitrogen and has a much shallower inflection due to capillary condensation, and also displays low and high pressure hysteresis. The BET surface area is calculated to be *ca.* 750 m\(^2\)/g. These observations together with those from PXRD, TEM and NMR suggest that the vacuum-dehydration pre-treatment prior to calcination substantially improves the degree of order and mesoporosity of the silica films.

![Figure 3.20](image.png)

**Figure 3.20.** Nitrogen isotherms of free-standing silica film: (a) after dehydration at 150°C, (b) calcined without dehydration treatment, and (c) calcined with dehydration pre-treatment.
It is worthwhile to mention that the approach of growing thick mesoporous silica films can also be applied to water-solid interfaces, such as glass slides and tubes, freshly cleaved Muscovite mica, and pyrolytic graphite. Discrete birefringence patterns were observed for the films grown on planar and curved glass substrates. The discrete patterns on glass appear to arise from the local nucleation and growth of silicate-surfactant assemblies.

Interesting birefringence patterns were observed for the thick films grown on freshly cleaved muscovite mica, Figure 3.22. Light gray and dark areas were observed. Careful inspection of these images showed that striations on the patches with the same brightness are aligned parallel to the film surface and that the lines on different color patches meet at 60° or 120°. Recall that oriented mesoporous silica films have been found to grow on this surface in a registered fashion. Thus the observed correlation of striations amongst similarly colored domains most likely originates from preferential alignment of the channels in the mesoporous silica film along the hexagonal $ab$-axes of the mica surface.
3.4 Discussion

3.4.1 Surfactant overstructures at air-water interface

The converging evidence from PXRD, TEM, and nitrogen isotherm measurements for thick mesoporous silica films shows that they have oriented and hexagonally close-packed mesopores with the channel c-axis aligned parallel to the growth interface. The as-synthesized and calcined films showed only (100) and (200) diffraction, while additional (110) and (210) diffraction can be observed for ground-up samples. This unequivocally establishes that the mesoporous silica films are hexagonal and oriented with the channels parallel to the growth surface.

A starting point for understanding the formation of oriented free-standing mesoporous silica films is to examine how surfactants organize at the air-water interface. The discovery of ordered organic amphiphile layers formed at air-water interfaces was first published by
Katherine Blodgett in 1935. The well-known Langmuir-Blodgett film involves transferring an insoluble monolayer from a solution surface to a solid substrate.

Long chain organic molecules packed at the air-water interface can often have ordered structures in the “liquid”-like range. In this concentration domain, hydrophobic alkane chains typically assemble into a quasi-two dimensional hexagonal structure at the surface. This idea first appeared in the late 1970’s and the surface structure was coined the hexatic phase. Such 2D structures often possess long range orientational order and have only short range positional order. Positional order is not preserved over time.

The arrangement of surfactant head groups surfactants in water soluble overlayers has been experimentally studied by X-ray and neutron reflectometry as well as equilibrium molecular dynamic simulations. In the case of CTACI, simulation studies have concluded that surfactant overlayers are in equilibrium with the underlying solution. The surface profile has a surfactant “hemimicellar” wavelike structure rather than a planar close-packed one as commonly expected. The surface roughness, as defined by the Gaussian distribution of CTACI head groups, is ca. 3-4 Å.

A recent study on the polymerization of n-octadecyl-trichorosilane (CH₃(CH₂)₁₇SiCl₃) monolayers formed at the air-water interface is worthy of attention. Such a monolayer has been transferred onto a silicon wafer and studied by electron diffraction and AFM. Closely packed hexagonal structures as well as point defects in the polymerized monolayer were observed.

Thus, it is reasonable to propose that the formation of a mesoporous silica film involves collective interactions between silicate building-blocks, micellar solution species and surfactant “hemimicellar” overstructures localized at the air-water interface, as illustrated in Figure 3.23. Under the synthesis conditions used, film formation is considered to involve polymerization of silicate in the surfactant head group regions of a hexagonal mesophase concentrated at the surface overstructure. The pre-organized CTACI overlayer facilitates the organization of a smooth oriented mesoporous silica film at the air-water interface. The observed AFM image of the films in Figure 3.7 presumably reflects the outcome of a cooperative surface process in which silicates undergo condensation-polymerization at the
Film growth is likely regulated by matching charge and geometry between micellar aggregates and silicates at the interface region.

The growth of the film may follow the same pathway as for mesoporous silica in powdered form, i.e., through the co-assembly of surfactant-silicate micellar aggregates into a silicatropic mesophase which undergoes condensation-polymerization to create a silica replica of the templating interface. The aggregates silicify and expand in size through the accretion of silicate-micelles and coalesce to form a continuous film.

Recently, in-situ X-ray reflection (XRR) studies on the formation mechanism of free-standing mesoporous silica films formed at the air-water interface have been published. Brown et al. have used cetyltrimethylammonium bromide (CTABr) and TEOS under acidic conditions (using HCl as an acid source) with a minimal amount of methanol present as their model system. Roser et al. have also employed CTABr and TEOS as their primary reactants but conducted the experiments under basic conditions using sodium hydroxide. The observed air-film and interface roughness are in the range of 4.5 to 6 Å, and 1 to 3 Å, respectively, during the induction period for an acidic system. This observation agrees well with the local roughness for free-standing films estimated from AFM images, if one takes into consideration the polymerization and condensation of the silicate and the drying effect. Both studies also confirmed that the mesoporous silica films grew from micellar "rods" organized parallel to the interface and packed as the hexagonal phase. Furthermore, this surface hexagonal phase directly forms from the surfactant-silicate precursor without any intermediate lamellar mesophases, as is the case for several other mesoporous metal oxide systems.
Figure 3.23. Graphical illustration of proposed model for the formation of a free-standing oriented mesoporous silica film at the air-water interface.
3.4.2 Growth and channel structure

Quiescent aqueous conditions are an essential prerequisite for the surfactant-templated synthesis of hexagonal mesoporous silica film at the boundary between air and water. The final film thickness is governed by the reactant ratio, temperature and acidity.

Although the hexagonal mesostructure and orientation of the film were maintained in all the preparations of the study, the porosity, wall structure, and other properties sensitively depend on the temperature and acidity. Lesser degrees of condensation-polymerization, evidenced by the larger \((Q_2+Q_3)/Q_4\) ratio of the silica in the thick films, were seen at higher pH and room temperature synthesis conditions. This may be attributed to lower thermal stability of such thick films compared to the thin films formed at higher acidity and enhanced temperature, though the order of the mesostructure in as-synthesized silica films did not vary much. Consistent with this proposal is the observed large contraction of the diameter of the mesopores for the calcined film samples. Thermal vacuum dehydration prior to calcination helps stabilize the mesostructure. It may also be interesting to point out that a lower degree of condensation-polymerization of the silica walls is observed in the thicker version of the films which is not commonly found in other mesoporous silica systems, thus quiescent conditions and surface confinement may be important factors. The as-synthesized silica films made by this approach therefore have a much larger population of unreacted hydroxide groups of the silicate wall regions, which may prove useful for making nanostructured materials.33

The observed POM texture represents the first example of optical anisotropy in ordered hexagonal phase mesoporous film. Although the formation of mesoporous silica film is thought to involve silicification of a lyotropic liquid crystal, the observed POM texture of the film does not arise from organized surfactant assemblies in the channels. The DSC trace of as-synthesized mesoporous silica films show no thermal events that can be associated with liquid-crystal or isotropic melting transitions of an imbibed surfactant liquid crystal. The first transition seen is \(ca. 250 \, ^\circ\mathrm{C}\), a temperature which is just below the decomposition temperature of the CTACl surfactant inside the structure. Also, the fan-type texture is retained upon removing the surfactant, therefore the optical birefringence of the film does not require the surfactant to be present in the channels. The annealing of the silica mesoporous
film at 450 °C during the calcination did not alter the birefringence texture, which means that strain anisotropy in the film is not the source of the fan-type texture. Finally, the PXRD data show no high angle diffraction from the silica implying that the channel walls are glassy. One may conclude that the birefringence is associated with the optically uniaxial nature of the oriented hexagonal mesoporous silica film.

The thick mesoporous silica film displays two dominant morphologies which give rise to distinct POM birefringence patterns. The free-standing films synthesized with stirring for 3 to 5 minutes at a low stirring rate have a structure in which discrete aggregates appear to have coalesced and show concentric birefringence patterns. Such morphologies have been observed for mesoporous silica films grown on gold and glass surfaces. By contrast, free-standing films with a continuous and fan-type texture were obtained from a synthesis mixture with a stirring time of about 10 minutes at a low stirring rates. The film shows good homogeneity and a smoother surface compared to those formed in shorter stirring periods. Films with continuous and fan-type textures can also be obtained from a synthesis mixture with a stirring time of ca. 5 minutes at a high stirring rate. The fan textures, however, did not transform into discrete textures on changing the vessel geometry, such as its shape and size. Thus, the difference in the POM birefringence patterns and surface morphologies might be best viewed as arising from a “switch” in the mode of formation of the free-standing film from one initiated by a small silicate liquid crystal domain at the air-water interface, involving local growth and coalescence, to one involving the formation of a continuous silicate liquid crystalline surface film. It is also noteworthy that the texture traverses the entire extent of the free-standing film implying that the mesoporosity is not confined to small domains.

The POM patterns and surface morphologies clearly not only depend on the synthesis conditions, they also change with the substrate properties. POM patterns for the films grown on mica differ from those on other surfaces or subphases. Discrete and fan-type textures are replaced by extensive areas of dark, gray and light patches. The patterns of parallel striations within the different color patches of mesoporous silica film meet at angles of 60° or 120°. This observation suggests that growth of the hexagonal mesoporous silica film occurs with the channel axis preferentially aligned along the hexagonal a, b-axes of the mica (001) surface.
The patterns and birefringence textures of free-standing mesoporous silica film show the same features as those observed for normal hexagonal phase organic liquid crystals.\textsuperscript{35} In this context, TEM images of early stage thin oriented film are extremely helpful. Compared to organic liquid crystals, the silicate liquid crystals have the advantage of having high thermal and mechanical stability due to their strongly covalently bound inorganic framework, allowing direct imaging of the structures of free-standing film lifted off the air-water interface in their early stages of growth by conventional TEM.

Macroscopic defect structures are the cause for those POM patterns observed in the oriented mesoporous silica films obtained through organic surfactant templates. Some examples of defects that are expected in the packing of silicate rod micelles and conserved through silicification in ultra-thin mesoporous silica are shown in Figure 3.2 and Figure 3.24. Defects associated with bending of the channel director fields, such as, $\pm \pi$ and $-\pi$ disclinations can be readily observed by TEM, and textures caused by $+\pi$ and $+2\pi$ disclinations, Figure 3.24 can be identified by POM.\textsuperscript{15,16,35} As in hexagonal liquid crystal films, combinations of several defects, such as pairs of two $+\pi$ disclinations, pairs of $+\pi/-\pi$ disclinations, two pairs of $+\pi$ and $-\pi$ disclinations, $+\pi$ disclination and dislocation are generated by the requirement that higher energy defects tend to split into several lower energy ones. Wall structures appear at the boundary regions, especially around $-\pi$ disclinations. The edge dislocation and wall structures may exist at the regions denoted * and **, respectively in Figure 3.24.

The observation of liquid crystalline textures in mesoporous silica films grown at the air-water interface under dilute aqueous acidic conditions provides direct evidence for a templating pathway based upon cooperative assembly and organization of silicate micellar species rather than a pre-formed silicate-liquid crystal.\textsuperscript{17,36}
Figure 3.24. TEM image of defect structures in an ultra-thin hexagonal mesoporous silica film.

Conclusions. Oriented free-standing films with controlled thickness can be synthesized at the air-water interface under quiescent acidic conditions. Optical birefringence patterns observed for free-standing mesoporous silica film are shown to originate from mesoscale optical anisotropy associated with the polarization response of electron density circumscribing a hexagonal array of glassy silica channels. The existence of the birefringence shows that the channel architecture is a silicified replica of the defect induced pattern of director fields in a silicate liquid crystal precursor. Alteration in synthesis conditions and substrates enables control over the film texture, which reflects changes in the channel structure arising from the operation of distinct film growth processes.
3.5. References

14 The "grinding" of the film sample for PXRD measurement was done in situ on a quartz cell surface by breaking apart the films to smaller pieces as much as possible. Grinding by using conventional methods failed due to the limited amount of sample.


Chapter Four
Formation of Curved Shapes in Mesoporous Silica

4.1 Introduction

The formation of silica mesoporous thin films on various subphases or substrates inspires one to examine the morphogenesis of this class materials in the bulk solution. In this chapter, the synthesis and characterization of hexagonal mesoporous silica which displays curved shapes and surface patterns is described. Reaction conditions that favor different curvature morphologies ranging from fibers to toroids, discoids, gyroids, spirals, and spheroids are presented. SEM is used to catalogue basic topologies and surface patterns, while TEM and AFM are used to establish the relationship between morphology and the underlying mesostructure. POM is also to define the connection between the optical anisotropy and the periodic mesoporous structures. The morphogenesis of mesoporous silica curved shapes can be rationalized in terms of the growth of a hexagonal cylindrical liquid crystal embryo subject to increasing degrees of curvature in space and time depending on the initial local reaction conditions.

A gyroid-to-sphere shape transition is also presented with an emphasis on the growth of mesoporous silica spheres under quiescent acidic aqueous conditions. Spherical mesoporous silica growth can be induced by lowering the acidity for a surfactant-based gyroid preparation. This approach of making mesoporous spheres is unique from two other recent reports on the preparation of mesoporous silica spheres in terms of the formation pathway and the size distribution. Millimeter spherical mesoporous silica made by Huo et al. depends largely on confinement of the growth process within a droplet emulsion, while micron size mesoporous silica spheres made by Grün et al. is a combination of the traditional Stöber dense silica sphere preparation with the surfactant templating method for making mesoporous materials. The strategy presented here involves just acidity and temperature control in an aqueous synthesis.

A preliminary understanding of the formation of curved mesoporous silica shapes with particular channel architectures is based largely on the theory of liquid crystal defects and and
concepts from colloid chemistry. In this context, the effect of solvent and ionic strength on shape are expected to be important.

4.2 Synthesis and characterization

4.2.1 Synthesis

The formation of curved mesoporous silica occurs simultaneously with film growth for both supported and free standing films. In order to obtain well-defined shapes it is important to conduct the reaction under quiescent and dilute aqueous acidic conditions. A typical reactant ratio used for making high curvature morphologies, such as gyroids and spheres is listed below:

\[ 100 \text{H}_2\text{O} : x \text{HCl} : y \text{CTACl} : z \text{TEOS} \]

Some reactant ratios for making particular shapes are listed in Table 4.1. The final products were recovered after a reaction time period of three to seven days or longer, and transferred from the vessel to a Buchner funnel and washed with de-ionized water. The material was then dried at ambient temperature. The disturbance of the quiescent synthesis by stirring the solution leads to similar, but broken, forms of the mesoporous silica morphologies, especially in the case of one dimensional fibers. No dramatic shape changes were observed for the curved shape preparation when gentle tumbling (with a tumbling rate of 8 cycles/minute) was applied to the reaction system at 80 °C.

**Synthesis-shape-size relationships:** The micron sized mesoporous silica spheres can form at either 80 °C or room temperature but at different reactant ratios, Table 4.1. The mesoporous silica growth process was allowed to proceed for a period of 7-10 days under static conditions at 80 °C. One set of reactant ratios that was employed for the sphere synthesis at 80 °C and characterized in detail is listed below:

\[ 100 \text{H}_2\text{O} : 0.9 \text{HCl} : 0.11 \text{CTACl} : 0.13 \text{TEOS} \]

Calcination of the gyroids and spheres was achieved by heating the sample from 25 °C to 540 °C at 1 °C/min. in air and then holding at 540 °C for 4 hours.
Table 4.1. Several representative synthetic ratios that favor the formation of mesoporous silica with curved shapes.

<table>
<thead>
<tr>
<th>sample</th>
<th>temperature (°C)</th>
<th>molar ratio</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>H₂O</td>
</tr>
<tr>
<td>fiber⁵</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>gyroid (small)</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>gyroid (medium)</td>
<td>80/RT</td>
<td>100</td>
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<tr>
<td>gyroid (large)</td>
<td>RT</td>
<td>100</td>
</tr>
<tr>
<td>hybrid-80</td>
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<td>100</td>
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<td>80</td>
<td>100</td>
</tr>
<tr>
<td>sphere 6</td>
<td>RT</td>
<td>100</td>
</tr>
</tbody>
</table>

a RT stands for room temperature.

b Pure fiber cannot be obtained for all compositions surveyed. A varied population of gyroids is always observed in different batch products.

Control experiments for mesoporous sphere formation were conducted with dense micron-sized silica spheres which were synthesized according to literature protocols.⁷ Acetic acid (glacial, 99.9%) was mixed with water followed by specified amounts of TEOS in approximately 5 minutes. The reactant ratio employed was:

\[ 1 \text{H}_2\text{O} : 4 \text{CH}_3\text{COOH} : 4 \text{TEOS} \]

The mixture was kept stirring for 10 minutes and then left under static conditions at room temperature for about 30 minutes. The product was transferred to a Buchner funnel and washed with ethanol followed by acetone.

The shape phase diagram was studied by systematically varying the reactant ratios of the system, \( 100 \text{H}_2\text{O} : x \text{HCl} : y \text{CTACl} : z \text{TEOS} \). Experiments were terminated after three days. The shapes were then checked either by SEM or by optical microscopy.
Yields of mesoporous silica with different shapes: The yield of the different shape mesoporous materials have been estimated based on silicon balance. TGA was used to estimate the weight loss due to the removal of imbibed water and water formed by polymerization and condensation, as well as the removal of the surfactant, Figure 4.1. The estimated yields of mesoporous silica for the fiber, gyroid and spherical shapes were generally over 90% based on gravimetric and TGA analysis, and a summary is listed in Table 4.2.

Since most systems were highly dilute and acidic, no dramatic change in pH of the system is seen during or after the reaction. It often requires several minutes to obtain a stable pH value (a Cole-Parmer® pHTestr BNC 59000-40 was used; the detectable range of the meter is from a pH of -1.0 to 15.0 with a resolution of 0.1). The measured pH values for the fiber, gyroid (medium size) and gyroid (large size)/sphere preparations were -0.6, -0.1 and 0.1, respectively.

Table 4.2 Yields of mesoporous silica with different shapes*

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<tr>
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<td>gyroid</td>
<td>sphere</td>
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<tr>
<td>91%</td>
<td>93%</td>
<td>96%</td>
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</tbody>
</table>

*: The compositions tested are 100 H₂O : nHCl : 0.11 CTACl : 0.11-0.14 TEOS. The “as-synthesized” and “calcined” refer to the as-synthesized mesoporous silica (with imbibed surfactants) and calcined mesoporous silica (up to >800 °C, weight is estimated from TGA data, see Figure 4.1), respectively. Yield calculation is based on SiO₂ and the error is estimated to be ca. ± 5% for the measurements.
Alcohol effect on the morphogenesis of mesoporous silica shapes were studied by using absolute ethanol as a co-solvent using the following reactant mole ratio:

\[100 \text{H}_2\text{O} : 7 \text{ or } 3.5 \text{HCl} : 0.11 \text{CTACl} : 0.13 \text{TEOS} : x \text{EtOH}\]

The acidified surfactant solution was first mixed with ethanol, followed by the addition of TEOS. After all the reactants were added, the solution was stirred for ca. 2 to 3 minutes at room temperature with a medium stirring speed and then transferred to a polypropylene bottle. The solution was then left at either room temperature or 80 °C for one week. Control experiments were done by replacing the added amount of ethanol with water in the system, i.e. by using the following reactant mole ratio:

\[100 \text{H}_2\text{O} : 7 \text{ or } 3.5 \text{HCl} : 0.11 \text{CTACl} : 0.13 \text{TEOS} : x \text{H}_2\text{O}\]

Salt effects on the morphogenesis of mesoporous silica shapes were studied by using sodium chloride as electrolyte with the following reactant mole ratio:

\[100 \text{H}_2\text{O} : 7 \text{ or } 3.5 \text{HCl} : 0.11 \text{CTACl} : 0.13 \text{TEOS} : x \text{NaCl}\]

The acidified surfactant solution was first mixed with NaCl, followed by the addition of TEOS.
Samples for early stage studies by TEM and AFM. The reactant ratio and composition used in the study are the same as those described in the previous chapter (100 H₂O : 7 or 3.5 HCl : 0.11 CTACl : 0.13 TEOS). To capture representative examples of early stage growing objects, copper grids coated with a thin-layer of carbon film (for TEM specimens) or freshly cleaved pyrolytic graphite supports (for AFM specimens) were dipped into the solution after stirring. All samples were grown at room temperature. Water on the grids or graphite supports was removed using filter paper and then allowed to dry in air.

4.2.2 Characterization

PXRD data was obtained on a Siemens D-5000 diffractometer using Ni-filtered Cu-Kα radiation with λ = 1.54178 Å. A plexiglass sample holder was used for recording the PXRD patterns.

SEM images were obtained with a Hitachi S-4500 field emission microscope using a low acceleration voltage of 2 kV. Samples were uncoated and imaged directly.

TEM images were typically recorded on a Philips 430 microscope operating at an accelerating voltage of 100 kV. A few TEM images of whole mounted samples on a holey carbon grid were taken on a JEOL 2010F field emission TEM operating at an accelerating voltage of 200 kV.

AFM experiments were conducted on a NanoScope® III microscope (Digital Instruments, CA) using silicon integrated tip cantilevers (Park Scientific Instruments, CA) for height mode scanning of the mesoporous silica shapes. The cantilevers were used as received. Images of the surfaces of the mesoporous silica were obtained using direct contact (dc) scanning mode. Images of early stage soft mesophase objects were obtained using a phase extender module, operating in tapping-mode. The A+B feedback signal was about 3 V while the RMS signal was set at around 0.3 V. Feedback gain parameters were set between 1 and 2 for both integral and proportional gains. NT-MDT UltraSharp silicon cantilevers SCS11 (resonance frequency 300-380 KHz) were used throughout the study. The drive amplitude was set between 600 - 800 mV while the working frequency was chosen to be about 360 kHz. The D scan head (maximum scan area is 12.5 × 12.5 μm², z-sensitivity of 9 nm/V) was employed throughout the study. Scan rates were chosen from 1 to 4 Hz.
Light scattering particle size analysis was conducted with a Malvern Mastersizer particle size analyzer using a 300RF lens suitable for the size range of 0.05 to 880 μm. Particle agglomeration was minimized by mixing the samples in de-ionized water, which functioned as a dispersing agent, and submerging the mixtures for 5 minutes in an ultrasound bath. Mie scattering theory was used to fit the measured scattered intensity to a particle size distribution.

Dynamic light scattering (DLS) experiments were carried out on a Brookhaven Instruments system consisting of a BI-200SM goniometer with a Lexel Excel 3000 argon-ion laser (514.5 nm green light was used) and a 2030AT multi-bit autocorrelator. Toluene was used as the immersion solution. All measurements were done at 20 °C using a water-cooled thermostat system. The study of initial growth was followed at a 90° scattering angle. A schematic of the set-up is shown in Figure 4.2.

![Figure 4.2. Illustration of the DLS set-up.](image)

All measurements were carried out in aqueous solution. The reactant ratio and composition used in the study was similar to those used in the previous chapter (100 H₂O : x HCl : 0.11 CTACl : 0.13 TEOS). After mixing, the reactant solution was immediately filtered through a 0.2 μm Millipore® filter with a plastic syringe and transferred into a 12 mm O.D. cell. Typical sample preparation times were between 5 and 60 seconds. The pinhole used
was normally set at 200 μm and the count rates of laser power maintained higher than 100 kHz in order to have a S/N value >0.15 and no overflow. The resulting time autocorrelation function of the scattered light intensity was analyzed by software from Brookhaven. The decay rate constant and effective hydrodynamic radius were extracted from the autocorrelation function through the fourth cumulant analysis (see below). The function was acceptable if the difference between the measured and calculated baselines was within ±0.2%.

From this time correlation function, the translational diffusion coefficient and the effective hydrodynamic radius of the particle can be obtained. The mathematical expression of this function, \( G_2(t) \), is given by

\[
G_2(t) = \langle I(t_0) I(t_0 + t) \rangle
\]

where the scattering intensity at time \( t_0 \) is compared with a delay time, \( t_0 + t \). The function can be further converted to an more useful term, the first-order scattered electric field autocorrelation function, \( g_1(q, t) \), by the Siegert equation:

\[
G_2(t) = A + [B g_1(q, t)]^2
\]

where \( A \) is a constant, \( B \) is an instrumental parameter close to unity and

\[
g_1(q, t) = B \exp(-\Gamma t)
\]

for monodisperse hard spheres. The value of the scattering vector \( q \) depends on the solvent refractive index \( n \), the wavelength of incident light \( \lambda \), and the scattering angle \( \theta \), which is given by

\[
q = \frac{4 \pi n}{\lambda} \sin\left(\frac{\theta}{2}\right)
\]

and \( \Gamma \) is the decay rate constant, which is related to the translational diffusion coefficient \( D_{\text{trans}} \) by the equation

\[
\Gamma = D_{\text{trans}} q^2
\]

In most of the cases, including micelles, systems show polydispersity and a cumulant expansion approximation can be applied

\[
g_1 = \sum_{n=0}^{-r_n e^{n^2}}
\]

or in a series expression
\[ \ln g_1(q,t) = -\Gamma_1 t + \frac{\Gamma_2 t^2}{2!} - \frac{\Gamma_3 t^3}{3!} + \ldots \quad \text{Eq. 4.7} \]

\( \Gamma_1 \), the first cumulant, is the most useful term in equation 4.7 as the collective translational diffusion coefficient at a given concentration, \( D_c \), can be obtained from the reduced form, \( \Gamma_1/q^2 \), through the equation
\[ \Gamma_1/q^2 = D_c (1+cR_g^2q^2 - \ldots) \quad \text{Eq. 4.8} \]
where \( c \) is a structure dependent coefficient and \( R_g \) is the radius of gyration. \( D_c \) can then be furthered approximated by the expression
\[ D_c = D_{\text{trans}} (1 + k_p c) \quad \text{Eq. 4.9} \]
where \( k_p \) is the effective interaction parameter.

The translational diffusion coefficient \( D_{\text{trans}} \) is one of the most important quantities determined through light scattering experiments. The effective hydrodynamic radius, \( R_h \), can be obtained from the Stokes-Einstein equation
\[ R_h = \frac{kT}{6\pi\eta D_{\text{trans}}} \quad \text{Eq. 4.10} \]
where \( \eta \) is the viscosity of the solvent. In this study the viscosity of water at 20 °C was used (\( \eta = 1.002 \, \text{cP} \)).

\textbf{TGA} was conducted on a Perkin Elmer Thermogravimetric Analyzer 7 Series apparatus. The samples were heated at a rate of 5 °C/min. under a flow of \( \text{N}_2 \).

\textbf{N}_2 \textit{ adsorption isotherms}. See Chapter 3 for details.

\textsuperscript{29}Si solid state \textit{MAS NMR} spectra were recorded on a Bruker DSX 200 MHz spectrometer at 40 MHz using a 90° pulse with a delay time of 600 seconds. Proton decoupling and magic angle spinning were used.

4.3 Results

\textbf{Formation of curved shapes}. The synthesis of mesoporous silica morphologies was conducted under quiescent aqueous acidic conditions using CTACl as a surfactant template and TEOS as the silica precursor. The materials obtained have the well documented hexagonal symmetry channel structure of MCM-41, which is shown by its diagnostic PXRD
pattern. Nevertheless, the quality of the pattern may vary with preparation conditions and reactant ratios.

A careful SEM study reveals that a diverse number of morphologies exist with exotic shapes and a broad range of curvatures, Figure 4.3. Field emission SEM images of the curved mesoporous silica morphologies show that they tend to fall into two classes: those that grow in one dimension and have a curved and twisted body based upon an elongated cylinder, and others that display no clear facets but instead have highly curved morphologies. These shapes are given the trivial names of fibers and gyroids, respectively.

It is found that certain concentration ranges favor low curvature fiber and related shapes, while others promote highly curved gyroid and related forms. The size of the gyroid family can be tuned by the varying the acidity as well as the reactant ratio of the synthetic mixtures. No pure fiber could be observed in any of the reactant systems.

TEM images of microtomed samples for the basic morphologies clearly depict the presence of hexagonally close-packed channels with a centre-to-centre spacing of around 50 Å. SEM and TEM images of whole mounted mesoporous shapes were used to establish the spatial relationship between the channel structure and the basic shape of the mesoporous silica morphologies.

Several EM images of fibrous mesoporous silica are presented in Figure 4.4. The fibers can display both arc and crankshaft body forms, show well-defined facets associated with body bending, and exhibit hexagonal basal faces. The facets imply that the hexagonal cylindrical fibers grow out from the basal planes. A 1000 Å width fiber is thin enough to be imaged directly using a high voltage electron beam without having to resort to microtome sectioning. Parallel curving lines with a spacing of about 25 Å run along the entire body length of the fiber or ribbon, the spacing being one half of the channel centre-to-centre distance. This is expected when the hexagonal mesostructure is viewed along the [210] direction of the hexagonal unit cell. Such clear images of the internal channel structure of the rope are only feasible if there exists almost perfect alignment of the channels throughout the body of the rope. Also noteworthy in the TEM images are pronounced surface irregularities predominantly located on the basal plane at the head of the fiber. This structure may portray the accretion and polymerization of surfactant-silicate micelles onto the growing hexagonal cylinder. The roughness of this growth front revealed by TEM is consistent with that
estimated from SEM images of similar regions of the rope, and is noticeably larger for the head (ca. 300 Å) than the body (ca. 100 Å) region. This observation agrees with the hypothesis that the deposition process is favored at the “sticky” surfactant-silicate ends of the evolving hexagonal cylinder.

Figure 4.3. SEM images of the product obtained by using 100 H₂O : n HCl : 0.1 CTACl : 0.1 TEOS at 80 °C: (a) n = 3.5 and (b) n = 7.4.
Figure 4.4. SEM of fibers showing a facet (top), head region (middle) and TEM image (bottom) for curving parallel channels as well as the structure at the growth fronts in the head and body regions (scale bar, 125 nm).
There are large variations in the shapes seen for gyroid morphologies. A typical gyroid shapes is shown in Figure 4.5a. To understand the channel orientation of mesoporous shapes with respect to the morphology, as-synthesized samples have been studied by AFM and TEM.

A TEM image of an entire mesoporous silica gyroid can be taken if the shapes are thin enough in at least one dimension or at the edge regions. These images reveal the relationship between the macro- and mesostructure. The pseudo-hexagonal arrangement of the edge areas implies that the channels wind around the toroids, Figure 4.5b. Viewing the head regions of a gyroid with a slight tilting angle with respect to the direction of the electron beam also shows swirling channel structures. The parallel lines arise from dense silica channel wall regions along the [210] direction (see Chapter 2). By careful inspection of the mesostructure located at the end of this morphology, one can further identify the smooth transformation of parallel curving channels into a hexagonal close-packed structure with a spacing of about 50 Å. These images show that the channels whorl around the rotation axis of the gyroids. AFM images of the gyroid at tip regions also reveals parallel stripes with a repeat spacing in the 50 to 90 Å range on the external surface, Figure 4.5c. These may represent the spacing between hexagonally close packed cylindrical channels when viewed in different directions of the periodic mesostructure. It is noteworthy that the hexagonal symmetry axis of the bulk mesostructure observed from TEM, SEM and AFM images is found to be associated with the surface mesostructure. This confirms the proposed spatial relationship between the mesostructure and the overall morphology.

The mesostructure of a discoid morphology, Figure 4.6a, has also been established by TEM. As in the case of gyroids, a TEM image of the [210] plane gives a representation of the channel directions. It was found that the channels of a discoid coil concentrically around the body, Figure 4.6b. By examining the image closely, one notices that the core of the discoid shows some mesostructural order which becomes more pronounced in the outer region.
hexagonal close-packed channel mesostructure of a whole-mounted sample.

Fig. 4.5. Cytoid morphology: (a) STEM, (b) AFM image that reveals parallel stripes and the TEM image that shows the relationship between the macrostructure and the 2D A
Figure 4.5. Gyroid morphology: (a) SEM, (b) AFM image that reveals parallel stripes, and (c) TEM image that shows the relationship between the macrostructure and the 50 Å hexagonal close-packed channel mesostructure of a whole-mounted sample.
Figure 4.6. TEM and SEM (inset) of mesoporous silica with a discoid shape.
It is most likely that the curved mesoporous silica morphologies are related to the growth of an archetype embryo in the synthesis system. This embryo is believed to be a hexagonal cylindrical liquid crystal which evolves into different morphologies through the accretion of silicate micellar species, developing varying degrees of curvature in the process. Although there is considerable variation in the spiral and gyroid morphologies, they all tend to be roughly spherical.

Anisotropy in mesoporous solids. Crystals with uniaxial symmetry display birefringence effects and show distinct patterns when viewed under cross polarizers. With the availability of the well defined hexagonal mesoporous morphologies, it was interesting to see if optical anisotropy exists in structures possessing only ordered void spaces.

Representative POM images for ribbon and discoid mesoporous silica morphologies are shown in Figure 4.7. They are optically anisotropic and show evidence for a common kind of optical birefringence pattern. When the discoid and related morphologies are observed with the incident light along their topologically unique rotation axis, one observes an image characteristic of an uniaxial system viewed along the optical axis.\textsuperscript{11} This image can be described as a roughly symmetrical black cross, consisting of the isogyres, which have arms parallel to the directions of the crossed polars. The central point is known as the melatrope, and the concentric colored rings in the four quadrants are the isochromes. When the discoids and gyroids are observed orthogonally to the topologically unique rotation axis, a broad diffuse cross that only occupies the centre of the field over a few degrees of rotation is observed.

Another simple morphology that can be easily aligned and correlated to its director field is the curved ribbon shape. The observed half cross seen, Figure 4.7b, is consistent with the expect channel directions as observed by TEM in fibre morphologies, Figure 4.4d.
There exists four major possibilities that can explain the POM images for the mesoporous silica: (i) a high degree of order from the surfactant head groups adjacent to the disordered silica walls of the meso-channels; (ii) strain induced anisotropy from the amorphous silica walls of the meso-structure; (iii) a high degree of regularity of the tetrahedral silica walls of the meso-channels; and (iv) the mesoscale periodicity of the channels. The first three possibilities can be reasonably eliminated based on experimental observations that the POM images are retained and even become sharper upon removing the surfactant-template. After annealing the template-free mesoporous silica morphologies at 540 °C, the $^{29}$Si MAS NMR spectra shows a $Q_3 : Q_4$ ratio of around 0.6, Figure 4.8, which is not significantly
different to ratios previously reported for mesoporous silica. Therefore, the observed optical anisotropy arises from the global polarization of an average electron density distributed around a hexagonal periodic array of mesopores. In other words, the optical birefringence is associated with the spatial anisotropy of the air-silica interface within the cylindrical channels.

Figure 4.8. $^{29}$Si solid state MAS NMR for mesoporous silica with fiber/gyroid (top) and pure gyroid morphologies (bottom).

Mesoporous sphere formation The curvature of the mesoporous silica morphologies can be tuned to the extreme limit, *i.e.* spherical shapes, by further decreasing the acidity of the solution. SEM images of as-synthesized and calcined sphere morphologies that have been synthesized at 80 °C using the reactant mole ratio of 100 H$_2$O : 0.9 HCl : 0.11 CTACl : 0.13 TEOS, are shown in Figures 4.9a, 4.9b. There were no detectable changes between the shapes of the as-synthesized and calcined materials. The surfaces of the spheres were
relatively smooth when viewed at high magnification by SEM. Spheres were synthesized in micron size ranges although they were not monodispersed, Figure 4.9c.

The corresponding PXRD patterns are displayed in Figure 4.10. A control experiment using dense micron-sized spheres\(^7\) showed no X-ray diffraction, Figure 4.10a. The PXRD trace of as-synthesized silica spheres corresponding to those in Figure 4.9a shows a broad low angle reflection with a \(d\)-spacing around 45 Å which is assigned to a hexagonal form of mesoporous silica with poorly ordered channels, Figure 4.10b.\(^{12,13}\) The absence of high angle reflections suggests that the composition of the silica wall is glassy. An expected shift of the low angle reflection to higher \(2\theta\) for calcined silica spheres corresponds to a ca. 4-5 Å decrease in the \(d\)-spacing due to the condensation and polymerization of residual hydroxyl groups and concomitant contraction of the pore center-to-center distance, Figure 4.10c. There is a considerable increase in intensity and narrowing of the PXRD peaks observed for the calcined spheres.

The PXRD pattern of the mesoporous silica gyroids aged at room temperature, show four reflections: (100), (110), (200) and (210), that are typical of a hexagonal mesoporous silica with well ordered channels. This is quite different from the single peak seen for the mesoporous silica spheres. The PXRD trace of the gyroids shown in Figure 4.10d displays a \(d_{100}\)-spacing of ca. 39 Å which is notably less than the \(d_{100}\)-spacing of ca. 45 Å for the spherical form of mesoporous silica. The \(d_{100}\)-spacing of the silicate-surfactant lyotropic liquid crystalline phase is reported to be ca. 47 Å and also undergoes a polymerization induced contraction of ca. 4-5 Å on transforming to the mesoporous silica phase.\(^{14}\) The full width at half maximum (FWHM) of the (100) reflection for the as-synthesized gyroid and sphere shapes is ca. 0.15° and 0.57° \(2\theta\), respectively, implying that the spheres have a less ordered mesopore structure than the gyroids.

A representative TEM image of an epoxy-embedded and microtomed thin section for a sphere is shown in Figure 4.11. The TEM images generally reveal a poorly organized mesoporous silica channel structure both in the body and the surface regions of the sphere. The pore center-to-center distance estimated from the TEM image is ca. 50 Å which agrees with the PXRD results. Only limited success was achieved in resolving mesopore order in ultrathin ca. 200-500 Å sections of the silica spheres, providing additional evidence that the mesopores were not well-ordered.
Figure 4.9. Representative SEM images of synthetic silica shapes for (a) as-synthesized spheres, (b) calcined spheres, and (c) spheres at high magnification.
Figure 4.10. Representative PXRD traces of (a) dense micron diameter silica spheres; (b) as-synthesized mesoporous spheres, (c) calcined mesoporous spheres and (d) as-synthesized gyroids.

Figure 4.11. TEM images of microtomed as-synthesized mesoporous spheres.
A selected area electron diffraction (ED) pattern of a thin section of a sphere displays a single diffuse ring with a d-spacing of ca. 43 Å, Figure 4.12, that corresponds to the observed PXRD d_{100}-spacing of ca. 45 Å. The diffuse ring ED pattern for the spheres provides further evidence that they have a poorly ordered mesostructure, consistent with PXRD and TEM observations.

Figure 4.12. A representative electron diffraction pattern of a microtomed as-synthesized mesoporous silica sphere

TGA traces of the silica sphere and gyroid morphologies are shown in Figure 4.13. The total weight loss was in the 20 to 40 wt. % range and the thermal transitions seen below 100 °C, around 300 °C, and above 350 °C correspond to the loss of imbibed water, removal of surfactant, and evolution of water from the condensation-polymerization of residual hydroxyls in the mesoporous silica, respectively.

The trend seen in the thermal events for the spheres is comparable to that of the gyroids made at room temperature with the same reactant ratio. In both cases, the loss of surfactant at ca. 300 °C is the major thermal event, Figure 4.13. Noticeably, the mass loss of surfactant from the spheres amounts to ca. 20-30 wt. % of the mesoporous silica while that of the gyroids is ca. 40 wt. %. This implies that the amount of surfactant in the silicate-surfactant
co-assembly that is required to make the spheres is significantly less than that needed to make the gyroids.

**Figure 4.13.** Representative TGA curves for mesoporous spheres and gyroids

Solid state proton decoupled $^{29}$Si MAS NMR was employed to determine the $Q_3$ ($SiO_3$OH) : $Q_4$ ($SiO_4$) ratio of the as-synthesized spheres. The observed (a), simulated (b), deconvoluted (c, d), and difference between observed and simulated (e) spectra are shown for $Q_3$ and $Q_4$ building-units which constitute the glassy silica channel walls of the mesostructure in **Figure 4.14.** The $Q_3 : Q_4$ ratio of 0.9 for the spheres compared to 0.6 for the gyroids implies a lower degree of silicate polymerization in the spheres.\textsuperscript{15}

The particle size distribution of the mesoporous silica spheres was measured by using a light scattering analysis technique. The size distribution of the silica mesoporous spheres according to surface area, volume and particle number are found to fall in the micron size regime. A distribution curve based on the particle surface area for calcined mesoporous spheres is shown in **Figure 4.15.** The mean diameter for this sample of mesoporous silica spheres is 6.8 μm which agrees well with SEM observations.
Figure 4.14. Solid state proton decoupled $^{29}$Si MAS NMR spectra of as-synthesized mesoporous spheres.

Figure 4.15. Particle size distribution of calcined mesoporous spheres based on particle surface area.
Nitrogen adsorption isotherms have been recorded at \(-196 \, ^\circ\text{C}\) for the calcined spheres and gyroids, Figure 4.16. They show a type IV isotherm, typical of mesoporous materials and display an initial steep slope at low partial pressures due to monolayer nitrogen adsorption in the mesopores, followed by an inflection at higher partial pressures around \(P/P_0 \sim 0.3\) arising from the capillary condensation of nitrogen in the mesopores. No hysteresis is observed which suggests that there is negligible obstruction of the channels in both the spherical and gyroidal mesoporous silica morphologies, thus allowing reversible adsorption and desorption of nitrogen to take place. The isotherms of these mesoporous silica spheres are distinct from those seen for porous samples made from sol-gel methods, where hysteresis is invariably present on Type IV and H2 isotherms.\textsuperscript{16}

![Graph of Nitrogen adsorption isotherms of mesoporous silica sphere and gyroid shapes.](image)

**Figure 4.16.** Nitrogen adsorption isotherms of mesoporous silica sphere and gyroid shapes.

There are obvious differences in the shapes of the isotherms for the spheres and gyroids. The mesoporous silica spheres show a smaller capillary condensation effect, indicative of a broader mesopore size distribution. This proposal is confirmed by a Dollimore-Heal analysis of both isotherms which provides estimates for the pore size.
distribution and pore volume of the mesoporous silica gyroids and spheres. The surface area was obtained by a standard BET procedure. A comparison of the adsorption results for the sphere and gyroid shapes is listed in Table 4.3. The surface area and pore volume of the gyroids are higher than those of the spheres. The width of the pore size distribution at half height for the gyroids is ca. 3 times narrower than that for the spheres, although both have comparable mean pore diameters. These values support the contention that the mesopores in the spheres are not as well organized as those in the gyroids.

Table 4.3. The surface area, pore volume, mean pore diameter and FWHM of the pore size distribution of mesoporous silica sphere and gyroid shapes made using the same reactant ratio.

<table>
<thead>
<tr>
<th>shape</th>
<th>BET surface area (m²/g)</th>
<th>pore volume (cm³/g)</th>
<th>mean pore diameter (Å)</th>
<th>FWHM (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sphere</td>
<td>750</td>
<td>0.59</td>
<td>33</td>
<td>19</td>
</tr>
<tr>
<td>gyroid</td>
<td>1200</td>
<td>1.01</td>
<td>35</td>
<td>6</td>
</tr>
</tbody>
</table>

It is noteworthy that the formation of sphere shaped mesoporous silica depends on both the ratio of reactants and temperature. Sphere shaped silica can be synthesized at room temperature using identical surfactant and TEOS concentrations with a lower acidity than those synthesized at 80 °C. However, the spheres made at room temperature show a larger degree of “necking” and much rougher surfaces than those made at 80 °C.

The surface microtopology of the spheres was studied by AFM. Interesting structural features were observed on the surface of the mesoporous spheres synthesized at room temperature that were absent in the 80 °C preparations. A contact height mode AFM image of an as-synthesized sphere formed at room temperature reveals a surface with a mottled texture, an average grain size of ca. 500-1000 Å, and a mean surface roughness of the same order of magnitude, Figure 4.17. The surface of each grain consists of parallel lines with a spacing of ca. 70-200 Å. There is no obvious correlation between the directions of the mesoscale corrugations of the grains. The surface morphology of the spheres is quite distinct to that of the gyroids where it was found that ca. 50-90 Å parallel lines whirl around the unique rotation axis in a manner that mirrors the internal channel architecture.
Figure 4.17. A representative AFM image of the surface morphology for the as-synthesized mesoporous silica spheres formed at the room temperature.

**Shape phase diagram** The effect of the ratio of reactants on the final shapes has been studied by creating a shape/phase diagram for syntheses with different H₂O/HCl ratios run at 80 °C for 3 days. A major experimental effort was placed on mapping the 100 H₂O/(1±0.1)HCl plane, as it is rich in information on shape formation in the CTACl systems.

A summary of the ternary phase diagrams is shown in Figure 4.18. For illustrative purposes, a plane number is given to particular ternary phase diagrams according to 100x(HCl/H₂O). The HCl-CTACl-TEOS ternary phase diagram at plane n, therefore, represents the system with a mole ratio of 100 H₂O : n HCl : x CTACl: y TEOS. The symbol and color codes for the experimental points shown on the phase diagrams are listed in Table 4.4.
Table 4.4 Color and symbol codes for the experimental points on the phase diagrams

<table>
<thead>
<tr>
<th>symbol</th>
<th>hexagon</th>
<th>diamond</th>
<th>circle</th>
<th>square</th>
<th>triangle</th>
<th>crosshair</th>
<th>band (thick line)</th>
</tr>
</thead>
</table>

Certain trends in the system can be seen by analyzing these semi-quantitative diagrams. All the shapes found were at relatively high acidity and always above the 60% level in the phase diagrams. Well-defined shapes often appear in regions with the TEOS/CTACl ratio > 1, implying that a sufficient concentration of inorganic species is needed. Finally, it appears that fiber morphologies only exist within certain acidity ranges and sensitively depend on the reactant ratio, i.e. there is a narrow window for the formation of these morphologies. In contrast, the less ordered mesoporous silica spheres can form in a relatively broader range of reactant ratios.

In the plane denoted as 0.5 spheres along with a mixture of other poorly-defined shapes were seen. This plane represents an extreme domain for shape formation. As the HCl/H₂O ratio increased, forms evolved from poorly-defined shapes and spheres to spheres, gyroids and fibers. At very high acidity, Figure 4.18e, TEOS polymerized very quickly, which led to low quality or non-mesoporous materials and the shape of the products was often ill defined. A schematic representation which encapsulates the essence of the observed data over all HCl/H₂O ratios, is shown in Figure 3.18f.
Figure 4.18. Ternary shape phase diagram of mesoporous silica with $n_{\text{HCl}}$ at (a) 0.5, (b) 1, (c) 1.5, (d) 2.0, (e) 3 of 100 H$_2$O/$n_{\text{HCl}}$ HCl, and (f) summary of the synthesis-shape results.
Figure 4.18. Ternary shape phase diagram of mesoporous silica with $n_{\text{HCl}}$ at (a) 0.5, (b) 1, (c) 1.5, (d) 2.0, (e) 3 of 100 H$_2$O/$n_{\text{HCl}}$ HCl, and (f) summary of the synthesis-shape results.
4.4 Discussion

4.4.1 Liquid crystal defects in hexagonal phases: generation of curved shapes

4.4.1.1 Theory of liquid crystal defects in hexagonal phases

Assuming that the packing geometry of the flexible rod-like micelles in the seed is more-or-less hexagonal, then translational topological defects can be defined. The defects pertinent to the hexagonal mesophase are transverse and longitudinal edge dislocations, and disclinations normal and parallel to the axes of the micellar rods. Disclinations in a liquid crystal may have large angles that relate to the symmetry of the medium, while disclinations in a regular crystalline solid possess small angles that exist at the ends of a dislocation wall.\textsuperscript{17}

The theoretical predictions for some simple shapes of a non-smectic hexagonal mesophase have been discussed by Bouligand based on the study of a lyotropic discotic system.\textsuperscript{18} The defect types are directly related to the symmetry of the hexagonal array. The rod-like 2-D hexagonal structures possess three packing layers along the (100), (110) and (210) planes, while the smectic or lamellar phase has only one stacking layer along the (001) plane, although both mesostructures may share common types of defects and optical textures. In general, there are three longitudinal axes (two, three- and six-fold) parallel to the director field and two transverse axes ($v_1$, $v_2$) that lie in the $ab$-plane of the hexagonal mesophase. The defect structures and final morphologies of a 2-D rod hexagonal liquid crystal can be generated by using any one of the above longitudinal and transverse axes as well as certain combinations thereof. For example, curved morphologies may originate from longitudinal disclinations with a rotation vector along the six-fold ($C_6$, $\pm \pi/3$), three-fold ($C_3$, $\pm 2\pi/3$), and two-fold ($C_2$, $\pm \pi$) axes. Similarly, transverse disclinations along the rotation axes ($v_1$, or $v_2$) produce $\pi$ or $2\pi$ related morphologies such as curved ribbons, discoids and flat toroids.
4.4.1.2 Defects in hexagonal mesoporous silica curved shapes

Early stage. The early growth of curved mesoporous silica at room temperature has been examined by dynamic light scattering (DLS). Since mixing and filtering were needed after all reactants were added, the first auto-correlation functions were normally measured ca. 10 minutes after the addition of all the components. Mesoporous silica with fiber shapes typically formed within 10 minutes and left little time for the measurements. The early growth of gyroid shapes with different sizes made from a mixture of 100 H₂O: n HCl: 0.11 CTACl: 0.13 TEOS at n = 3.5, 2.1, and 0.9 have been followed in situ by DLS. A control experiment was done with an acidic surfactant solution with a molar ratio of 100 H₂O : 3.5 HCl : 0.11 CTACl. The autocorrelation functions after the initial period of accretion for the
systems are shown in Figure 4.20. With time evolution, the autocorrelation function is slightly higher for \( n=3.5 \) and 2.1. In the case of \( n=0.9 \), the induction period was longer than four hours. Clearly, the acidity of the solution strongly affect the nucleation of mesoporous silica.

![DLS autocorrelation function](image)

**Figure 4.20.** DLS autocorrelation function for mixtures of 100 H\(_2\)O : 3.5 HCl : 0.11 CTACl : 0.13 TEOS measured at different times after mixing.

The time dependence of the first cumulant, \( \Gamma_1 \), and the hydrodynamic diameter, \( 2R_H \), based on the fourth cumulant are shown in Figure 4.21. Typical diameters of the solution aggregates are in the range of 5.5 to 7.5 nm, presumably micelles or silicate-micellar species. With time there was a slight decrease in the \( \Gamma_1 \) values which gives rise to a slight increase in the effective diameters, Figure 4.21. Recently, dynamic EPR probes have been used to tackle the kinetics of micelle-templating mesoporous silica formation by using the same surfactants, CTACl or CTABr, and silica precursor, TEOS, under basic conditions.\(^{19,20}\) These *in situ* studies suggested that the formation of mesostructural silica starts with exchange of the counter ions of the surfactants, such as Cl\(^-\) or Br\(^-\), by much large silicates at the head group regions, effectively “freezing” the surfactant micellar templates. The observed changes in the
DLS measurement might represent early events in the induction period of the growth process, supporting the proposed initial growth model of mesoporous silica in basic conditions.\(^{20}\)

It is noteworthy that at high acid molarities the induction period drops dramatically. For systems with \(n = 3.5, 2.1\) and 0.9, the induction periods were \(ca. 20, 40\) and \(> 260\) minutes, respectively. Once the formation of silicate-surfactant mesophase begins, the growth of the mesostructured materials was so fast and the particle size increases so rapidly that no useful autocorrelation functions could be obtained, \(i.e.\) the growth kinetics can no longer be followed by the DLS technique.

Alternate approaches such as AFM and TEM were also used to study the "frozen" early-stage silicate-surfactant mesostructured objects. The samples for AFM studies were made by dipping freshly cleaved pyrolytic graphite into the synthetic solution containing 100 H\(_2\)O: n HCl : 0.11 CTACl : 0.13 TEOS where \(n = 7\) (fiber) or 3.5 (gyroid). Representative AFM images of the dried objects are shown in Figure 4.22. AFM tapping mode was used to minimize the damage and deformation of the soft silicate-surfactant structures. Samples which grow in \(ca. 3-10\) minutes give elliptical shapes with diameters in the 50 - 100 nm range. Silicate hexagonal mesostructures in the same size range have been previously observed by cryo-TEM and may represent the core assembly units which serve as seeds for the mesoporous growth.\(^{21}\) No drastic differences were observed for specimens collected at different acidities, \(i.e. n= 7\) and 3.5. Larger objects (several hundreds of nanometers in size) have been observed for samples with longer growth times.

The internal structures of these soft objects have been studied by conventional bright-field TEM. Along with dense silica spherical objects in the ten to hundred nanometer range, silicate mesostructures with a relatively narrow size distribution of 60-150 nm were observed.\(^{22}\) The size range of the mesostructured silica was comparable to those seen by AFM, Figure 4.23. The mesostructured silica could have been destroyed by the electron beam during the imaging as the seeds have very soft surfaces. This is expected as the silicate would only be loosely assembled around the head regions of surfactants during the initial growth stages.\(^{23}\) Mesostructures in these small seeds are not as well ordered as the structure observed in the core regions of the discoid mesoporous silica. Objects imaged by both AFM and TEM represent the early growing subunits which were frozen \(in situ\) on the specimen supports.
Figure 4.21. *in situ* DLS experiments for the early growth of gyroids with a reactant ratio of 100 HCl : n HCl : 0.11 CTACl : 0.13 TEOS where n = 3.5, 2.1, and 0.9: (a) $\Gamma_t$ vs. time, and (b) $2R_h$ vs. time.
Figure 4.22. AFM of early stage objects: (a) $n = 7$, (b) $n=3.5$, and (c) $n = 7$ longer time.
Figure 4.23. TEM of early-stage objects for mesostructured silica at low (top) and high (bottom) magnification.
In essence, the early stage study of the shape formation points to the existence of nanoscale seeds which govern the further growth of mesoporous silica with curved shapes.

**LC defects in curved shapes.** The above studies on the curved morphologies of the final mesoporous silica products show that the unusual forms exhibited by these mesoporous silica morphologies not only appear to be related to the faceted and geometric polyhedra of regular crystals but also are quite similar to the contour surfaces predicted by defect initiated growth.¹⁸ The mesoporous silica formed can be viewed as two dimensional hexagonal arrays of long rodlike shapes. The phase of this 2D hexagonal phase mesoporous silica is $P6m$ with no symmetry element associated with the $c$-axis. By increasing the degree of curvature of the faceted rope morphologies, it is possible to generate discoids and gyroids with periodic faceting on their outer surfaces.

The illustrations and observed synthetic shapes are presented in Figure 4.24. The lines on the illustrations represent the director fields delineated by the channels of the mesoporous silica. It is noteworthy that most of the simplest curved morphologies could arise from disclination defects.

These morphologies are represented by discoids and flat toroids which could be initiated from a $+2\pi$ disclination rotated along the transverse axis in the $ab$-plane (wedges), Figures 4.24a, b, and single point knots and spirals from application of a $+2\pi$ screw dislocation, Figure 4.24c. The twist observed in hexagonal fibers can be thought of as the consequence of $+\pi/3$ or $-\pi/3$ disclinations around the longitudinal axis $C_6$, Figure 4.24d. TEM images that define the mesostructure-morphology relationship in both discoid and gyroid mesoporous silica shapes provide compelling evidence for the proposed defect structures.¹²⁴

Some representative TEM images for mounted fiber samples are shown in Figure 4.25. The black lines in the images are the silica walls, which show the channel direction within the fiber morphology. Dislocations appear to be common in mesoporous silica. These defects have the tendency to exist in the bending regions of a fiber morphology by inspection of the TEM images. Even if a large population of edge dislocations existed, they would not be expected to induce substantial morphology changes or bending, Figure 4.25b. Several defect types, including dislocations and disclinations such as, $+\pi$, and pairs of $+\pi/\pi$, or $+\pi/-\pi$, have been described for powder forms of mesoporous silica.²⁵
Figure 4.24. SEM images of hexagonal mesoporous silica morphologies that could arise from single defects (left: SEM images; right: illustrations): (a) discoid (v axis, +2\pi disclination), (b) flat toroid (v axis, +2\pi disclination), (c) spiral (v axis, +\pi screw dislocation), (d) rope (C\textsubscript{3} axis, 1/3\pi disclination).
Figure 4.25. TEM of mesoporous fibers with dislocation defects.
Hybrid structures based upon a combination of two defects can lead to a variety of mesoporous morphologies, **Figure 4.26**. Three possible combinations predicted by Bouligand have been observed: the first involving two $+\pi$ screw dislocations, the second two $+\pi$ disclinations, and finally a combination of a $-\pi/3$ disclination normal to the main rotation axis and a $+2\pi$ disclination orthogonal to this axis.\(^{18}\) If growth is initiated by a parallel pair of $+\pi$ screw dislocations, a dual-center spiral will be generated, **Figure 4.26a**. Growth initiated by two $+\pi/+\pi$ disclinations having their transverse axes at different angles gives a bagel shape, **Figure 4.26b**. An irregular bagel shape appears when the two axes are at any angle other than $0^\circ$ or $90^\circ$, **Figure 4.26c**.

The third variety of defect involves the fusion of a $-\pi/3$ disclination normal to the main rotation axis with $+2\pi$ disclination orthogonal to the this axis; this defect could initiate the development of a twisted toroid, **Figure 4.26d**. The $-\pi/3$ defect can be best seen by following the rotation direction of the inner plane.

The defect-shape-channel structure relationship manifests itself through characteristic textures when the shapes are viewed between cross polarizers in an optical microscope. The textures of elongated discoids can be viewed as two parallel $+\pi$ disclinations, **Figure 4.27a**, and bagel shapes as two orthogonal $+\pi$ disclinations, **Figure 4.27b**, with at least one transverse axis parallel to the optical axis of the hexagonal mesoporous silica. Clearly, all POM patterns for these forms of mesoporous silica bear a close resemblance to those observed for organic liquid crystal defect structures and agree well with theoretical predictions for materials with uni-axial symmetry.

In conclusion the collection of hexagonal mesoporous silica morphologies presents a close relationship between the channel patterns, defects, and textures present in the mesophases. The appearance of a particular mesoporous silica shape is associated with the existence of specific kinds of dislocation and disclination defects which initiate growth and determines the final form of a germinating and polymerizing silicate mesophase.
Figure 4.26. SEM images of hexagonal mesoporous silica morphologies that arise from combinations of two defects: (a) dual center spiral (a parallel pair of $+\pi$ screw dislocations), (b) bagel (a pair of orthogonal $+\pi$ disclinations grown to different extents), (c) irregular bagel (a pair of orthogonal $+\pi$ disclinations with the two axes at an angle other than $0^\circ$ or $90^\circ$) (d) a twisted toroid arising from a combination of $-\pi/3$ and $+2\pi$ disclinations.
Figure 4.27. POM images of hexagonal mesoporous silica: (a) elongated discoid (ν axis, a pair of parallel +π disclinations), (b) bagel (ν axis, a pair of orthogonal +π disclinations).

The model that emerges from these observations shows that a hexagonal cylindrical surfactant-silicate seed\textsuperscript{26} undergoes polymerization and growth through the accretion of surfactant-silicate micelles. The diversity of mesoporous silica with curved morphologies reflects the underlying liquid crystal defects. The geometrical shapes and surface patterns that emerge represent the morphogenesis of mesoporous silica that has been frozen along the reaction co-ordinate. Thus supramolecular templating is able to create inorganic materials with natural form.\textsuperscript{27}

4.4.2 Tuning the shape in the “colloidal domain”

The experimental observations suggest that gyroid mesoporous silica can transform into spherical shapes simply by enhancing the aging temperature. Gyroid-to-sphere transformations also happen with decreases in the acidity of the system. A catalogue of SEM images for samples made at 80 °C depicts representative synthesis-shape transitions induced by decreasing the acidity Figure 4.28.
Figure 4.28. A series of SEM images illustrating various mesoporous silica shape transitions from (a) gyroids to (f) spheres.
The following trend is seen from (i) gyroids displaying smooth surfaces with well-ordered hexagonal closely packed structures, to (ii) gyroids co-existing with similar shapes possessing a multi-granular texture with less ordered channels akin to a "molten" mesostructure,\textsuperscript{28} (iii) mixtures of these multi-granular shapes co-existing with spheres exhibiting smooth surfaces, (iv) smooth spherical shapes, and ultimately (v) shapeless forms. The shapeless end-products formed at low acidity in this synthetic system consist of dense and glassy forms of silica.

Highly acidic quiescent conditions promote a reaction mechanism based on the rapid growth and polymerization of a silicate liquid crystal embryo. Conditions near the isoelectric point of silica (pH = 2.0 - 2.2 at 25 °C)\textsuperscript{29} favor protonation of the silicate precursors and a [(CTA)\textsuperscript{+}Cl\textsuperscript{-}H\textsuperscript{+}(Silicate)\textsuperscript{-}] type of co-assembly.\textsuperscript{30} As the acidity is lowered, the growth process changes from one involving deposition of silicate-surfactant micellar species onto specific regions of a growing silicate liquid crystal seed, to one in which deposition occurs on non-specific regions of the evolving subunits. The lower acidity growth process could involve a slower and non-directional silicification of silicate-surfactant mesophase "floc". Surface tension effects would affect the final shape of the particle.

**Effects of ethanol on the shape formation.** The cooperative assembly mechanism is the most reasonable formation pathway for mesoporous materials using cationic surfactant templates under dilute conditions.\textsuperscript{31} Qualitatively, any van der Waals and electrostatic forces that involve counterion, surfactant and silicates, can effect the surfactant assemblies and the surfactant-silicate interfacial interactions at the head group region of the assemblies.\textsuperscript{31}

A calculation of solute-surfactant interactions on micelle formation has been examined using a finite number of surfactant types. The study suggests that the structure and coordination number of the inorganic solute is an important factor in the formation of mesostructured materials with a particular phase.\textsuperscript{32} That is, the strength of the interaction of the inorganic with an organic surfactant at the boundary region effects which mesophase is produced. This has also been experimentally observed.\textsuperscript{13,33} Profound effects on the formation of mesoporous silica are seen by modifying the charges on the inorganic species and surfactant headgroups or adjusting the dielectric constant of the solution.

If this model is qualitatively applicable to the formation of mesoporous materials, one may expect the forces that effect the cooperative interactions between the surfactant head
groups and inorganic species may also effect the morphogenesis of the inorganic-organic mesophase. Thus the shapes of mesoporous silica could be controlled by reagents which alter these forces. This is the rationale for examining whether tailoring the dielectric constant of the synthetic mixture through the addition of alcohol affects the mesoporous shape formation.

The effect of adding different amounts of absolute ethanol to the preparation (100 H$_2$O : 7.4 and 3.5 HCl : 0.11 CTACl : 0.13 TEOS: x EtOH, fiber/gyroid) was examined. As one increases the amount of ethanol in a synthesis which normally creates a mixture of fibers and gyroids, the mesoporous shapes transform into pure gyroids. Spherical mesoporous silica was obtained by the further addition of ethanol to the reaction mixture. PXRD and SEM images of spheres made at room temperature and 80 °C with x = 12(fiber/gyroid) are shown in Figure 4.29. Along with transformation of the shapes to gyroids and spheres, the FWHM of the (100) diffraction peak for the hexagonal phase increases and all the higher angle diffraction peaks gradually disappear. The shape change of mesoporous silica when ethanol is added to the synthetic mixture is similar to the effect seen when the acidity is decreased.

A systematic study of the effect of cosolvents on the formation of surfactant templated silica mesophases using tetramethoxysilane and cetyltrimethylammonium bromide under aqueous basic conditions has recently been published. Fourteen cosolvents including ethanol were tested. Spherical and ellipsoidal mesoporous silica was observed with increasing amounts of the co-solvent. The micelles in highly concentrated cosolvent systems were thought to be less elongated, thus leading to the formation of spherical mesoporous shapes.

Salts such as NaCl, show no dramatic effects on the final shapes for the gyroid formation, even at saturation. These observations are summarized in Figure 4.30.

In summary, 1) increasing the pH of the synthesis mixture to the isoelectric point can transform mesoporous silica from fiber, and gyroid into sphere shapes; 2) Similar effects can be accomplished by gradually adding ethanol into the synthetic system; 3) Enhanced temperatures tend to give less ordered mesoporous materials; and 4) Monovalent salts, such as NaCl, do not have dramatic effects on morphology, that is, fibers do not transform to spheres even at saturated NaCl conditions.
Figure 4.29. PXRD (left) and SEM (right) of shapes of mesoporous silica in the presence of ethanol made at (a) room temperature and (b) 80 °C.
Figure 4.30. Illustration of ethanol and salt effects on morphogenesis of mesoporous silica.
Acid plays several important roles in the system, including: 1) catalyzing the polymerization and condensation of TEOS,\textsuperscript{29,35,36} 2) serving as an electrolyte that tunes the solution properties and interaction of the assemblies, especially at head group regions through a charge screening effect,\textsuperscript{37,38} and 3) changing the interaction between inorganic silicate species and the head groups of the surfactants, Figure 4.31a. The charge and size of tetrahedral silicate species can be effectively tuned by changing the acidity, which in turn changes the size of the head groups, the packing parameters, and the curvature of the assemblies. Since the hexagonal phase of the mesoporous silica under dilute surfactant conditions exists only when inorganic species are involved, the absence of strong interactions between silicate species and the surfactant head groups leads to the absence of long range assembly.\textsuperscript{36} The direct consequence of short range micellar packing with slow condensation of silicate around the head group regions results in the formation of spheres rather than faceted gyroid structures.

To a less dramatic extent, formation still requires a liquid crystal templating route. However, the growing silicate-surfactant seeds have different degrees of surface charge, \textit{i.e.} different electrical double layer thickness and charge densities, with changing pH conditions and thus possess distinct growth pathways, Figure 4.31b.

Addition of ethanol to the synthetic mixture affect the morphogenesis of mesoporous silica much like the effects seen by lowering the acidity. A by-product of the hydrolysis of TEOS is ethanol which is expected to have an effect on the hydrolysis reaction according to Le Chatelier's Principle\textsuperscript{39} and the addition of ethanol will shift the equilibrium towards the reactant side, resulting in silicate species with a lower degree of hydrolysis and condensation. Such building blocks will have a lower degree of interaction with the surfactant head groups.

Surfactants do not typically form well ordered self-assembled structures in low dielectric organic solvents, as the hydrophobic chain interacts with the solvent molecules, impeding the chain-chain hydrophobic interactions.\textsuperscript{40} Therefore, adding ethanol into an aqueous system effectively lowers the ability of the surfactant to self assemble and promotes mesophases with little long range order. With increasing amounts of ethanol, van der Waals interactions become the main governing forces which leads to non-directional flocculation of seeds, leading to the formation of spherical mesoporous silica.\textsuperscript{41} Thus, ethanol, with a
dielectric constant or permitivity of 25.3 ($\varepsilon_{\text{H}_2\text{O}} = 80.1$) at 20 °C, could have large effects not only on the surfactant head group regions through charge screening, but also at the hydrophobic chain regions.

By comparison, salts such as NaCl can play only a limited role in the cooperative silicate-surfactant assembly. The hydrolysis and condensation of TEOS is not expected to be sufficiently altered due to the presence of electrolytes. In organic supramolecular systems, NaCl can increase the aggregation numbers and lower the critical micelle concentrations through charge screening at the ionic head group regions. Thus it may be not surprising that no gyroid to sphere transformation was observed, since charge screening typically does not obstruct the ability of surfactant to assemble into micelles. In this regard, the effect of surfactant counterions on the morphogenesis has also been tested at reactant ratios of 100 H$_2$O : 3.5 HCl : 0.11 surfactant : 0.13 TEOS. For all three cationic surfactants tested, i.e., CTACl, CTABr and cetylpyridinium chloride, at mole ratios that favors the pure gyroid formation, only gyroid related shapes were observed. The change of counterion hardly has any impact on the surfactant assembly.

In conclusion, the picture that emerges from the studies of the morphogenesis of shape in hexagonal mesoporous silica is that there exists a logical relation between the synthesis conditions, polymerization, growth, and curvature of a silicate liquid crystal growth nucleus. The shape-transition of the gyroid to the sphere with intermediate stages of multigranular hybrid structures is interesting because it unveils acid, cosolvent and temperature dependent switches in the mode of formation of these morphologies. It appears that the faceted fiber and gyroid shapes form by rapid local silicification and the curvature of an evolving silicate liquid crystal seed initiated by defects. By contrast, a slower and non-directional silicification process, in which surface tension forces dominate, promotes sphere formation. Altering the silicate polymerization and solution dielectric constant seems to have strong effects on the mode of formation and the types of defect seen.

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Figure 4.31. Illustration of (a) the effect of some colloidal forces and hydrolysis rate on the morphogenesis of mesoporous silica, and (b) shape formation trends.
4.5. References:


22 Since no objects larger than 10 nm were observed in DLS experiments, the observed mesostructures in AFM and TEM images could only form after the induction period in the samples, i.e.: after been transferred onto the grids or graphite surfaces.


Chapter Five
Concluding Remarks

5.1 Conclusion

Mesoporous silica forms were studied under quiescent aqueous acidic conditions. Low dimensional shapes of mesoporous silica, predominantly the ordered hexagonal phase, as fibers and films, as well as three dimensional curved shapes including gyroids and spheres have been made.

Mesoporous silica films can be grown on various solid substrates. Films grown on atomically flat surfaces such as Muscovite mica and pyrolytic graphite were found to be oriented and registered with respect to the substrate. In situ tapping-mode AFM of surfactant assemblies on the graphite surface suggested the formation of a surface liquid crystalline film growing from a hemimicellar monolayer assembly. The channel structures of the films can clearly be altered by using different substrates. No clear registry of film growth was seen on glass substrates or pristine and SAM modified gold layers deposited on mica. Patterned SAMs on gold can be used to create a hierarchical macro-meso two dimensional design.

Free-standing ordered mesoporous films grown at the air-water interface also show preferred orientation with respect to the interface. Film thickness and the degree of polymerization of the silica wall for both free-standing and supported films can be tuned by altering the acidity and temperature of the synthesis mixture. Fan-type POM images were observed for the films which were caused by the ordered channel structure of the films. The optical anisotropy for the mesoporous films arises from the uniaxial array of hexagonal cylinders with glassy walls.

Curved shapes were also made under quiescent acidic conditions. The relationship between channel structure and morphology was established by PXRD, SEM, TEM, AFM and POM. The origin of observed birefringence patterns was the anisotropic array of hexagonal cylinders with amorphous silica walls. It was found that acidity and the use of cosolvents such as ethanol, can have important effects on shape formation. Liquid
crystalline defects are believed to be the major reason for the formation of a large population of curved shapes and the mesoporous silica sphere were formed through the flocculation of smaller mesostructured units.

Unquestionably, form in ordered mesoporous materials has emerged as a new avenue of investigation. The ability to intentionally synthesize a particular shape with tunable properties will represent a big step towards the design of functional inorganic mesostructures for a range of perceived applications.

5.2 Future work

The guest-host chemistry of mesoporous materials has been extensively studied since their discovery not only because of the fundamental interest, but also because of potential applications. In this context, ordered mesoporous hosts with well defined morphologies should have an important position in the field of supramolecular materials. It should be interesting to investigate how these well-defined forms of mesoporous silica act as host structures.

A case in point concerns the deposition of luminescent silicon within the mesoporous film. Photoluminescence has been reported for nano size silicon clusters in MCM-41. Although still under debate, quantum and spatial confinement effects have been widely accepted as the origin of the observed luminescence. Disilane (Si\textsubscript{2}H\textsubscript{4}) has been used as a silicon source for chemical vapor deposition into oriented hexagonal mesoporous silica films. The deposition procedure is a modified version of that used for powdered hexagonal mesoporous silica. The appearance and photoluminescence of mesoporous films with deposited disilane in a sealed quartz cell are shown in Figure 5.1. Yellow to brown colors can be observed for films with different thickness in white light and the film remains intact. Under UV irradiation at ca. 77 K, bright yellow-orange photoluminescence could be observed from the films. The dependence of luminescent intensity on temperature could be detected by the naked eye.

PXRD patterns of the silicon-silica mesostructured film have been taken before and after disilane treatment. After the CVD process, a contraction of the hexagonal unit cell by
3-4 Å occurs due to anchoring of disilane to SiOH sites on the walls of the channels. PXRD shows that the high loading of disilane tends to decrease the order of the mesoporous silica film. Polarized optical microscopy images of the film before and after disilane deposition, display the expected optical birefringence from the pattern of channels organized in the plane of the film. This implies that the disilane deposited film still maintains its channel orientation.

Figure 5.1. Photograph of Si₂H₆ treated films under white light at room temperature (left) and under UV irradiation at liquid nitrogen temperature (right).

For the mechanistic concern, although the connection has been made between liquid crystalline defects and some curved mesoporous shapes, and channel structures of the film the subject of morphogenesis of mesoporous silica are far more complex than those cases identified in this work. It also seems certain that colloidal forces, such as electrical double layer forces and solvent dielectric constant effects, play important roles in shape formation. In this context, one may need to carefully examine how colloidal forces effect the morphology of mesoporous materials. Thus, a better understanding of shape and surface patterns requires insight from researchers in materials chemistry, colloidal chemistry, liquid
crystal physics, mathematics, and physics. Nevertheless, the basic control and understanding of morphology and channel structure for hexagonal mesoporous silica fibers, films, and curved shapes provides a fascinating springboard from which to orchestrate future experiments and formulate and test theoretical models that are aimed at understanding and controlling the polymerization, growth and form of silicate liquid crystal seeds.

While the involvement of topological defects in the silicate mesophase seems assured, it has yet to be established to what extent reaction-diffusion processes contribute to the overall silicified library of shapes. The surface patterns observed in this system are aesthetically beautiful and puzzling. Experimental and theoretical studies are needed to examine the possibility that thermally excited surface vibrational waves contribute to the pattern formation. Such waves often contribute to the formation of surface patterns for bilayer vesicles. Channel buckling could also contribute to the creation of surface patterns.

The subject of mesoporous silica shares aspects with biomineralization processes. In Nature, biosilicification occurs at organic-inorganic interfaces in aqueous systems under mild conditions. Natural and synthetic silica assemble hierarchically in two or three dimensions and the connection may serve to inspire inorganic materials chemists in the search for new materials.

It is interesting to imagine how the paradigm developed in this study for mesoporous silica forms can be extended to a broader range of compositions. The possibility of controlling the shape of mesostructured transition metal oxides should be a rewarding future research direction.
5.3 References


