
Amy Rue

Virginia Commonwealth University

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Virginia Commonwealth University.

by

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<td>Anodic aluminum oxide membrane</td>
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<tr>
<td>Ag/AgCl</td>
<td>Silver chloride coated silver wire</td>
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<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<td>CV</td>
<td>Cyclic voltammetry or cyclic voltammogram</td>
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<td>DDMOS</td>
<td>Dimethyldimethoxysilane</td>
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<tr>
<td>OTMOS</td>
<td>n-octyltrimethoxysilane</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>Ru(NH$_3$)$_6^{3+}$</td>
<td>Hexaammineruthenium (III) ion</td>
</tr>
<tr>
<td>SAM</td>
<td>Self-assembled monolayer</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>SDS</td>
<td>Sodium dodecyl sulfate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron Microscopy</td>
</tr>
<tr>
<td>SPM</td>
<td>Scanning Probe Microscopy</td>
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<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>STMOS</td>
<td>3-mercaptopropyl trimethoxysilane</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
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<tr>
<td>TEOS</td>
<td>Tetraethoxysilane</td>
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<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
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<tr>
<td>TMOS</td>
<td>Tetramethoxysilane</td>
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<tr>
<td>UV-Vis</td>
<td>Ultraviolet/visible molecular absorption spectroscopy</td>
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Abstract

DEVELOPMENT OF NANO-SCALE FEATURED SILICA MATERIALS FOR ELECTRODE MODIFICATION AND SOLID SUPPORTS

By Amy Rue, PhD

A Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor in Philosophy at Virginia Commonwealth University.

Virginia Commonwealth University, 2012

Major Director: Maryanne M. Collinson, Professor, Department of Chemistry

This work utilized the sol-gel process in two ways. First, macroporous silica thin films were developed using a combination of casting techniques and templating. Macroporosity was introduced to the silica thin films by either doping the silica sol before casting or by ordering the template on a substrate and then casting a sol over it. These techniques were first used to create silica thin films with long microchannel pores (200 nm x 60 μm) from a doped sol with the bacteria, B. Megaterium, as the template for nanomaterial formation. To enable the formation of long microchannels, the flexible bacteria chains were aligned by using light scratches on the substrate surface as anchors for the bacteria’s adhesive cell capsule. Polystyrene (PS) sphere templates were then used in several studies to obtain silica thin films with well-ordered “nanowells,” single-layer hemispherical pores that allowed direct access to the substrate beneath...
the film. Copper and gold nanoparticles were integrated into moderately packed films by electrodeposition and monolayer self-assembly, respectfully. The size of the nanoparticles was controlled by the time of the electrodeposition or the time of exposure to an electroless growth solution. The final study with polystyrene latex sphere templates produced high quality, well-packed films containing well-defined nanowells over almost the entire conductive substrate. This was accomplished by separating the ordering of the templates on the substrate from film formation. Electroless growth was used to control the size and shape of the gold nanoparticles and the electrochemical properties of the resultant films were studied, showing an enhanced response to negatively charged redox probes.

Sol-gel techniques were then used to create high aspect ratio silica nanotubes and pillars. The electroassisted deposition of silica was carried out in the pores of track-etched membranes, allowing supported nanotubes with dimensions of 100 – 400 nm x 10 µm to be obtained. The mechanism of silica formation in the tubular template was studied and it was found that growth occurred first by nanotube formation, followed by further growth through tube from the electrode to the other side of the pore. This allowed for partially filled tubes and solid pillars to be obtained. The method was found to be flexible and characteristics such as tube length, chemical functionality and porosity to be controlled.
Chapter 1: Introduction to Sol-Gel Science and Templating Techniques

1.1 Introduction

The major focus of this dissertation is on the intersection of analytical chemistry and material science and how the specific techniques of electrochemistry, templating and sol-gel science can be used to develop novel electrodes and nanoscale materials. In chapter three of this work, bacteria in sol-gel derived thin films were investigated as exotemplates for the formation of high aspect ratio nanomaterials. In chapters four and five, the sol-gel process was utilized to create thin films on surfaces for the purpose of electrode modification. Both chapters utilized the integration and subsequent removal of ordered, hard templates to control diffusion through silica films and improve the electrochemical response. In chapter four, metal nanoparticles were integrated into silica “nanowell” templated films through electrodeposition and particle self-assembly. The goal of this work was to control the size and location of the metal nanostructures. Chapter five describes how silica thin films templated with PS spheres were cast on gold electrodes and further modified with gold nanoparticles. The electrodes were then used to study the influence of charge interactions between the silica film and common redox probes on the system’s electrochemistry. In chapter 6, electrochemistry was used to influence the sol-gel process for the creation of high aspect ratio silica nanostructures. Scaffolding-type track-etched membrane templates were modified with gold to form electrodes and the effect of changes in experimental conditions on the final material was studied. Experiments ultimately showed that the dimensions, porosity, type of structure (tube vs solid pillar), and chemical functionality could be controlled. In the present chapter, a detailed background of sol-gel chemistry and templating is given and in chapter two, electrochemistry and other important instrumentation is explained.
1.2 Sol-gel Chemistry

Since the discovery by Ebelman in 1846 that, under acidic conditions, tetraethyl orthosilicate (TEOS) formed a silica gel, the formation of inorganic network materials though the sol-gel process has been the subject of much study.\textsuperscript{1} With the advent of more advanced technology, sol-gel chemistry has been modified for the creation of a variety of ceramic materials, such as threads, monoliths, nanoparticles, and thin films.\textsuperscript{2}

![Diagram of sol-gel process]

**Figure 1.1**: Common materials formed through the sol-gel process. (Adapted with permission from reference 2. Copyright 1999 American Chemical Society)

Ceramics are defined as non-metallic, inorganic, non-chalcogenic materials and include a wide range of important materials such as metal oxides, nitrides, and carbides.\textsuperscript{1} Traditional methods for creating ceramics often involve application of significant pressure or heat, whereas sol-gel derived ceramics are primarily created at or near room temperature and pressure.\textsuperscript{1, 3} While the sol-gel process can and has been used to synthesize ceramics with a variety of metal centers (ex. Ti, Zr, and Ta) in the literature, silicon and silica materials remain a primary area of study and they will be the focus of this dissertation.\textsuperscript{1, 4} The sol-gel process has many attractive
characteristics such as tunable porosity, chemical inertness, resistance to swelling in aqueous solutions, and, perhaps most importantly, simple preparation under bench top conditions.\textsuperscript{2,5}

The sol-gel process describes the general process by which sols undergo gelation. A sol is a colloidal solution where the particles suspended in solution are solid. The definition of a gel is less concrete, but for the purpose of this dissertation Brinker’s definition of “[a] substance that contains a continuous solid skeleton enclosed in a continuous liquid phase” over at least a micron range will be used.\textsuperscript{1} Material formation takes the general form of (1) sol formation/polymerization, (2) gel formation, (3) aging, (4) drying and an optional final (5) densification step through the application of heat (Fig. 1.2).\textsuperscript{1}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{sol-gel-process.png}
\caption{The major steps of the sol-gel process: (1) sol formation, where precursors react to form a colloid; (2) gelation, where the sol particles form a single, solution spanning network; (3) aging, where polymerization continues to occur in the gel network; (4) drying, where liquid is removed from the gel; (5) heating, where the gel undergoes densification. (Adapted with permission from reference 1, Copyright Elsevier (1990))}
\end{figure}

Variation in the method can be introduced at any point in these steps, creating the opportunity for tailoring a wide range of characteristics in the final material. The following sections will describe the first four steps in detail and will provide background relevant to the conducted research.
1.2.1 Sol formation/polymerization

The sol-gel process generally begins with mixing one or more chlorosilanes or alkoxyssilanes with water.\textsuperscript{1, 5, 6} The basic sol-gel precursor is a metal that is bonded to two or more labile groups. Silica precursors range from the relatively simple tetrachlorosilane, tetramethoxysilane (TMOS), and tetraethoxysilane (TEOS) to more complex compounds like 3-mercaptopropyl trimethoxysilane and (3-aminopropyl)-triethoxysilane and are commonly chosen for their reactivity and/or their functionality. The most studied class of sol-gel precursors are the metal alkoxides, which are metal-organic compounds where the metal and organic ligands are linked through oxygen rather than through carbon.\textsuperscript{1, 4} Understanding the chemistry of the silicon-oxygen bond is fundamental to the sol-gel process for most silica materials, as it is the location of cleavage after a nucleophilic attack by either water or hydrolyzed precursors. As explained, a sol is a colloid of solid particles and these particles are created by a series of hydrolysis and condensation reactions taking place between the precursors and water. Generalized reaction schemes for the reaction of metal alkoxides and water are as follows,

**Hydrolysis** →
\[(1) \text{M(OR)₄} + \text{H₂O} \leftrightarrow \text{OH-M(OR)₃} + \text{ROH}\]
\[\leftarrow \text{Esterification}\]

**Alcohol Condensation** →
\[(2) \text{(OR)₃M-OR} + \text{HO-M(OR)₃} \leftrightarrow \text{(OR)₃M-O-M(OR)₃} + \text{ROH}\]
\[\leftarrow \text{Alcoholysis}\]

**Water condensation** →
\[(3) \text{(OR)₃M-OH} + \text{HO-M(OR)₃} \leftrightarrow \text{(OR)₃M-O-M(OR)₃} + \text{H₂O}\]
\[\leftarrow \text{Hydrolysis}\]

where the organic ligands facilitate hydrolysis reactions (Equation 1) with water to form hydroxylated metals, (1) that in turn undergoes condensation (Equations 2 and 3), resulting in oxygen linking the metal centers.\textsuperscript{1}
Silica materials dominate the sol-gel literature primarily due to their unusually favorable, or rather, unusually unfavorable properties for these reactions.\textsuperscript{1} The greatest control over the final material in the sol-gel process is achieved by careful monitoring and controlling the many steps throughout, which is most easily achieved with relatively slow reaction rates. In the hydrolysis reaction, water acts as a nucleophile and silicon, with its small partial positive charge (+0.32 in Si(OEt)_4), is more resistant to nucleophilic attack relative to other similar metal alkoxides such as Ti and Zr (+0.63 in Ti(OEt)_4 and +0.65 in Zr(OEt)_4).\textsuperscript{4} The reactivity of other metal oxides can be mitigated through the use of complexing agents, such as acetylacetone to retard the hydrolysis of titanium n-butoxide in the development of TiO\textsubscript{2} materials, but even then they are generally more difficult to work with than silica.\textsuperscript{7, 8} It should be noted, however, that in some situations the ease of use of silica cannot overcome the need for more hardy or chemically resistant materials that can come from the use of other metal oxides.\textsuperscript{8}

The chemistries of the hydrolysis and condensation reactions of silanes are largely dominated by several important variables: the alkoxyilane precursor, the secondary solvent, the ratio of water to precursor, the nature of the catalyst, and the pH of the solution.\textsuperscript{1, 2} Because of its importance and relevance to this dissertation, the influence of pH in particular will be discussed in some detail.

The silane precursors are the monomer building blocks of a silica polymer, and as such, their selection is very important. First, equation 1 shows that the leaving group in the hydrolysis reaction is an alcohol in the form of ROH. The R functional group of the alkoxide ligand on the precursor can influence the reaction in several ways. The kinetics of hydrolysis is influenced by the type of R group attached to oxygen; electron donating or electron withdrawing groups can strengthen or weaken the Si-O bond, decreasing or increasing reaction kinetics respectively.\textsuperscript{9}
Bulky R groups can also slow kinetics by adding steric hindrances to the reaction. The use of organotrialkoxysilanes or diorganodialkoxysilanes of the general formula $R_mSi-(OR')_n$ will limit the polymer functionality of the material. Organoalkoxysilane precursors have substituents (R) that are bound to the central silicon atom by a carbon, and thus cannot be hydrolyzed under normal experimental conditions. Therefore, the organic character of the selected precursor will be retained within the resulting gel. In addition, the presence of functional groups that have acidic or basic characteristics, such as (3-aminopropyl)-triethoxysilane, on the organic ligand of an organoalkoxysilane can play a role in the reaction because of the pH sensitivity of the hydrolysis and condensation reactions. Precursors with low functionality ($m = 1\text{-}3$, in the general formula above) are also particularly useful for surface modification, where they readily react with hydroxyl groups on the surface of a silica material. For organosilanes that have single functionality, or long hydrocarbon chains as their organic ligand, their formation at the surface will be in a single layer. Most other organosilanes can produce branched arrangements on the surface of a silica structure, but the additional chemical functionality can still be useful.

The structure of metal alkoxides, where a metal center is surrounded by organic ligands, results in most silane precursors having low solubility in water and thus a secondary solvent becomes necessary to prevent phase separation. The most popular choice for the secondary solvent is short chain alcohols due to their success as solvents in the common water/tetrafunctional silane (TMOS, TEOS) system. In addition to improving solubility, alcohols can also play a role in the reverse reaction of condensation (Equation 2), through the pH dependent solvation of polymerized silica and the regeneration of precursor monomers. Alternative secondary solvents such as DMF and THF are also available for use with precursors that are relatively polar due to alkyl-substitution. DMF and THF are aprotic and therefore lack
the ability to form hydrogen bonds with the linking oxygens on the silica structures. As a result, their roles in the reaction chemistry are severely diminished and they are generally considered to be inert solvents.

The next variable for consideration will be the concentration of water in the solution, which should influence the hydrolysis of the silica precursors according to Equation 1. The water concentration is generally expressed in terms of the molar ratio of water-to-silane. This value can have a substantial influence on the hydrolysis and condensation reactions, and is heavily influenced by the pH of the solution. In general, acidic conditions coupled with low water-to-silane ratios result in sols that are weakly branched and appear more polymeric. Coupling basic conditions with large water-to-silane ratios, on the other hand, results in strongly branched materials that are either particles or particulate in nature. In addition, the kinetic effects of the water-to-silane ratio are more strongly felt under acidic conditions. For example, the hydrolysis of TEOS under acidic conditions was determined by Aelion et al. to be first-order with respect to water concentration whereas it was found to be zero-order under basic conditions. The reason for the difference between these trends will be discussed in more detail later, but briefly, the silica precursors can be regenerated much more readily from the polymer under basic conditions, lessening its kinetic dependence on the amount of water present. Under acidic conditions, the condensation reactions are generally irreversible. There is a limit, however, to the amount that the water can be increased in acidic solutions while still increasing the hydrolysis rate and decreasing the time required for a gel to form. To retain good solubility between the water and the silane precursors, a large increase in the water-to-silane ratio can require a simultaneous increase in the amount of secondary solvent needed. Increasing both the
water and secondary solvent results in an overall decrease in the silane concentration; this in turn decreases the hydrolysis rate and increases the amount of time needed for a gel to form.

1.2.1.1 Influence of pH on sol formation

The pH of the solution has been shown to have a major influence on the hydrolysis and condensation reactions at almost every level. This is largely due to subtle but important differences in the reaction mechanisms under acidic and basic conditions and the implications they have on polymerization. The discussion of pH will address its role in both hydrolysis and condensation and its importance in relevant particle growth models.

The mechanism for hydrolysis under both acidic and basic conditions follows an SN2-Si scheme, where the silica precursor undergoes nucleophilic displacement. Acids act as catalyst in this mechanism by first protonating one of the alkoxides on the precursor. The central silicon becomes more electrophilic as electron density is drawn away by the newly protonated ligand. Figure 1.3 shows the generally accepted mechanism for hydrolysis with an acid catalyst.

![Figure 1.3: The mechanism for acid-catalyzed hydrolysis.](Adapted with permission from reference 9, Copyright Elsevier (1988))

The water acts as the nucleophile, attacking the silicon opposite from the protonated ligand. An intermediate is formed and the incoming water develops a partial positive charge that corresponds to a reduction of the charge on the protonated ligand. This results in the protonated ligand becoming a good leaving group and forming an alcohol. The hydrolyzed precursor now takes the form of SiOH(OR)₃ and has undergone inversion. This mechanism agrees with trends
described previously, where increasing the electron-donating character or steric bulk in R will slow down the rate of hydrolysis.

Under basic conditions, however, the mechanism cannot begin with the protonation of the precursors. Rather, the addition of a base results in the dissociation of water into hydroxide ions that then act as the nucleophile in the mechanism (Fig. 1.4). Similarly to in the acid catalyst mechanism, the nucleophile attacks opposite of the eventual leaving group.

![Figure 1.4: The mechanism for base-catalyzed hydrolysis. (Adapted with permission from reference 9, Copyright Elsevier (1988))](#)

An intermediate is then formed, with partial negative charges forming on the hydroxyl and ligand groups, resulting in a compound that has undergone inversion and released an alcohol.

Because the overall rate of hydrolysis is slow, condensation will proceed concurrently under most conditions. First, in sol-gel science, the rate of condensation is defined as the inverse of the time required for the system to reach the gel point \((1/t_{gel\ time})\). The influence of pH on condensation is perhaps the most dominate variable in determining the characteristics of the final material and the general trends are described in Figure 1.5.
Figure 1.5: The pH dependence of gel time for silica sol-gel materials. Below pH 2 (the isoelectric point of silica) gel time is directly proportional to the increase in pH. Between pH 2 and 6, the gel times are inversely proportional to the pH. Above pH 6, the gel time rapidly increase with pH in systems with no additional salt, eventually reaching stability as particles before true gels form. The addition of salt to basic sols decreases the gel time in proportion to their concentration. (Adapted with permission from reference 1, Copyright Elsevier (1990))

Gel formation can be split into three pH regions: acidic pHs below the isoelectric point of silica; acidic pHs above the isoelectric point of silica; and basic pHs. Very low pHs were not utilized in this study, so they will be described very briefly. At very low pHs (<2), condensation rates are relatively slow and silica has low solubility, resulting in small particle formation (>2 nm). The particles then undergo aggregation, which is aided by the small total charge on the silica particles, especially between pH 0 and 2.

Although the pH environment greatly influences how polymerization and particle growth proceeds, above the isoelectric point, condensation occurs through a single base-catalyzed mechanism whether the pH is acidic, basic or natural.\(^1\)
Figure 1.6: The base-catalyzed mechanism for condensation. Base catalysis occurs for all condensation reactions above the isoelectric point of silica (~ pH 2). (Adapted with permission from reference 1, Copyright Elsevier (1990))

In the mechanism, hydroxyl ions deprotonate one of the hydroxyl groups on either a silica monomer or larger silica precursor. The deprotonated ligand then reacts with a neutral silane, likely through a hexacoordinated intermediate, to form a new Si-O-Si link and expel a OH⁻ or OR⁻ during the rate determining step. The decrease in condensation rate between pHs 2 and 7 shown in Figure 1.5 supports a base-catalyzed mechanism for polymerization in the acidic ranges above the isoelectric point. A side effect of the first step of the condensation mechanism being the fast deprotonation of hydroxyl groups is that deprotonation is most highly favored on ligands that are already attached to condensed silica. This is due to the SiO ligand having more electron withdrawing character compared to OH or OR ligands. As a result, the most acidic structures are the large silica fragments and the least acidic are the precursor monomer and the reaction between the two is highly favorable. This trend is not the complete exclusion of other combinations, particularly under acidic conditions where deprotonation is incomplete, but will have significant consequences on the overall polymerization of silica materials.
Despite having a consistent mechanism over the pH range of 2 to 12, Figure 5 shows there is a clear boundary between the condensation above and below a neutral pH and that the boundary is reflected in the properties of the final material. The trend of increased condensation rate that is seen in the acidic region proceeds logically from the corresponding increase in hydroxide concentration. Extending this argument would suggest that further increasing the hydroxide concentration into basic pHs should decrease gel times even more, but that is not what is observed. Instead, gel times increase sharply and the type of gel produced shifts from being polymeric to being particulate. In the absence of added salt, the particles can continue to grow to as large as 2 µm and will remain stable. So in the absence of mechanistic differences, the dramatic change in material structure that occurs at pH 7 must be somehow accounted for, and this answer can be found by exploring several particle kinetic growth models.

The two classes of growth models that will be presented, monomer-to-cluster and cluster-to-cluster growth, are extremes and experimental silica systems can and do undergo both types of growth, especially those in the intermediate pH range (4-7). I will begin by describing each as theoretical models, and then explore specific relevant experimental examples. The first class, monomer-to-cluster, occurs under neutral and basic conditions. The requirements for this model are that an unending supply of monomers must be available and that condensation reactions do not always occur when monomer interacts with reaction site on the cluster (known as Reaction-limited monomer-cluster growth (RLMCA)). The first requirement is met by the fact that silica readily dissolves in this range, continuously resupplying regenerated monomers. The second requirement is met both by silica’s tendency to dissolve from less energetically favorable sites on the structure and by the slow reaction kinetics. The slow kinetics are important because they result in the whole cluster being effectively available for condensation, rather than just the outer
shell where growth would occur if the monomer reacted with the first available site on the cluster that it came into contact with. Silica growth through the monomer-to-cluster pathway was successfully modeled using the Eden model, with additional modifications known as the ‘poisoned’ Eden model for neutral pHs. The Eden model was first used to describe the growth of cell colonies and according to this model; all of the positions on the silicons in the cluster are available for growth. Growth begins by filling in a random place on a lattice, after which all of the nearest neighbors become available for the next step in formation. Growth then occurs at one of these newly activated locations and their nearest neighbors are added to those from the previous step (Fig. 1.7).

Figure 1.7: Simplified schematic of growth by the Eden and the ‘Poisoned’ Eden Model. In the Eden Model, each of the nearest neighbors of an added point becomes available for further addition in the next growth step. In the ‘Poisoned’ Eden Model, only selected nearest neighbors will be available for growth and others will remain forbidden.

The cycle continues, and while the possible number of sites for growth increases, all of the nearest neighbors retain their ability to be filled no matter how large the cluster gets.
This model is appropriate for basic conditions, as almost all of the silica will be deprotonated at higher pHs.\textsuperscript{1} Monomers will be continuously regenerated from the large silica clusters, leaving less stable positions. As discussed before, it is favorable for the condensation reactions to occur between the more acidic superstructures and the monomers, resulting in limited additional nucleation occurring with the newly made monomers. This process shares many elements with traditional Ostwald ripening, although there are some notable differences. Although traditional ripening certainly does occur, the influence of curvature on the solubility of silica becomes negligible for particles larger than 5 nm.\textsuperscript{1} Instead, growth occurs by the aggregation of small particles (~ 10 nm), where the reduction in surface area aids in overall stability.\textsuperscript{16} For the distinctive large silica particles (45 nm+) typically seen at basic conditions, a two-phase process of ripening would be the most accurate, where initial small particles are formed and then, in turn, become ‘monomers’ that aggregate and form larger smooth particles.

Under more neutral conditions, the hydroxyl ligand on the silica clusters are only partially deprotonated and growth is therefore better described by the ‘poison’ Eden model (Fig. 1.7).\textsuperscript{19} In this model, there are blocked or ‘poisoned’ sites within the cluster that cannot be reacted. As the cluster grows, these sites will remain within the structure and steric hindrance can make it even more difficult for them to undergo hydrolysis, thereby forcing them to remain poisoned to future condensation. This should result in the final gel having an increased fractal character.

Under extreme acidic conditions, the growth class that best describes it is cluster-cluster growth.\textsuperscript{1, 20} The requirements for this model are a limitation in the amount of monomers available and the favorability of the reaction between very large and small particles being minimized. At very low pHs, these requirements are met because most of the precursors
hydrolyze almost completely. The precursors then condense to form dimers and other short chains. Once all of the monomers are gone, the dimers (the least acidic) will want to react with the more highly condensed middle chains (the most acidic), increasing factual branching.²⁰

![Monomer-to-Cluster Growth (Eden Model)](A)

![Cluster-to-Cluster Growth](B)

**Figure 1.8:** Typical clusters grown from the monomer-to-cluster (Eden) and cluster-to-cluster growth models. The monomer-to-cluster system produces dense, highly branch clusters and the cluster-to cluster model produces weakly branched fractal clusters. (Adapted with permission from reference 9, Copyright Elsevier (1988))

Also, under acidic conditions, silica resists being dissolved, and thus formation of the branched structures are effectively irreversible.¹ Typical clusters that result from cluster-to-cluster and monomer-to-cluster growth are illustrated in Figure 1.8.

These models fit growth under the extremes of pH very well, but most sols are made under more mild conditions. The processes in these models can be combined to describe mildly acidic conditions as well and basic conditions in the presence of salts.²¹ Because the condensation that occurs between pH 3 and 6 is base catalyzed, increasing the acidity of the solution suppresses the ability of the silica to dissolve and regenerate monomers once it has formed. That means that mildly acidic solutions (pH 4-6) will tend towards the neutral poisoned Eden model in the early stages.¹ Eventually, however, the suppressed regeneration of monomers leads their to concentration becoming heavily depleted, and growth occurs predominately between clusters. Under stronger acidic conditions (pH<4), however, silica solubility is
suppressed to the point that the condensation reactions can be considered irreversible, resulting in weakly branched, polymeric materials that grow almost entirely by the cluster-cluster model.\textsuperscript{1}

As seen in Figure 1.5, the addition of salt to a basic solution can have a dramatic effect on the condensation rate. The silica clusters formed in base are largely deprotonated, giving them an overall negative charge. This results in mutual repulsion between the particles, allowing the particles to grow without aggregation. The addition of salt, however, decreases the distance of the double layer and allows the larger particles to aggregate and fuse together.\textsuperscript{21} As a result, the particles will act as clusters in the cluster-to-cluster model, forming branched ‘polymers’ or large silica spheres.

1.2.2 Gel formation

As the sol particles grow larger and form extended cluster networks, the viscosity of the solution will begin to increase rapidly until a single, solution spanning network is formed.\textsuperscript{1, 13} The completion of this solid network is considered to be the system’s gel point. At this point, the system is no longer a colloid of solid particles in a solution, but two mutually continuous solid and liquid phases (Fig. 1.9).

\textbf{Figure 1.9:} Gel formation occurs at the moment that the final linkage in the single, solution spanning network occurs.
In simple terms, the gel can be considered to be formed when the system can no longer be poured and an inserted probe tears rather than flows through the system.\(^1\) The change from sol to gel can be very abrupt, with systems that appear to shift from ‘liquids’ to ‘solids’ in seconds, or it can occur very slowly, happening over the course of even months, with the system gradually increasing viscosity until the gel point it reached.\(^2\) The inverse relationship between the gel time and the condensation rate indicates that the same variables used to control condensation can be used to increase or decrease gel time.

The shift from sol to gel generally proceeds as the larger sol particles begin to connect with one another, either by the long polymeric branches tangling together or clusters and particles colliding.\(^1\) Bonds can form between them, creating even larger structures. As the clusters size increases, viscosity also increases as liquid becomes trapped in the clusters, decreasing the amount available for flow.\(^2\) As more and more clusters aggregate and become entangled, the overall structure of the gel takes form and eventually the gel will set. Despite taking on some properties of a solid as a gel, molecular transport through the gel changes little. For example, Gits-Leon did diffusion studies of NaCl transport through silica gels and determined that the decrease in the diffusion rate was not significant.\(^3\) Molecular transport can be affected by charge interactions between the negatively charged silica and an diffusing species, but in these case molecular movement is not limited by the actual formation of the gel.\(^4\) The continued passage of compounds through the gel allows for further strengthening of the network through aging and, as will be explained in detail in section 3.2, allows for silica gels to find applications in electrochemical studies.
1.2.3 Aging

Because gels are solid networks amongst continuous liquid networks and diffusion through the system is not significantly impeded, the formation of a gel does not affect the process of hydrolysis and condensation adding to and changing the newly formed structure. This phenomenon, known as aging, is defined as the changes and restructuring that the material undergoes after reaching the gel point. The effects of aging can be quite dramatic, such as in the case of silica gels that can lose up to 25 percent of their volume without noticeable liquid evaporation. More subtly, the aging process greatly influences the strength and pore size of the final material by adding strength to newly formed networks. The main classes of transformations that the gels undergo are polymerization, syneresis, and ripening.

The level of connectively found at the gel point is the minimum required to create the single, solution spanning network. In the polymerization process, additional links are formed between the silicons in network. The more interconnected the structure is, the more stiff and stronger it will be. In some cases, extensive polymerization can result in the process known as syneresis, which is responsible for the dramatic shrinking sometimes found in sol-gel materials. In syneresis, the further condensation reactions result in the pores shrinking, pushing out liquid as a result. These condensation reactions can either be between groups close together in a pore, resulting in a small amount of shrinkage or between large polymeric chains, resulting in larger amounts of shrinkage (Fig. 1.10).
Figure 1.10: Typical reactions in a gel that result in syneresis. (A) Hydroxyls in close proximity on the surface of a pore can undergo condensation, bringing the walls of the pore closer together. (B) As long polymeric chains flow close to each other, bonds can form between them, restricting their further movement in the gel. (Adapted with permission from reference 1, Copyright Elsevier (1990))

As illustrated in the second example, if the chains in the gel are flexible, they can come into close contact with each other, which sometime results in condensation occurring between them.

The gel will lose some of its flexibility after this bond forms and less liquid is able to exist between them. Syneresis does not always require polymerization to occur, such as in basic systems were particles reversibly aggregate based on the electrolyte concentration.

Ripening as a concept was already been addressed in the discussion of condensation and cluster growth models, but it is also an important concept for aging. Despite the dramatic changes in physical characteristics that take place during gelation, the basic chemistry of the system remains the same. So, while polymerization continues to occur, so does
depolymerization under conditions that are not too acidic. This means that silica will continue to
dissolve from locations that are less energetically favorable and recondense on other areas of the
structure.\textsuperscript{28} Areas where solubility is generally more favorable in the silica systems are at
locations of high positive curvature and are least favorable at negative curvature.\textsuperscript{1} Over time,
very small particles will completely dissolve and larger particle aggregates will undergo growth
at the connection points between particles (Fig. 1.11).

\textbf{Figure 1.11}: During aging, Ostwald ripening strengthens the walls of the network by adding
support the weak connections between fused silica particles. Very small particles dissolve,
creating additional monomers for growth. Silica on convex surfaces can also dissolve and
transfer to concave areas of curvature, where the solubility is the lowest.

Ripening results in the overall structure being strengthened, because the weak connection points
between particles receive additional support.

1.2.4 Drying

The transition from a gel to the final solid material occurs as the gel dries, and the drying
process can have a dramatic effect on the porosity and structure of the final material. The
common effects of drying are shrinkage, decreases in porosity and, in some cases, cracking or
warping in the final material. They largely come about due to the development of capillary forces
in the system.\textsuperscript{1} Dried sol-gel materials can be split into two main classes, aerogels and xerogels.
If drying occurs under supercritical conditions, an aerogel is formed.\textsuperscript{29} Supercritical drying
prevents the development of capillary forces by heating the system past the critical point before the liquid is removed. Therefore, the liquid/vapor interface never attempts to enter the silica network and the surface tension that would otherwise accompany the interface is not present and pore collapse is minimal. The resulting material is extremely light and can have pore volumes of up to 98%. Conversely, drying under standard condition results in a xerogel, a dense material that has porosity that is a partially a function of the amount of pore collapse experienced during drying. 

Drying under standard conditions occurs in several steps (Fig 1.12). First, the gel will shrink in proportion to the amount of evaporated liquid, resulting in all evaporation occurring at the surface of the solid/liquid structure. In this stage, the gel is relatively weak and the capillary force that wants to push the evaporating liquid to the surface is enough to pull the pore walls together. This results in the volume of silica shrinkage being equal to that of the liquid evaporating.
As liquid begins to evaporate from the system, liquid from the interior of the gel will flow to cover the surface and menisci will form along the outer most pores. The menisci have a negative...
The amount of force is a function of the curvature of the meniscus, which is related to pore size. The effect of capillary pressure on sol-gel derived systems is dramatic because of their unusually small pores. In traditional ceramics, the average pore size is in the micrometer range, but is in the nanometer range for sol-gel materials, leading to pressures of up to 100 MPa being placed on the gel.\(^1\)

As the pore sizes shrink, more silica surfaces come into contact and form bonds. This results in the network gaining strength as it shrinks.\(^1\) Eventually, the gel will have gained enough strength that the capillary forces are not enough to compress it any further. Here, the menisci will enter the pores of the silica itself and the drying is considered to have reach the critical point.\(^{30}\) The drying of the interior system is not consistent, however, because the porosity throughout the film is not uniform.\(^1\) As a result, drying occurs at different rates in the gel, which can lead to warping in the material or cracking, as the material fractures under the added stress of uneven contraction and relaxation that occurs in the wet and dry areas of the material, respectfully.

The initial conditions used to form the gel and degree of aging it undergoes is an important factor in the drying of a gel, as the strength it develops allows it to resist pore collapse.\(^{28}\) The weakly branched polymeric strains of acidic conditions result in both weaker initial gel structures compared to their more basic counterparts, as well as smaller initial pores (Fig. 1.12). This combination results in these gels being very dense, as they are highly susceptible to the strong capillary forces.\(^1\) Gels formed under basic conditions, however, are more resistant to compression because of their higher degree of branching and denser clusters. The ripening effect seen in aging similarly increases a gel’s ability to withstand capillary forces by filling in weak points in the network.\(^{28}\) High porosity, however, is not the goal for every
material and techniques such as spin coating can be used as a drying method to force the steps of the sol-gel process to proceed very quickly, resulting in very dense thin films.

In spin coating, the sol is placed on a substrate before it begins to gel. As rotation begins, the solvent (i.e., ethanol) evaporates very quickly, resulting in a sharp increase in the water and sol concentration at the interface (Fig 1.13).\textsuperscript{32, 33}

![Figure 1.13](image)

**Figure 1.13:** Casting of silica films on a substrate through spin coating. A drop of hydrolyzed is spun at very fast speeds, resulting in excess material being flung off the substrate and the sol solvents being evaporated at an accelerated rate. The extremely dense silica film produced undergoes a truncated version of the sol-gel process, where the system proceeds from gelation to drying with virtually no aging.\textsuperscript{32}

The sol particles undergo rapid condensation and as spinning continues; the remaining water will evaporate off the gel. This process can occur in seconds, resulting in almost no time for further aging after the gel forms as well as the evaporation of the liquid in the system happening very quickly. This results in the gel structure being very weak and thus leads to pore collapse and the formation of very dense films.\textsuperscript{34} The loss of porosity of the thin films can be dramatic, with pore sizes of less than 0.4 nm and surface areas equal to the geometric areas being reported for some systems.\textsuperscript{32} For reference, silica monoliths can have pore sizes ranging from 3.8 nm to 40 nm, depending on the experimental conditions.\textsuperscript{24} This loss in pore size can inhibit diffusion through the film, which is necessary for electrochemical applications.\textsuperscript{35} Methods for controlling pore size will be discussed in section 1.3.
When coupling sol-gel techniques with electrochemistry, both the porosity of the silica material and as well as its net negative charge will play a role. For example, the incorporation of a positively charged precursor in monolith can inhibit the diffusion of negatively charged redox probes compared to a monolith made only from TMOS. The electrostatic interaction between the positive probe and the negative silica pores resulted restricted diffusion within the pore. In thin films, the influence of charge appears to be the opposite. When comparing the entrapment of the positive and negative redox probes such as potassium ferricyanide (Fe(CN)$_6^{3-}$) and ruthenium(III) hexaammine (Ru(NH$_3$)$_6^{3+}$) encapsulated in acid catalyzed thin films, it was seen that the cationic probes suffered more leaching out of the film into solution over time. It was postulated that anionic movement was limited by the charge interaction between the probe and the silica resulting in movement through the film being a high energy process. In the same study, it was also determined that the decreased pore size of the silica thin films prevents a substantial portion of the entrapped redox probes from being electroactive, with some probes showing electroactive fractions as low as 3-9%. This is most likely linked to the pore collapse typical in thin films, preventing easy movement within the films. As will be described in more detail in chapter 4, the small pore sizes also inhibit the movement of an analyte from the solution through a thin film in similar ways, necessitating the development of methods to increase silica thin film porosity.

1.2.5 Conclusion

The previous discussion gives an overview of sol-gel material chemistry. In chapter 3 and 4, the chemical trends and unique properties of silica were manipulated to create dense, thin films from intermediately acidic sols. The challenges associated with cracking and material defects arising from the drying process was addressed for films fabricated in chapter 3. Finally,
silica nanostructures were created from basic sols, and showed novel growth patterns by utilizing the basic sol’s preference for monomer-cluster growth in chapter 5.

1.3 Templating

The second material science technique that was instrumental to the creation of the silica materials developed in this work was templating. A template in material science is a structure-directing agent that generally serves as a placeholder during the formation of the desired primary material.\textsuperscript{5, 36-39} Templates are commonly used to introduce additional porosity into a material in a controlled and reproducible manner. The size of the added pores are dependent on the size of the template and in the case of a “true” template, the pores will have its exact inverse dimensions.\textsuperscript{36} Several desirable characteristics in a template/material system include: the templates can be easily removed by a method that is both mild and that the primary material is completely resistant and the primary material has the mechanical stability to prevent pore deformation or destruction after template removal.\textsuperscript{36} These characteristic are found in many silica sol-gel/template systems. Silica is inert with respect to organic solvents, allowing for their use in the removal of organic templates under mild conditions.\textsuperscript{40} In comparison, silica nanoparticles or porous silica structures can be used as templates for organic polymers, but require HF or strong bases to completely dissolve.\textsuperscript{41} The inorganic nature of the silica structures also gives it additional mechanical stability. As described in section 1.2.4, as a xerogel undergoes shrinkage, it will continue to polymerize and eventually will reach a critical point, after which the network has gained enough strength to combat compression. At this point, the material’s shape becomes set, and if the template is then removed, it will normally keep its shape with minimal effect on the xerogel. Most organic polymers, however, will undergo complete
pore collapse due to the plastic deformation of the pore walls and thus only the most highly crossed-linked polymers easily benefit from template integration.\textsuperscript{36}

The advantages gained through templating include: marked increases in available surface area, improved diffusion through a material, spatially ordered chemical character, and controllable nanoscale material morphology.\textsuperscript{42} The ability to impart additional porosity to traditionally non-porous materials, such as metals and dense thin films, can open up these materials to additional types of applications or can greatly improve their existing function. Applications that have found benefit from templated materials include catalysis, separations, coatings, electrodes and chemical sensing.\textsuperscript{36, 39} The produced porous structures are classified by size, where microporous material have pore sizes of less than 2 nm, mesoporous materials have pore sizes between 2 and 50 nm and macroporous materials have pore sizes larger than 50 nm.\textsuperscript{5} A summary of the classes of pores and examples of templates that produce pores in each range is given in Table 1.

### Table 3.1: Common templates classified by pore size

<table>
<thead>
<tr>
<th>Pores by size</th>
<th>Example templates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microporous, &lt;2 nm</td>
<td>Zeolites\textsuperscript{43}, covalently bonded organic templates\textsuperscript{44}, metal alloying\textsuperscript{45}</td>
</tr>
<tr>
<td>Mesoporous, 2-50 nm</td>
<td>Surfactants\textsuperscript{35}, block copolymers\textsuperscript{39}, periodic mesoporous silica\textsuperscript{36}, anodized aluminum oxide membranes\textsuperscript{46}, biological materials (ex. tobacco mosaic virus)\textsuperscript{39}</td>
</tr>
<tr>
<td>Macroporous, &gt;50 nm</td>
<td>Polymer or silica nanoparticles\textsuperscript{41}, colloidal crystals\textsuperscript{36}, carbon nanotubes, track-etched membranes\textsuperscript{47}, biological materials (bacteria, yeast, DNA, wood tissue)\textsuperscript{39}</td>
</tr>
</tbody>
</table>

Silica materials, which are the focus of this dissertation, generally do not require the use of templates to introduce microporosity, as it is an intrinsic property of most sol-gel derived materials.\textsuperscript{48} Briefly, however, the microporous nature of silica can be enhanced by using
organoalkoxysilanes as covalently bonded organic templates. The unhydrolyzed organic ligands remain embedded within the silica network and, after removal by heat treatment, leave behind pores on order of less than 10 Å, the size of the molecule. The addition of mesopores and macropores into the system, on the other hand, have received a great deal of attention from the sol-gel community and will be discussed at length.

The scope of templating is vast, both in the potential entities that can be used as templates and the potential materials that can be templated, which has led to the wide range of applications found in the literature. The range of applications and the speed at which the templating method has grown over the last few decades, however, has led to inconsistencies in the definition of common terms in the literature. For example, the distinction between “hard” and “soft” templates has been used both to describe the way templates direct the growth of the primary material (as physical scaffolding vs molecular self-assembly) or to describe the type of material found in the secondary template (organic vs inorganic), resulting in some templates that would be considered hard by one definition and soft by another. Therefore, the discussion of each templating method will begin with a basic definition for the purposes of this dissertation, followed by a detailed explanation and pertinent examples. The major classes of templates that will be explored are soft and hard templates, with additional detail given to endo- and exo- hard templates. Molecular imprinting and encapsulation will also be described briefly.

1.3.1 Soft Templates

Soft templating methods involve the use of molecules that will self-assemble within the primary material and are largely used for the formation of mesoporous materials. This is commonly accomplished through micelle formation from surfactants, although phase separation in block copolymers has also been established in the literature as an alternate method.
1.14 shows a simplified schematic of the formation of mesoporous silica through surfactant micelles.

**Figure 1.14:** Simplified method for the formation of mesoporous materials from surfactants. Upon mixing, the surfactants will form micelles within the precursor solution, and if the concentration of the surfactant is sufficient, the micelles will self-order. Polymerization then occurs around the micelle, leaving a porous structure after they have been removed. (Adapted with permission from reference 37. Copyright 1996 American Chemical Society)

The structure of the formed micelle is concentration dependent, allowing for a variety of shapes to be formed. At low concentrations just above the critical micelle concentration, surfactants form a traditional spherical micelle. Moderate increases in concentration then lead to cylindrical structures that can form close packed arrangements (Fig. 1.14). Further increases in concentration lead to cubic liquid-crystals, where the pores interconnect, and finally, a stacked lamellar structure. The exact size of the mesopores can be correlated to the length of the tail of the surfactant. For example, it was determined that increasing the length of an imidazolium based surfactant could result in an increase in pores size from 2.6 nm to 5.6 nm in a silica gel. Mesopores structures have found applications as molecule sieves (close-packed cylinders) and in silica thin film modified electrodes, where the interconnected pore system created by the CTAB cubic liquid crystal has been shown to improve current responses by up to 100 times.

1.3.2 **Hard Templating**

In contrast to soft templating, hard templating begins with a preexisting solid material with a defined size and shape. The hard template serves as a scaffold for the formation of the
primary material. After the formation of the primary material is complete, the hard template is removed, leaving behind a structure that is the inverse of the original template. One of the greatest strengths of the hard templating method is the wide range of potential templates available.\textsuperscript{36, 39} While common templates include silica nanoparticles, colloidal crystals, and AAO membranes, almost any material that can be submerged into or filled with the primary material, and then subsequently removed, can be used as a hard template.\textsuperscript{37, 47} Therefore, unlike soft templates, hard templates cover all three pore size ranges, from the microporous zeolites to extremely large biological templates, like wood tissues.\textsuperscript{37, 39}

1.3.2.1 Endotemplating:

Endotemplating is a hard templating method in which the primary material forms around the template, such that the templates become encased inside the forming material.\textsuperscript{36} Figure 1.15 shows a typical endotemplating procedure.

Figure 1.15: Simplified schematic of the hard template method termed endotemplating. Templates are ordered and the spaces between them are filled with monomers. Polymerization then leads to material formation around the template and pores with inverse dimensions remain after the templates are removed. (Adapted with permission from reference 36. Copyright 2008 American Chemical Society)
As illustrated, the endotemplates will be organized in some manner and the primary material will infiltrate around them. After the space between the templates has been filled, the individual components of the primary material will form into a solid through means such as polymerization or electrodeposition. At this point, the templates are removed, and a structure with pores that are the inverse of the templates is left. The template organization step often comes before monomer infiltration, such as in the case of infiltration of a sol through a colloidal crystal to make macroporous monoliths, but it is not necessary. In the case of some sol-gel spin coating and dip coating methods, the template is doped into the sol prior to casting. The sol/template mixture can then be cast onto the substrate, where organization occurs (Fig. 1.16).

Figure 1.16: Simplified method for template integration into a silica thin film system through spin coating. The templates are added to the sol solution and then cast onto the substrate. Conditions between the template, the substrate and the solution will determine the ordering arrangement undergone by the template.

One of the most commonly used methods for templating, endotemplating allows for a large degree of variation in the method. The types of materials that can be used as endotemplates range from spherical nanoparticles, to nanotubes, to biological materials like yeast and bacteria. The primary material can also form around these templates in several ways. Monomers or sols can be infiltrated through filtration or casting in the template system, where they then undergo polymerization. Inverse opals are commonly produced through this method, and the introduced porosity gives them unique optical properties such as a photonic band gap. Metals can be electrodeposited around endotemplates that have been formed on the surface of an electrode. This procedure will lead to increases in the electrode surface area, potentially increasing sensitivity and enhancements in the surface roughness. Endotemplates that remain in solution
can also be used as scaffolds for the formation of hollow capsules. In this method, silica or polymer spherical nanoparticles are suspended in solution and the primary material forms around them through layer-by-layer self-assembly.

1.3.2.2 Exotemplating:

In exotemplating, host/guest polymerization or formation is used, such that the primary material forms inside the pores of the selected template (Fig. 1.17).

**Figure 1.17**: Simplified schematic of the hard template method exotemplating. Monomers fill the pores of the exotemplate and polymerization then leads to material formation. Upon removal of the template, individual structures with the inverse dimensions of the template pores remain. (Adapted with permission from reference 36. Copyright 2008 American Chemical Society)

Common exotemplates include zeolites, mesoporous silica, aluminum oxide membranes, and polymer track-etched membranes. In all of these cases, the primary material is formed inside the pores of the template, and upon removal produce porosity that is the inverse of the template. In some cases, this leads to large periodic structures, such as the formation of an inverse mesoporous polymer made from MMA and EDMA within a mesoporous silica template. Often, however, exotemplates are used to obtain nanostructures such as nanotubes, wire, fibers
and spheres. Exotemplates can produce a wide variety of sizes of nanostructures, depending on the template chosen. For example, zeolites, which are microporous, can produce so called “molecular wires”, which are isolated polymer strands; the mesoporous aluminum oxide membranes have been shown to make metal and silica nanotubes with diameters between 15 and 100. Finally, track-etched membranes, with macropores between 100 and 1000 µm, make excellent templates for metal nanotube electrodeposition.

1.3.3 Other templating methods: molecular imprinting/encapsulation

During the templating process, it is possible to not only organize the primary material around the template physically, but it can also be organized chemically. One of the earliest developed forms of templating, molecular imprinting, is the process by which the chemical functionality and its arrangement in a material is influenced by the chemical character of the template and in turn allows for enhanced analyte selectivity (Fig. 1.18). Imprinting occurs by influencing the size and shape of the pore, and by providing it specific chemical functionality, either by leaving behind a bonded group or by influencing the properties of the primary material during formation.

The imprinting process mimics molecular recognition in biology and a main goal in templating research is to one day reach the efficiency and variety found in nature. Early work

Figure 1.18: Simplified schematic of the molecular imprinting template method. (Adapted from reference 55 with kind permission from Springer Science and Business Media.)
was done on methyl orange dye molecules, where a silica gel was formed around the dye and then the dye was removed. When the gel was reintroduced to a solution of methyl orange, the template pores showed a higher affinity for reabsorption of the newly introduced dyes relative to a control. Since then, molecular imprinting has grown to include a variety of applications such as templated monolayer SAM films. For example, hexadecane was used as a template in OTMOS SAM films, which were found to selectively detect vitamin K\textsubscript{1} over vitamins K\textsubscript{2} or E through binding between the produced pore and K\textsubscript{1}’s isoprenoid tail. Other examples of imprinting include metal ion and molecular recognition, imprinted silica gels for chromatographic column packing and chemical sensors.

Encapsulation, while not strictly a templating technique, shares many similarities with templating and thus its role in silica materials will be discussed here. In encapsulation, the integrated foreign material is intended to remain within the silica matrix. For example, silica films can become electrically conductive by adding carbon powder, metal nanoparticles, or redox probes, such as ferrocene derivatives, to the sol before film formation. Encapsulated compounds can be integrated into the film either through chemical bonding directly to the silica backbone, such as in the case of gold nanoparticles attached to thiol functionalized silicon atoms, or by simply being surrounded by the silica network. The latter is common for redox probes, which can experience leaching if the encapsulated compound is small enough to diffuse out of the matrix to any great degree.

Another class of molecules for encapsulation that have received a great amount of attention in the past few decades is biomolecules. Biomolecules such as enzymes are large enough that they cannot diffuse out of the film once entrapped; however, the much smaller molecules required for their function can diffuse from solution into the film. Because the
enzymes are introduced to the system before the gelation, the silica network creates large pores around the entire structure. These pores can be large enough for the enzyme to conduct its normal biological functions, which can then be measured by analytical means. This discovery had led to a variety of biological sensors based on sol-gel methods.

While neither molecular imprinting nor encapsulation were used in the following work, their discussion was deemed important as they represent possible future developments that the materials described herein could follow. Each process described in this dissertation allows for easy integration of addition templates or encapsulated compounds, an advantage of their flexible procedures.
Chapter 2: Instrumentation

2.1 Introduction

In this chapter, the major analytical techniques used in this work are reviewed. Electrochemistry, which along with sol-gel science forms the foundation of the presented research, will get particular attention. In addition, the major techniques for sample characterization are reviewed. The imaging techniques atomic force microscopy and scanning electron microscopy will be described, followed by ultraviolet/visible molecular absorption spectroscopy.

2.2 Electrochemistry

Electrochemical theory and applications are either the end goal or a major element in all aspects of the work presented in this dissertation. In chapters 4 and 5, sol-gel science and templating methods were used to design or improve novel electrodes. In chapter 4, the effects of the devised electrode design on fundamental electrochemical processes were also studied. In chapter 6, the directional diffusion produced by track-etched membrane electrodes was found to be instrumental in the production of unique sol-gel derived silica nanotubes and nanopillars. Therefore, electrochemistry will be discussed in some depth, with a focus placed on fundamental processes, the specific techniques of cyclic voltammetry, amperometry, and electroplating, important properties of ultramicroelectrode arrays, and the electro-assisted production of silica.

2.2.1 Electrochemistry Fundamentals

The primary focus of electrochemistry is the study of charge transfer at chemical interfaces, most commonly between an ion rich liquid, known as an electrolyte, and a solid metal, called an electrode. Many reduction or oxidation processes at an electrode can be simplified to three basic steps. First, the analyte species must travel from the bulk solution to
the electrode through some form of mass transport. Once the species reaches the electrode, it either gives up (oxidation) or receives (reduction) a stoichiometric number of electrons from the electrode. The newly produced species then diffuses away from the electrode, making room for new molecules to approach. This process can be complicated in several ways, either through the addition of an absorption or desorption step, where the species becomes temporally or permanently attached to the electrode surface; a crystallization step, where a deposited species becomes part of the electrode structure; or a competing reaction step, where the species reacts with another compound in solution.  

As stated, the reaction results in a stoichiometric exchange in electrons between the electrode and the redox species. Current produced in the cell due to this process is considered to be faradaic, because charge transfer, or the amount of electricity passed through the cell, is proportional to the number of chemical reactions occurring in the system, as outlined by Faraday’s law. The reactions in a cell can be either spontaneous (galvanic) or non-spontaneous (electrolytic), but the chemical systems studied in this work were electrolytic. Because of the complexity of the electrochemical cell system, electrical responses that result from sources other than chemical redox reactions must be considered. Processes that lead to these additional responses are collectively referred to as non-faradaic, because they are not in accordance with Faraday’s law. The interface of the electrode is complex and the application of potential results in the interface restructuring, even in the absence of a redox species. Figure 2.1 gives a simplified schematic of the electrode interface. The applied potential results in a buildup of charge along the electrode surface with an equal but opposite buildup of charge from the solution. This charge system acts as a capacitor and accounts for much of the non-faradaic current seen in experiments, as current will flow until the ‘capacitor’ is charged.
**Figure 2.1:** Simplified schematic of the electrode interface. Charge accumulates at both the solid and liquid interface, creating a capacitive double layer. The electrode surface and the bulk solution are also separated by a gradient of ions called the diffuse layer. (Adapted from reference 63 with kind permission from Springer Science and Business Media.)

The two main transport processes, mass transfer and charge transfer, will next be discussed. First, in order for the continued generation of current to occur in a cell, the redox species must be able to travel from the bulk solution to the electrode. Mass transfer can occur by three processes within the electrode cell: diffusion, migration and convection.\(^{63}\) Diffusion occurs in the cell system because redox species depletion takes place at the electrode following oxidation or reduction, leading to a concentration gradient at the interface. The gradient occurs in both directions, resulting in one form of the redox species moving towards the electrode and the other moving towards the bulk. The movement of ions in a solution due to the application of an electric field leads to migration while convection is the result of a mechanical force, such as stirring. Generally, diffusion is the desired form of mass transport for electrochemical studies and thus migration and convection effects are often minimized. Migration is minimized by including large concentrations of an inert, supporting electrolyte in solution. Convection is prevented by ensuring that the cell is not stirred and is free from outside vibrations. It is not necessary, however, to limit mass transfer to diffusion and convection will be used in the
amperometric studies in chapter 6 of this work for reasons not related to the system’s electrochemistry.

Mass transfer considerations are of particular importance for silica thin film modified electrodes such as those designed in chapters 4 and 5 of this work, as the negatively charged, insulating silica thin films can interfere with the mass transfer of some species, influencing the electrochemical response.24 Specifically, in chapter 5 it will be shown that, while the mass transport of neutral species were unaffected by the unmodified, macroporous silica thin films, negatively charged species were repealed from the film, preventing the expected charge transfer at the electrode. Film modification, however, will be shown to improve the transport of the negative species and thus the electrochemical response.

Once the redox specie reaches the electrode, it can then undergo a electron transfer reaction. In an electrolytic cell such as those used in this work, non-spontaneous reactions are driven through the application of a potential. Reduction occurs when the electrode potential is made more negative than a reaction’s standard electrode potential (E°), increasing the energy of the electrons in the metal.62 If the energy of the electrode electrons is raised sufficiently, then the electrons will be able to transfer from the electrode to an unoccupied orbital position on the analyte in the electrolyte solution. Oxidation occurs by lowering the energy of the electrode electrons by applying more positive potentials, resulting in the flow of electrons from the solution to the electrode as it becomes more energetically favorable. This process is illustrated in Figure 2.2.62
To make electrochemical studies both accurate and reproducible, it is necessary to have reliable current and potential measurements. Potential, in particular, can be challenging to monitor and control because practical limitations require potentials to be measured as differences, where the experimental potential value is measured with respect to an electrode with a known, constant value. In an electrochemical cell, the electrode where the experimental processes occur is called the working electrode and the electrode that its potential is measured against is called the reference electrode. Ideally, the reference electrode will remain unaffected.
by changes in the experimental conditions and thus the experiment can be carried out with only two electrodes, but in practice this is often not the case. The ability of a reference electrode to hold a constant potential can be compromised by the flow of more than a small amount of current. To avoid this, a third electrode, call the counter or auxiliary electrode, can be added. In a three electrode system, the potential of the working electrode is measured with respect to the reference electrode, but the actual current flow occurs between the working and the counter electrode. The three electrode cell system is used in all electrochemical experiments in this work. The working electrode material is varied based on the needs of the experiment. The counter electrodes used are either a platinum wire or a graphite carbon rod. The references used for most experiments were saturated Ag/AgCl fritted electrodes in 3 M KCl, except in chapter 6, where a Ag/AgCl wire was used to avoid silica formation occurring in the reference frit.

2.2.2 Cyclic Voltammetry

Cyclic voltammetry (CV) is a powerful tool for qualitative and quantitative electrochemical studies. CV can be used to determine the identity and concentration of compounds within a solution, to study the mass and charge transfer conditions of a system, and to probe reaction rates and mechanisms. In this work, CV served two primary functions. First, the current response of an analyte at various potentials on the CV curve was used to determine the ideal potential for electrodeposition and amperometric studies. CV was also used to study the mass transfer at an electrode, specifically through PS sphere templated silica thin films.

CV is a voltammetric technique, where the potential of the cell is the independent variable and current is the dependent variable. The current response is studied with respect to a cyclic potential sweep, represented by the potential waveform found in Figure 2.3 A. The initial potential is chosen such that it will not result in a Faradaic redox reaction at the beginning, thus
producing a minimum amount of current (position A: Fig. 2.3 B). The potential is then either increased or decreased to cause the analyte to undergo oxidation or reduction (reduction in figure 2.3 B). This reaction results in the flow of electrons through the cell and an increase in Faradaic current (position B). The current that flows is proportional to the concentration gradient at the electrode surface.\(^6\) The Faradaic current increases rapidly as \(E^0\) is approached because there is a high concentration of the redox species at the electrode interface; the concentration gradient is thus very steep. Eventually, depletion takes place, the concentration gradient extends further into solution, and current drops. The potential is then swept back to its initial point (position D), leading to the same process occurring, but now with the reverse reactions. In an ideal system, sweeping the potential back to its initial value will result in a second similar peak of opposite flow of current as the redox system returns to its original state.

**Figure 2.3:** A typical waveform (A) and cyclic voltammogram (B) for a reversible electrochemical reaction.

The CV presented in Figure 2.3 B represents a reversible reaction. In a reversible reaction, returning the potential to its original value results in the regeneration of the original redox species at the electrode surface.\(^6\) Ideally, this means that the ratio of the peak current at
the oxidation and reduction peak is 1. In addition, the difference between the two peaks, or the peak splitting, is equal to $59/n$ mV and is independent of the scan rate (the change in the voltage per second in the waveform). If the system cannot recover from the initial redox reaction, it is considered to be irreversible and does not show a peak after the switching potential. The electrochemical generation of hydroxide is an example of an irreversible reaction and a typical CV is given in Figure 2.4. CVs can also appear electrochemically quasireversible, where the peak splitting is greater than $59/n$ mV and the peak positions depending on scan rate.

![Figure 2.4: A cyclic voltammogram of the reduction of oxygen into hydroxide. This process is irreversible.](image)

2.2.3 Ultramicroelectrodes

The CV in figure 2.3 is typical for a reversible reaction at conventional planer electrode. The diffusion profile that dominates the mass transfer is assumed to be linear because the size of the electrode is assumed to be sufficiently large that any radial diffusion at the electrode edge is negligible. This assumption, however, does not hold as the area of the electrode surface is decreased. At an electrode radius of below 50 µm, the diffusion profile at the electrode shifts from linear into radial. The change in diffusion profile can be seen in a typical CV done with an ultramicroelectrode. An ultramicroelectrode is an electrode that has micrometer or less...
dimensions at which diffusion at the electrode can reach steady state. An example of a typical ultramicroelectrode CV is found in Figure 2.5.

**Figure 2.5:** A cyclic voltammogram of the reduction of ferrocyanide. This shape is typical for ultramicroelectrodes at slow scan rates.

The characteristic ‘duck’ shaped of the curve has been replaced with a sigmoidal curve. The diffusion at the ultramicroelectrode reaches steady-state rather than falling off because the radial diffusion layer allows for more of the unreacted species to reach the electrode unimpeded, thus preventing depletion experienced by an electrode under planar diffusion (Fig. 2.6 A). This effect, however, is scan rate dependent, and at very fast sweeps, the diffusion will behave in a planar manner.

**Figure 2.6:** Schematic of the diffusion layers at a large planar electrode vs. an ultramicroelectrode (A) and at ultramicroelectrode array whose individual electrodes are far apart vs. close together (B). (Adapted from ref. 64 with permission from Elsevier/)

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Ultramicroelectrodes are attractive because they limit iR drop, allow for the establishment of steady-state current, and can produce increased signal-to-noise ratios, but they have the clear disadvantage of low currents.\textsuperscript{64} To address this, ultramicroelectrode arrays have been created. In such an array, many ultramicroelectrodes are electrically connected, but their surfaces are separated in some manner.\textsuperscript{64} The spacing of the electrodes in the array is important as is scan rate, leading to very different voltammetric peak shapes depending on these values. As the spacing between two ultramicroelectrodes decrease and/or the scan rate decreases, their diffusion profiles will overlap (Fig. 2.6 B). Eventually, if enough arrays have been brought together, their individual radial diffusion profiles will blend to form a single linear profile, resulting in the CV appearing like that observed at a large planar electrode.\textsuperscript{64} Ultramicroelectrode arrays with planar diffusion were developed in chapter 4 and 5 and utilized in chapter 6 in the form of track-etched membrane electrodes.

2.2.4 Amperometry

The second class of electrochemistry techniques used in this work was amperometry. In amperometry, a given potential is applied and kept constant over the course of the experiment and the current is recorded as a function of time.\textsuperscript{62} A typical amperometric curve and waveform are shown in Figure 2.7.
Figure 2.7: Typical amperometric waveform and corresponding $i$-t curve.

2.2.4.1 Electrodeposition

Amperometry provides a means to produce continual reduction or oxidation reactions over a period of time.\(^6\) For example, application of a sufficient reducing potential in a solution of metal ions will result in a phase change, where the reduced metal forms a solid on the surface of the electrode. If amperometry is conducted such that metal ions in solution are constantly being reduced onto the electrode surface, then the process is known as electroplating or electrodeposition.\(^6\) In this work, copper was electrodeposited onto the surface of exposed glassy carbon electrode modified with a macroporous silica thin film. The degree of control over the rate of deposition comes from controlling the amount of current that is produced. This can be achieved by galvanic procedures, where the desired current is held constant and voltage is varied over time, but the instrumentation required was not available at the time the experiments were complete. As an alternative, amperometric techniques can be used with potentials that have been carefully selected. Higher potential values result in faster deposition, so selecting a potential that provides for optimal growth of the nanostructure is important. The CV profile is a useful tool for helping to select the correct potential for electrodeposition. By selecting a potential just past the
point that the current starts to increase on the voltammetric curve, the deposition rate will be lower, allowing for more control over the amount that has been deposited.

2.2.4.2 The electro-assisted deposition of silica

Amperometry has also been shown to allow for the controlled formation of silica at the electrode surface, often in the form of thin films.\(^6^5\) In this process, the electrochemical cell is filled with a sol containing supporting electrolyte. The catalyst (OH\(^-\)) is electrochemically generated via application of a potential sufficient to reduce oxygen (\(E_{\text{applied}} \sim -0.8 \, \text{V}\)) or water (\(E_{\text{applied}} \sim -1.2 \, \text{V}\)).

\[
\begin{align*}
(2.1) \quad & \quad O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \\
(2.2) \quad & \quad 2H_2O + 2e^- \rightarrow 2OH^- + H_2
\end{align*}
\]

To confirm that oxygen is an important source of the produced hydroxide, it has been shown in the literature that deoxygenating the sol prior to deposition does not result in silica formation.\(^6^5\) As will be discussed in more detail in chapter 5, hydroxide ion diffuses from the surface of the electrode and catalyzes the hydrolysis and condensation of silica onto the electrode surface. Unlike traditional metal electrodeposition, these reactions do not strictly take place on at the electrode surface as the hydroxide ions are able to diffuse through the solution of partially hydrolyzed monomers quickly. This effect will play a major role in the growth of high aspect ratio nanostructures, as described in chapter 6.

2.3 Imaging Techniques

The ability to image features in the nano-scale region in many modern materials, such as those developed in this work, necessitate the use of advanced imaging techniques. Traditional light microscopes are limited to a resolution of \(\sim 200 \, \text{nm}\) because image resolution, as described by Abbe’s law, is approximately one half of the wavelength used to view the sample.\(^6^6\) For the
materials developed in this thesis, the much better resolution provided by scanning electron microscopy and atomic force microscopy were needed. A description of these imaging methods is given below.

2.3.1 Atomic Force Microscopy

Atomic Force Microscopy is a Scanning Probe Microscopy (SPM) technique developed by Binnig in 1986. Atomic Force Microscopy (AFM) distinguishes itself from other imaging techniques because they are based on the interaction between a stiff probe and a surface, rather than the interaction between the sample and some form of radiation. Scanning Tunnelling Microscopy (STM), the first of these techniques to be developed, produces images by measuring the current decay in electron tunneling between a conductive surface and the probe. While the resolution and quality produced by STM is very high (0.1 nm wide, 0.01 nm deep), it is limited by several factors. First, the sample must be conductive. Second, the range over which electron tunneling occurs is very limited and thus restricts STM’s usage to samples with minimal roughness. The introduction of AFM, however, greatly expanded SPM’s applicability to image in both air and liquid and allowed for imaging of larger, particularly, nonconductive samples. AFM, while it often has lower resolution relative to STM, has found wide application in the realms of biology, electrochemistry and material science by providing an alternative technique that avoids some of the weaknesses of STM while still giving the potential for sub-micron resolution. Figure 2.8 illustrates the basic apparatus of the AFM as used in this work.
AFM instruments interact with the sample through the use of an extremely sharp probe (commonly called ‘tip’), which is located on the bottom side of a cantilever and is typically made out of silicon or silicon nitride.\textsuperscript{67} Due to the controlled bending that the cantilever experiences during the function of the AFM, cantilevers generally have very low spring constants. Specific characteristics of the tip/cantilever chosen will depend on the mode selected (Contact, Tapping, Non-contact) and will be discussed later. The sample specimen is placed on a piezo transducer, which controls the sample position by utilizing the reverse piezoelectric effect. This means that the application of a controlled potential difference onto the piezo results in the material expanding or contracting in the z direction or bending in the x and y direction. The ability of the piezo to move the sample in an accurate, reproducible fashion is vital to the function of the AFM. Under ideal conditions, the movement of the piezo can be accurately controlled in atomic dimensions.\textsuperscript{68} Finally, the AFM’s detector is a combination laser/photodiode that determines the cantilever’s position by measuring the deflection of a laser focused on the end of the cantilever onto a four quadrant photodiode. Imaging occurs by coordinating these three elements such that

\textbf{Figure 2.8:} Simplified schematic of the AFM apparatus\textsuperscript{70} (Digital Instruments, Nanoscope IIIi) (adapted from ref. 70)
the position of the tip is exactly matched to its location relative to the surface at a single moment in time and both are accurately detected.

The AFM creates an image by measuring the attractive or repulsive force between the tip and the sample. Van der Waals or in some cases electrostatic forces occur between the AFM tip and the sample as the distance between them changes. Figure 2.9 A gives an exaggerated force/deflection curve for an AFM tip at variable distances from the surface.

Figure 2.9: (A) Graph of cantilever deflection verse the distance from the tip to the surface. (B) Graph of the Lennard-Jones function for two particles r distance apart. (adapted from ref. 71 kind permission from Springer Science and Business Media.)

When the tip is far from the surface, the forces between them are very small, resulting in no tip deflection. As the tip approaches the surface, however, attractive forces begin to draw the tip to the surface, resulting in a slight bend in the cantilever. Eventually the tip and the surface will touch and the cantilever will experience significant bending. When the distance between the sample and the tip is decreased further, the cantilever will straighten out and then eventually curve outward as the sample is pushed into the surface. The pattern of attraction and repulsion between the tip can also be modeled as a function of the potential energy between particles on the tip and the surface by using the Lennard-Jones function (Fig. 2.9 B). By largely relying on
these interactive forces, the AFM can image a much wider range of materials compared to STM or other high magnification techniques, such as SEM, without sample modification. These conditions have resulted in particular interests in the realm of biology. In this work it was used to follow individual, undisturbed samples at each step throughout the fabrication process, which is particularly advantageous in multi-step material development.

The interaction between the tip and the sample can be measured in several ways. The first method developed was contact mode, where the tip remains in contact with the sample during the entire duration of the image scan. Contact mode is best used for hard, flat samples and uses relatively soft, short cantilevers to minimize the force on the surface and to prevent undesired tip oscillation. Constant contact between the tip and the sample, however, has some disadvantages. Moving a hard tip along a soft or rough surface can damage the sample. The next two modes, non-contact and tapping, avoid this by minimizing the physical contact between the tip and the sample. In both modes, the tips are under oscillation and thus require relatively stiff cantilevers. For non-contact mode, the oscillations have small amplitudes and shifts in the tip’s frequency are measured as it approaches, but never touches, the surface. In tapping mode, by contrast, the tip is oscillated near its resonate frequency. The tip is brought close enough to the sample so that the oscillating tip repeatedly engages and disengages with the surface. Depending on the topography of the surface, the amplitude of the oscillating tip will either increase or decrease, information which is then used to construct the image. Tapping mode tips require particularly stiff cantilevers because, as they disengage, they must overcome capillary forces produced by the condensation of water as the tip first approaches the surface. The samples studied in this work generally had height differences of about 300 nm, making tapping mode the most appropriate choice for study.
Despite the many attractive qualities of the AFM, there are several challenges and disadvantages to be overcome or accepted. First, by relying on physical or near-physical contact between a probe and an object, the features on the sample can become defined by the tip geometry. In the process known as tip convolution, portions of the sample are not displayed in the image because the tip is not sharp enough or cannot reach to properly trace the features.

**Figure 2.10:** Illustration of tip convolution and low-aspect ratio vs. high-aspect ratio tips. (adapted from ref. 72 with permission from Elsevier.)

Deep recesses in a surface can similarly create challenges for imaging with an AFM tip. In order for the tip to image the recess, the tip must be sharp enough to actually fit inside the recess. In many situations, this can be achieved by using high aspect ratio tips, but these are expensive, can be hard to work with, and become dull quickly. Ultimately, there is a limit to how rough the samples can be and even the advantages of the AFM over the STM are not enough for some samples to be examined with probe microscopy. Also, AFM falls short compared to SEM when imaging large areas. The AFM can produce images up to 100 µm², but they require long collection times (upwards of an hour) while an SEM can take much larger images in as little as a few seconds. Overall, the AFM is a very useful technique for imaging small areas on a sample under atmospheric conditions and can provide information about surface roughness and depths of small pores.
2.3.2 Scanning Electron Microscopy

The introduction of electron beams to the field of microscopy in the 1930’s dramatically increased the resolution of images and resulted in the technique of electron microscopy (EM). At 0.1 nm, electrons have significantly shorter wavelengths than light photons and modern EM instruments can produce resolution of up to 0.1 nm. Transmission electron microscopes (TEM), the first type of electron microscope to be developed, utilize the electron beam in a similar manner to light in traditional microscopy, by producing a true image. A true image is produced by detecting the radiation that is transmitted through a sample, rather than by being absorbed by it. However, samples must be very thin (<~200 nm) to be imaged in the TEM, which is not possible for the majority of samples in this work. The alternative EM method, scanning electron microscopy (SEM), however, does not have the same restriction on sample thickness and can readily image sample topography over long ranges; SEM was thus an attractive imaging method for many samples in this work.

SEM images, unlike true image techniques, are produced by point by point reproduction. As the electron beam scans a surface, energized electrons escape to the detector. The larger the number of escaping electrons, the lighter the area will be represented in the image. The ease or difficulty of the electrons’ escape is determined by the sample’s work function, which is influenced by both the sample’s physical and chemical properties. First, roughness in the topography will lead to an increase in electrons escaping, as will sample cleanliness. Roughness is a dominating factor in the number of electrons escaping, but in areas of similar roughness, elements with higher atomic numbers will produce more electrons, sometimes allowing for crude differentiation between components in a sample. The emitted electrons can
be divided into two main classes, backscattered electrons or secondary electrons. Other types of emission can and do occur, but they will be addressed during the discussion of energy dispersive spectrometers. The two types of electrons are defined by the amount of energy they possess, where electrons with over 50 eV are classified as backscattered electrons and electrons with energies less than 50 eV are classified as secondary electrons. The difference in energy is accounted for by examining the two types of interaction the beam electrons generally have with the sample’s atoms. The first interaction occurs between a beam electron and the electric field of the nucleus in a sample atom. The difference in mass between an electron and a nucleus results in this interaction being largely elastic, where the electron can be deflected but undergoes little to no loss of energy. Elastic events produce the higher energy backscattered electrons. An interaction between the electron beam and the electric field of a sample atom’s electrons, conversely, is inelastic. Because the interaction is between electrons, they have the same masses and thus the beam electron can transfer some energy to the atomic electron, leading to an energized electron being emitted as a secondary electron.

In practice, there is a discernible difference between the emission of electrons from conductors and insulators, resulting in it being necessary to coat insulating samples with a thin layer of metal before imaging. The samples in this work all involve insulating silica, making this distinction an important one. In conductors, the high number of electrons in the conduction band results in the emitted electrons having a much greater probability for experiencing collisions compared to those in an insulator. The greater number of collisions undergone in conductors has implications for image resolution. The high number of collisions occurring in conductors results in only electrons close to the surface having enough energy to be emitted from the sample. This leads to insulators being able to emit electrons from up to 50 nm from their
surface but conductors only 5 nm (Fig. 2.11). Not only is the depth at which electrons can be emitted greater for insulators, but also the diameter beyond the electron beam (Fig. 2.11). In metals, this diameter is only an additional 0.5 nm larger than the electron beam, but in insulators the emitting surface area increases by an additional 5 nm. Pixel size is proportional to the area from which the electrons are emitted, so minimizing this value results in better resolution.

**Figure 2.11:** Illustration of the effect of sputter coating a thin conductive layer onto an insulating sample. The escape volume of emitted electrons decreases in both depth and radius from the exciting electron beam. (Adapted from 75 with permission from Elsevier.)

Insulating materials also pose another challenge in imaging due to an effect known as charging. If the number of electrons entering and leaving the sample is the same, then the overall charge on the samples surface will be neutral, which is the ideal condition for imaging. If there is an imbalance, however, the sample will become charged, leading to interference in the imaging process. Conductors mitigate this imbalance by adding or removing electrons through its connection to ground. Uncoated insulators, however, will retain this charge, which can lead to light or dark streaks in the image. Therefore, insulating samples are coated with ~10 nm of gold or platinum to minimize the escape volume of the sample and reduces the effects of charging.
The bombardment of the sample with high energy beam electrons and the detection of the emitted electrons to create an image occur inside the SEM column. Figure 2.12 shows a simplified schematic of an SEM column.\(^6\)

![Simplified schematic of a SEM column](adapted from ref. 77 with permission from Elsevier).

The electron beam is produced at the top of the column by the electron gun. The SEM used in this experiment was primarily the Hitachi SU-70, and it used a ZrO/W Schottky emission source.\(^7\) The electrons produced by the gun are then accelerated downwards due to the potential difference between the high voltage cathode and the anode at ground. The beam is then focused and brought to its desired diameters by several magnetic lens and apertures, including two condenser lens and one objective lens. Each magnetic lens consists of an electromagnet created by flowing current through wound copper wire. The apertures are gold plates with holes of predetermined diameters that control the diameter of the beam by absorbing electrons that stick...
it. The scanning deflection coils are often contained within the objective lens and are responsible for moving the beam in the x and y direction to create the imaging raster pattern. The sample holder and the detector are at the bottom of the column. The Hitachi SU-70 uses a secondary electron detector.78

2.3.2.1 Energy Dispersive Spectroscopy

Elemental analysis can also be conducted if the SEM instrument is equipped for X-ray microanalysis. There are two types X-ray microanalysis devices, wavelength dispersive spectrometers and energy dispersive spectrometers.69 The former measures the wavelength of emitted x-rays; this was not used in this work so it will not be discussed. The energy dispersive spectrometer, conversely, measures the energy of X-rays emitted from the sample. To produce X-rays, the sample is bombarded with high energy electrons.69 When an electron with sufficient energy strikes a non-valence electron, the electron will be emitted from the atom. This leaves behind an electron hole that is then filled by an outer shell electron falling to the lower energy level. The difference in energy between the level that the falling electron began at and the level it fell to is released in the form of an X-ray, which has energy that is roughly the difference between the two levels. Because elements have distinctive differences between their energy levels, the X-ray can be used to identify them.

In the case of energy dispersive spectrometers (EDS), the X-rays are detected through an insulating semiconductor system.69 The semiconductor in an EDS system has been setup such that the $pn$-junction diode has the $p$-type semiconductor connected to the negative terminal and the $n$-type semiconductor connected to the positive terminal. Under ideal conditions, this would be enough to prevent the independent flow of electrons within the crystal, but the effects of thermal energy and defects must be accounted for. EDS systems are generally cooled by liquid
nitrogen, which prevents the occasional thermal promotion of a silicon electron into the conduction band. The cooling system also aids in correcting for defects. Li\(^+\) ions are introduced into the \(p\)-type side of the silicon semiconductor system and then used to compensate for the doped B\(^-\) atom, thus preventing the production of unwanted current. The cooling system is needed to prevent the Li\(^+\) ion from leaching out of the semiconductor.

At this point, the only electron holes that are produced are the result of the semiconductor being hit with an X-ray. The X-ray is absorbed by a silicon atom, resulting in an electron being pushed to the conduction band, known as a photoelectron, and a hole being produced.\(^{69}\) The energized atom then can emit either an outer orbital electron, known as an Auger electron, or it can emit a silicon X-ray. Eventually, all the energy from the initial X-ray will be used in the production of electron-hole pairs and the produced voltage is proportional to the energy of the original X-ray, allowing it to be identified.

2.4 Ultraviolet/Visual Molecular Absorption Spectroscopy

Ultraviolet/visible molecular absorption spectroscopy (UV-Vis) was used in chapter 4 to identify gold nanoparticles on the film. A brief description of the function of the UV-Vis will be given followed by a discussion the phenomena of plasma resonance, which was used in the study of the nanoparticles.

In UV-vis spectroscopy, the transmittance or absorbance through a sample is measured.\(^{79}\) Practically, this means that the radiant power detected after radiation has passed through a sample is compared to the radiant power through a suitable control or solvent blank. Transmittance and absorbance are thus defined as

\[
(2.2) \quad T = \frac{P_{\text{sample}}}{P_{\text{control}}}
\]

\[
(2.3) \quad A = - \log \frac{P_{\text{sample}}}{P_{\text{control}}}
\]
where $T$ is transmittance, $A$ is absorbance and $P$ is radiant power. While UV-Vis is often used to study solutions, solids and gases can also be examined, as was the case in chapter 4 where nanoparticles attached to glass slides were studied. When testing a monolayer on a substrate, the blank for the determination of transmittance and absorbance become the untreated substrate.

Figure 2.13 gives a block diagram of the UV-Vis system used in for the work in this dissertation, which had a single-beam configuration.

**Figure 2.13**: Block diagram of a single-beam UV-Vis instrument.\(^{79}\)

The UV-Vis was used to confirm the presence of a monolayer of self-assembled gold nanoparticles on glass sides and silica template films. It was also used to determine the size of the particles and the quality of the assembled layer on the film, respectfully. Gold nanoparticles can be studied with UV-Vis because they have characteristic absorption/scattering peaks due to the plasmon resonance effect.\(^{80, 81}\) Plasmon resonance in metal nanoparticles is the result of the interaction of the particle’s electron cloud with light.\(^{80, 82}\) Because the size of the nanoparticles compared to the wavelength of light that it has been irradiated with is much smaller, oscillations within the electron clouds occur in the opposite direction from the light’s electric field (Fig. 2.14).
Gold is an ideal element to study with plasmon resonance because its characteristic absorption occurs in the visible spectrum. For spherical gold nanoparticles within 20 nm diameter, the approximate size used in this study, the light extension is mostly due to absorption and produces a characteristic peak at 520 nm, giving gold nanoparticle colloid solutions their distinctive red color. It was showed by Natan et. al that attaching a gold nanoparticle to a glass surface through a mercaptosilane linker did not have a notable effect on the absorption peak of the gold nanoparticle, and that trend continued for the gold monolayers formed on silica films in this work. As the gold particles increase their aspect ratio, however, their appearance shifts to a blue color and an addition broad absorption peak appears at wavelengths greater than 600 nm, depending on the particles length. The shift from red to blue was a useful indicator for gold monolayer quality, as aggregation of spherical particles leads to an increase in their aspect ratio, resulting in the film surfaces taking on a blue or purple color.
Chapter 3: Ordering of *B. Megaterium* in Silica Thin Films

3.1 Introduction

In this chapter, a novel method for ordering and arranging the biological template, *B. megaterium*, within a silica thin film was devised. The embedded bacteria templates were then removed to create high aspect ratio macropores within the film for possible applications, such as chemical sensors, microchannel arrays or for use as exotemplates.

3.2 Background

It has been shown in the literature that the pores of a material could be used as an exotemplate for the creation of nanostructures.\textsuperscript{46, 47, 49} Examples include the use of track-etched polymer membranes or anodized aluminum oxide membranes for the creation of metal nanowires, mesoporous silica structures such as MCM-41, for the creation of poly(phenolformaldehyde) measofibers, and the creation of polypyrrole hollow nanospheres through surfactant microemulsion fabrication.\textsuperscript{46, 84, 85} Biological templates, in particular, have the potential to add a wide range of unique shapes to the template canon.\textsuperscript{39, 48, 86, 87} An example of a biological material that has found use as a template is bacteria.\textsuperscript{87, 88} Bacteria make useful templates because of their many unique sizes and shapes, and ability to be easily replicated.

Preliminary studies completed in the Collinson group on the use of bacteria as hard templates in silica thin films successfully showed that the bacteria *Bacillus subtillis, Escherichia coli, Listeria monocytogenes*, and *Bacillus megaterium* could be easily integrated into a silica film by simple mixing into a silica sol prior to casting on an electrode. It was also shown that copper can be grown at the bottom of some of the rectangular macropores that were formed after the bacteria templates were removed by applying -0.35 V to the electrode in a solution of 5 mM copper sulfate in 0.1 M sulfuric acid for 180 seconds (Fig. 3.1).
Figure 3.1: AFM images of silica films templated with \textit{B. subtilis} before template removal (A), after template removal (B) and after copper deposition (C). (z scale: 1200 nm)

The bacteria template \textit{B. subtilis}, having the dimensions \(\sim 1 \times 4 \ \mu\text{m}\), creates long channels that are \(4 \ \mu\text{m}\) long and approximately \(350 \ \text{nm}\) deep. These can be used as microchannels or framework for other material formation, such as seen in the electrodeposition of copper. It would be beneficial, however, to expand the range of dimensions available for this method. The bacterium \textit{B. megaterium} is an attractive candidate as an alternative bio-template because of its large size and ability to form bacteria chains due to the adhesive nature of \textit{B. megaterium}’s cell capsule, potentially increasing the length of the channels several times.\(^{89}\)

The cell capsule is an extracellular structure that is part of some bacteria’s cell envelope and both protects the bacteria from phagocytes and improves their adhesion to surfaces.\(^{90}\) The cell capsule is a layer of polysaccharides attached to the outside of the cell wall and unlike other extracellular structures such as the slime layer, is difficult to remove (Fig. 5).\(^{90}\)
Figure 3.2: Simplified schematic of a *B. megaterium* bacterium cellular structure\textsuperscript{90} (adapted from 90). The common arrangement of the bacteria after spin coating is illustrated, as well as the ideal arrangement for this work.

The adhesive nature of the cell capsule presented both challenges and opportunities for the ordering of *B. megaterium*. When freshly grown, the cell’s capsule does not just improve the adhesion between the bacteria and a surface; it also allows several bacteria to link together, forming long chains. When used as templates, these chains can produce long, trough-like pores. The disadvantage of the chain structure is that it gives the templates several points of articulation that can result in folding and curling in the structures when cast onto a substrate (Fig. 3.2).

When high aspect ratio structures that are inflexible, such as carbon nanotubes or nanocrystalline cellulose, are spun across a surface, they typical exhibit radial ordering along the vector of centrifugal force.\textsuperscript{91, 92} It was thought that if the adhesive bacteria could be anchored to something on the substrate, the centrifugal force that is produced by spin coating could straighten out the chains, while also giving the bacteria a more consistent overall directional ordering. A common ordering technique for liquid crystals provides a promising alternative.\textsuperscript{93, 94} In the ordering of liquid crystals, light scratches are applied to the substrate by directional rubbing with an organic fiber cloth prior to spin coating. Similar light scratches were added to the substrates in the following work in attempt to improve bacteria alignment. In this work, *B. megaterium*’s
tendency to form long bacterium chains will be used to create ordered, high aspect ratio pores that could then been used as vessels for nanoparticle formation.

3.3 Methods

A sol was prepared by stirring a mixture of 0.25 mL tetramethoxysilane (TMOS, 99%, Acros), 1.2 mL ethanol, 1.15 mL water, and 0.15 mL 0.1M HCl for 30 minutes. The sol was then aged for two days and 100 µL of sol was mixed with 100 µL of B. megaterium prior to casting. The bacteria were obtained from Professor Ohman’s group where it was grown by standard protocols. Briefly, 50 mL of LB broth in a 250 mL flask were inoculated with the bacteria. Following overnight incubation at 37° C in a shaking water bath, bacteria were removed and placed into sterile microcentrifuge tubes and spun down at 10K for 10 minutes. The supernatant was then removed and the pelleted cells were resuspended in 15-mL of 0.85% NaCl solution (concentration of bacteria was ca. 10^9/mL). 1-mL of the suspended cells was centrifuged at 4000 rpm for 4 minutes. The supernatant was removed, and 0.5 mL of sterile, deionized water added.

The glass substrates were prepared by securing slides cut into approximately 1.5 cm x 1.5 cm squares to a flat surface and applying 20 light scratches on their surface in a single direction with 1500 grit sand paper. The glass was then cleaned by successive sonications in soap, water and water for 10-15 minutes each. The suspension was then cast onto the modified slides at 8000 rpm for 30 seconds. The film was allowed to dry overnight and then the bacteria were removed by exposure to oxygen plasma (Southbay PE-2000, DC bias of -500 V) for 32 minutes. Because of the size of B. megaterium, the etching step was repeated until the bacteria appeared to be completely removed, which in some cases was up to four times. The alignment of the bacteria
was determined by viewing in an optical microscope (DC Instruments) and the removal of the templates was confirmed via AFM (Digital Instruments, Nanoscope IIIa).

3.4 Discussion:

Optical studies of the alignment of *B. megaterium* in the silica films showed a marked improvement in the overall order of the templates with the addition of the unilateral scratches. Spin coating a mixture of the bacteria and sol without modifying the glass substrate resulted in curling of the bacteria strands and the bacteria being aligned in inconsistent directions (Fig. 3.3 A).

**Figure 3.3:** 450 x 600 μm optical image of *B. megaterium* immobilized in a thin silica film on a smooth (A) and unilaterally scratched (B), (C), and (D) glass surfaces. Figures B, C, and D reflect the radial nature of the bacteria alignment.
In the films cast onto scratched surfaces, however, the majority of the bacteria formed straight lines and were aligned in the same direction. The ‘head’ of the bacteria was generally located at a scratch and the body and tail extend from it. The orientation of the bacteria over the whole substrate was radial with a central point coinciding with where the glass had been positioned on the spin coater chuck. This is demonstrated in comparing Figure 3.3 B, C and D. In Figure 3.3 B, the bacteria are largely perpendicular to the scratches, whereas in Figure 3.3 C, they are at approximately 45° and in Figure 3.3 D they align along the scratches themselves. The orientation of the bacteria results from the contrast between the radial centrifugal force propelling the bacteria across the slide and the scratches on the glass being aligned linearly, resulting in the bacteria’s ordering now being comparable to other more rigid, high aspect ratio structures (Fig. 3.4).  

![Figure 3.4: Simplified schematic of the relationship between the bacteria arrangement, the linear scratches on the glass substrate, and the direction of the centripetal force vector.](image)

AFM studies were also conducted on the ordered films and it was determined that the changes in the procedure did not interfere with the process of template removal. Figure 3.5 shows the silica film before and after template removal by plasma etching.
Figure 3.5: Typical AFM images of silica thin films created from *B. megaterium* immobilized on a unilaterally scratched glass surface before (A) and after (B) the bacteria were removed. (C) Depth of channels is approximately 130 nm.

The AFM images confirm that the “sticking” point from which the bacteria extend are the scratches. This results in the formed microchannels from the chain of bacteria being very straight, despite at times being made up of several separate bacteria. The channel’s length was dependent on the number of bacteria in a strand, with a single bacterium having a length of about 10 µm. The upper limit of chain length was observed to be six, resulting in channels with the dimensions 200 nm wide and 50 to 60 µm long, depending on the lengths of the individual bacterium and if they were linked completely end to end.

There are several challenges that still must be overcome for *B. megaterium* to be used as an exotemplate for electrochemical growth, or for any other electrochemical application. As seen in Figure 3.5, it appears that the bottom of the microchannel is slightly raised above the level of the film. This can be attributed to two possible reasons. Either the bacteria are still not
completely removed or silica is forming underneath the bacteria. Either of these situations would prevent full access to the underlying electrode. To address the first possible challenge, more extreme removal techniques could be used. The plasma etching used in this work employed a moderate bias of -500 V. This bias could be raised as high as -800 V, which could potentially aid in removal of any excess bacteria. If the silica was forming below the bacteria template, a two-step film formation method could be used, where the bacteria could first be ordered on the substrate and then the sol spun over the template separately. Because the bacteria would already be in contact with the surface, there would be a smaller chance of either silica condensing on that bacteria surface in the sol or a small amount of sol remaining underneath the bacteria when spun.

3.5 Conclusion

By taking advantage of the natural complexities of biological templates such as B. megaterium, a new template orientation method was devised. The combination of the adhesive nature of the bacteria’s cell capsule and the introduction of ‘sticking’ points on the substrate allowed for radial alignment of the bacteria. Suggested future aims for this project would be to form nanostructures within the pores, either through electroless or electrochemical growth and to explore less destructive methods for modifying the surface. Possible alternative methods include patterning by photolithography or patterned SAMs, which could provide opportunities for more complex arrangements.
Chapter 4: Metal Nanoparticle Modification of Macroporous Silica Thin Films

4.1 Introduction

The major objective of the work presented in this chapter was to improve the conductivity of macroporous silica thin film electrodes through the use of metal nanoparticles. The films were modified either through the electrodeposition of copper at an exposed area of the electrode in the macropores or through the self-assembly of gold nanoparticles on the film surface.

4.2 Background

One area of sol-gel research that has received particular interest is sol-gel modified thin film electrodes. Modifying an electrode with a metal oxide thin film such as silica is attractive for many reasons. The inorganic nature of the silica results in the films being rigid and mechanically stable and the sol-gel process allows for the use of straightforward bench-top casting techniques, such as spin-coating and dip-coating. The simple addition of templates before casting can give the resulting film tunable porosity with a high degree of reproducibility and can even control the local chemistry of pore surfaces through template imprinting. Chemical modification of the films is also straightforward. Organic character can be added to the films through the use of precursors (R_m-Si(OR)_n, where m + n = 4) with carefully chosen ligands that are resistant to hydrolysis, such as 3-mercaptopropyl trimethoxysilane or n-octyltrimethoxysilane, either by integrating them into the sol during the initial film formation or by having them react with the surface of an existing film.

The increased interest in sol-gel modified electrodes has led to electrodes with a wide range of properties and characteristics being developed. For example, silica films can be modified with dopants that have a high affinity for the target analyte in a process known as pre-
concentration, where the analyte is encouraged to diffuse into the film, leading to an increase in sensitivity of the electrode.\textsuperscript{5,99,100} If the functional group is well chosen, it can also increase the experiment’s selectivity by preventing interferants from entering the film and diffusing to the electrode. For example, pre-concentration factors of 10 to 50 were found by the addition of polyelectrolytes such as poly(dimethyldiallylammonium chloride), polystyrene sulfonic acid and Nafion into a sol that was then spin coated onto an electrode surface.\textsuperscript{100} These films showed enhanced sensitivity for compounds such as Re[1,2-\textit{bis}(dimethylphosphino)ethane]\textsuperscript{+} and 8-hydroxy-1,3,6-pyrenetrisulfonic acid trisodium salt. The same mechanism that allows for the films to be doped with templates by simply adding them to the sol prior to casting can be applied to the entrapment of biomolecules for the creation of biosensors.\textsuperscript{39,48,57} For example, sol-gel based biological sensors have been created by entrapping enzymes such as glucose oxidase into a silica matrix and have proved to make robust sensors with enhanced enzyme stability and resistance to leaching.\textsuperscript{58}

For sol-gel derived thin film electrodes to move beyond the laboratory, however, several important challenges must be addressed.\textsuperscript{96} While the porous nature of the silica films allow for some diffusion through the network, the size and arrangement of the pores has an influence on the analytical response.\textsuperscript{35} For example, electrodes modified with 300 nm entrapped enzyme films (Fig. 4.1 A) have shown optical response times of up to 2 hours, which is generally not acceptable in commercial settings.\textsuperscript{59}
Figure 4.1: Simplified schematics of common sensor designs found in the literature. The enzyme is directly embedded into the silica film in design A, where it is sandwiched between two films in design B. (modified from ref 59 with permission from Elsevier)

Generally, the analytical response in a silica thin film system has a positive correlation with the film’s pore size and order, and the degree to which the pores are interconnected. Another important factor in the application of silica thin film electrodes is the film rehydration time required before experiments can be run. For optimum response, all of the pores in the dry film must be refilled with liquid, which can be a lengthy process for the dense thin films, despite their small thicknesses. For example, more acceptable optical and amperometric response times of 4 minutes and 30 seconds, respectively, have been reported for films where the enzyme is sandwiched between two thin silica layers (Fig. 4.1 B). The top silica layer has an average thickness of 100 nm, allowing for faster diffusion from solution to the enzyme. The improvements in response times, however, were only achieved after the sensor was allowed to hydrate for an hour. Therefore, a design that provides fast hydration rates and quick response times would improve the applicability of sol-gel thin film electrodes.

The challenge presented by the slow hydration into and diffusion through silica thin film electrodes has been addressed by the Collinson group and others through the integration of templates into the film. Common templates include surfactants and soluble microparticles, which are used to create films with defined mesopores or macropores, respectfully. As explained in section 1.3.1, the addition of a surfactant to the sol will result in micelle formation; the resulting pores size and pore organization that results from the micellar
template (or structure directing agents) then can be controlled by modifying the concentration of surfactant and rate of film evaporation.\textsuperscript{35} The work conducted previously by the Collinson group, however, has focused on creating macroporous films by using soluble microparticles or biological templates.\textsuperscript{40, 102, 103} In this work, the endotemplates were only partially submerged in the silica, resulting in large, open macropores being formed in the film after template removal. These macropores, or “nanowells”, will increase the film’s total surface area and expose more of the micropores intrinsic to silica directly to the solution. The film structure also decreases the diffusion distances between the bulk solution and the interior of the film. These factors can decrease the often long film rehydration times that are found in conventional silica thin films and improve sensor response times (Fig. 4.2).

**Figure 4.2:** Comparison of typical properties found in silica thin film made through conventional spin coating techniques and those found in “nanowell” modified film.

In addition to increasing the film surface area and decreasing diffusion distances, the templated films generally have small areas of exposed electrode where the template came into contact with the electrode, giving a direct link to the electrode surface (Fig 4.3).\textsuperscript{40} Previous works by the Collinson group has used PS spheres as templates for this method.\textsuperscript{102} PS spheres are an attractive template selection because they are soluble in many organic solvents and the
wide range of commercially available sizes (30 nm to 3 µm). The templates were mixed with an acid catalyzed sol and then cast onto an electrode. After the film was allowed to dry completely, the templates were removed with chloroform, exposing a small portion of the electrode at the bottom of the nanowell and thus forming a new conductive domain.

**Figure 4.3:** Simplified schematic of a nanowell formed in a silica film on an electrode by templating with a polystyrene latex sphere. At the bottom of the nanowell is a small area of exposed electrode, giving direct access for electrochemical reactions.

The electrochemical properties of the newly exposed conductive domain are dependent on several factors: the packing of the nanowells, interaction between the silica and the analyte, and the amount of exposed electrode at the bottom of the nanowell.\(^{95, 102}\) For example, Figure 4.4 shows typical electrochemical responses for films with poor PS sphere packing (A) and improved PS sphere packing (B) that resulted from the addition of the surfactant SDS to the sol prior to spin coating.\(^{40, 102, 105}\)
Figure 4.4: CV data previously published by the Collinson group. Figure A is a CV of 1 mM ferrocene methanol in 0.10 M KNO₃ at a scan rate of 100 mV/s at a silica film of randomly located 0.5 µm PS sphere templates before (dashed line) and after (solid line). Figure B shows the comparison of CVs taken in 1 mM ferrocene methanol in 0.1 M KCl at a bare electrode and film modified electrodes before and after the removal of the close packed PS colloidal crystal. Each film electrode had pinholes blocked with OTMOS. (scan rate: 100 mV/sec) (Reprinted with permission from ref 102 and 105 with kind permission from the American Chemical Society. Copyright 2004.)

The difference in the current response shows the effect of diffusion layer overlap in the thin film modified electrode. Each individual nanowell can be considered to be an ultramicroelectrode, and as such has a radial diffusion profile. In Figure 4.4 A, the individual nanowells are spaced far enough apart such that their diffusion layers do not overlap resulting in a sigmoidal shape CV. Upon improving the packing density of the nanowells on the surface, the CVs were greatly improved (Figure 4.4 B). In this case the diffusion layers of electrode’s nanowells overlapped and thus behaved as a single bulk electrode. In addition to the change in shape, the current response increased over three times. These results show the importance that packing plays in electrode design and this will be reflected in the following work.

It should be noted that the improvements in sphere packing density were not without consequences, however. The closely packed films required an additional blocking step before template removal. It was found that, unlike with the films where the spheres were largely
separated, pinholes were forming in the densely packed film, exposing unintended areas of the electrode to solution. Pinholes and minor cracking in the densely packed films is likely due to stress resulting from uneven drying in the film. Soaking the films in n-octyltrimethoxysilane before template removal was found to eliminate the majority of the pinholes and suppress the current response (Fig. 4.4 B).  

The other factor affecting the electrochemistry in the nanowells that will be addressed in this chapter is the size of the conductive domain at the bottom of the nanowell. Increasing the conductive domain in an ultramicroelectrode array can potentially increase electrochemical sensitivity. In addition, the incorporation of metal particles into the film as described in this chapter could also potentially decrease the distance that an entrapped molecule has to diffuse before encountering an electrode surface, further improving response times. The addition of metal nanoparticles has other advantages as well, such as decreasing the influence of the negatively charged silica on electrochemical systems. For example, the self-assembly of 5 nm gold nanoparticles into a 15 nm silica thin film was shown to improve the reversibility of the potassium ferricyanide through the film. Potassium ferricyanide is normally a reversible system at a standard electrode, but its negative charge limits its ability to interact with a negatively charged silica film due to electrostatic repulsion. This limitation could be overcome, however, by adding 3-mercaptopropyl trimethoxysilane to the sol and then letting the film soak in nanoparticles for a given time. It was determined that the return of reversibility could be correlated with the amount of time the gold was allowed to self-assemble in the film. This effect will be explored in more depth in chapter 5.

In this work, the silica thin films were modified with metal nanoparticles by two methods, electrodeposition and nanoparticle self-assembly. In section 4.3, the study of the
formation of copper nanodeposits at the bottom of the nanowells was expanded from previously published work.\textsuperscript{102} These electrochemical deposition studies, originally conducted to prove that the bottom of the nanowells were open, were expanded to assess the degree of control that could be achieved over the growth of copper nanoparticles through variations the deposition time. Changes in the film formation method necessitated the redesigning of the method used to block pinholes. This was accomplished by switching from the surface condensation of n-octlytrimethoxysilane (OTMOS) to the electro-assisted deposition of silica from a sol.\textsuperscript{65} In section 4.4, the type of metal nanoparticles integrated into the PS templated thin films was broadened to include gold. In this case, however, the nanoparticles were prepared separately and then integrated into the film through the use of thiol-based silane linkers.\textsuperscript{81} Electroless deposition was used to increase the diameter of the gold nanoparticles and attempts were made to selectively cover the electrode surface with the gold nanoparticles.

4.3 Controlled copper growth in silica films

The electrochemical growth of copper nanostructures at the bottom of silica nanowells prepared by templating latex spheres served as the foundation of the following study, which demonstrates that the size of the copper particles could be controlled.\textsuperscript{102} The major variables that play a role in the growth of the copper deposits are potential, copper ion concentration and deposition time. The extent of copper growth will be determined by areas of exposed electrode, either intentionally though template removal or unintentionally through pin holes and other defects in the film. In this work, deposition time was selected as the variable to be controlled and it was shown that longer times lead to larger copper deposits. Deposition time was selected because it could be more easily controlled than potential, where very small changes can result in a huge increase in the deposition rate and thus the size of the formed copper deposit. Deposition
time also has the advantage of requiring minimal changes to the procedure, whereas varying the copper ion concentration would require multiple solutions to be prepared. Through the experimental process, it was also found that the previous published method for blocking defects in the film was insufficient for the new, larger electrodes described herein. Because it was important to limit the deposition to only the conductive domains located at the bottom of each nanowell, other methods for the removal of these defects in the film were explored. This ultimately led to the filling in of defect sites in the electrode through electrodeposition of silica at these areas.

4.3.1 Methods

A sol was prepared by stirring a mixture of 0.25 mL tetramethoxysilane (TMOS, 99%, Acros), 1.2 mL ethanol, 1.15 mL water, and 0.15 mL 0.1 M HCl for 30 minutes. The sol was then aged for two days and mixed with 0.4 µm polystyrene spheres (PS from Invitrogen, formally Interfacial Dynamics Company (IDC), sulfate stabilized, 8%) in a 1:1 ratio. 5 mM sodium dodecyl sulfate (SDS, 98%, Acros) was added to improve wettability and the suspension was cast at 3000 rpm onto a ~1.5 cm x 1.5 cm square glassy carbon electrode that had been polished with 0.05 µm alumina particles on a napless polishing cloth (Buehler). The film was allowed to dry at least 12 hours before any electrochemical studies were conducted. All electrochemical studies were completed on a CH instruments potentiostat using a three electrode cell with a horizontally mounted working electrode (Fig. 4.5).
Figure 4.5: Simplified schematic of the electrochemical cell used in the deposition of silica and copper onto glassy carbon electrodes. The glass cell, which contained an open internal tube, was placed onto an o-ring on the glassy carbon electrode. A thin piece of brass served as the electrical connection. This assembly was sandwiched between two pieces of plastic and screwed finger tight to form a good seal. The solution and the reference and counter electrodes were placed inside the internal tube.

The electrochemical experiments proceeded as follows: The electrode was mounted in a cell with an 8 mm internal tube and the pin holes were blocked by electrochemically depositing silica from a sol (1 mL TMOS, 4 mL 0.1 M KCl, 4 mL ethanol, stirred 10 mins) for 3 minutes at -0.9 volts vs a silver/silver chloride (1.0 M) reference with platinum wire counter. The electrode was then removed from the cell, rinsed well with water and dried overnight. The PS spheres were removed by dissolving them in chloroform for 3 hours, followed by a chloroform rinse. Once dried, the electrode was put in a smaller cell with an internal diameter of 6 mm that was carefully placed over the silica deposited film. Copper was deposited from a solution of 5 mM copper sulfate (Fisher) in 0.1 M sulfuric acid for two lengths of time: 30 and 60 seconds. The electrode was removed, rinsed with water and dried and then imaged using atomic force microscopy (AFM, Nanscope IIIa).

4.4.2 Results and Discussion

A silica film with a close packed arrangement of polystyrene spheres was produced on a glassy carbon electrode that was comparable to those produced by Deepa et al (Fig. 4.6 A).
Figure 4.6: Silica film before (A) and after (B) PS template removal. The nanowells showed depths of ~250 nm and diameters of ~400 nm. (z scale: A=700 nm, B=600 nm)

However as previously discussed, the close–packed arrangement of spheres on the surface leaves pinhole in the film, resulting in exposed electrode. These pinholes (or defect sites) provide a site for copper deposition as does any other exposed area in the film. It is thus very important to block these pinholes/defects before the templates are removed to limit the deposition only to the desired conductive domains exposed upon sphere removal.

The first two blocking methods attempted were adapted directly from the literature. The method used in the previously published silica nanowell studies was tried first, where the films containing the polystyrene latex spheres were soaked in a 5 % OTMOS/dry ethanol solution. In this procedure, the hydrophobic silane will react with exposed hydroxide bonds at the defects, effectively knitting the film together. This method, however, was originally designed for use with a 5 mm diameter chip glassy carbon electrode; the current method uses a much larger 1 cm x 1 cm square glassy carbon electrode. It was observed that copper deposition continued to occur outside of the nanowells, signifying that the blocking attempt was not as effective as it needed to be (Fig. 4.7).
Figure 4.7: (A) Schematic of the desired location of deposition, at the conductive domains vs. defects. (B) AFM image of 30 second copper deposition with a failed blocking attempt. (z scale: 600nm). It can be seen that copper growth inside the nanowells is limited and that copper growth at defects in the film can be unpredictable and particles can be larger than the nanowells themselves.

At this point, both higher concentrations of OTMOS and larger solution volumes were also evaluated. It was postulated that a larger amount of OTMOS may be needed to cover the much larger surface area. The increase in concentration, however, did not appear to block the pinholes to the extent needed. The highest concentrations also used interfered with the clarity of the AFM images. In the second method, a technique that had been used to block titania thin films was attempted, whereby a very thin layer of TMOS sol was cast over the dried film before template removal. This method was not successful, as the second layer covered the templates completely, thereby preventing their removal.

The third method attempted was the electrodeposition of silica onto the dried film prior to template removal and it was found to be the most effective of the three methods tried. In the electrodeposition of silica, hydroxide, a catalyst for the hydrolysis and condensation of silica (Equation 1.1 and 1.2), is produced via the reduction of oxygen or water (Equation 4.1 or 4.2).
These reactions will take place first at the exposed areas of the electrode (pin holes and defect sites), resulting in a local change in pH and the localized deposition of silica.

\[
(4.1) \quad O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \\
(4.2) \quad 2H_2O + 2e^- \rightarrow 2OH^- + H_2
\]

First cyclic voltammetry (CV) was used to confirm the reduction potential of oxygen in the presence of the sol, showing the expected peak at -0.8 V for oxygen reduction (Fig. 4.8 A).

**Figure 4.8** Typical CV of the reduction of oxygen/water in a sol comprised of 1 mL TMOS, 4 mL 0.1 M KCl, 4 mL ethanol. (scan rate: 10 mV/sec)

The deposition was carried out using amperometry, where a potential of -0.9 V was applied for 3 minutes (not shown). Previous studies of the electro-assisted deposition of silica on bare electrodes used much longer time scales. For this work, smaller times were used to minimize changes to the overall film. To test if the electro-assisted deposition of silica results in the filling of defects and pin holes, an unblocked and blocked film was placed in 1 mM ferrocene methanol in 0.1 M KCl and a CV acquired. As can be seen, no (or little) Faradaic current was observed for a blocked films and high Faradaic current observed at an unblocked film. The blocked film clearly shows suppression of the faradaic current for a diffusing redox species.
Figure 4.9: CVs showing reduced current after silica deposition onto a silica film before sphere removal. Blue: Silica film with spheres before silica deposition; Pink: Silica film with spheres after silica deposition. Scan taken in 1 mM ferrocene methanol and 0.1 M KCl at a scan rate of 10 mV/sec.

After electrodeposition, the PS templates were removed by soaking the electrode in chloroform for 3 hours. AFM images (not shown) confirmed that under these deposition conditions, the silica films were not significantly altered. Longer silica deposition times, however, could result in excess silica forming on the templates.

Once the defects in thin films were successfully blocked and the templates completely removed, the influence of deposition time on the size of the electrodeposited copper particles was investigated. To determine the specific influence of deposition time, other important parameters such as deposition potential and copper ion concentration were held constant. Cyclic voltammetry was used to determine the potential at which copper ions were reduced to copper (Fig. 4.10 A).
Figure 4.10: A) A typical CV of copper ions (5 mM in 0.1 M H$_2$SO$_4$) at the surface of a glassy carbon electrode modified with a “nanowell” template silica thin film. (10 mV/s)  B) An amperometric response curve for copper deposition for 30 seconds. A similar result was seen for the 60 second deposition (graph not shown).

The potential -0.2 V, where the current due to copper reduction peak begins to increase, was selected as the deposition potential. It was observed that using more negative potentials resulted in larger particles growing over prohibitively short periods of time. Amperometry was then used to electrodeposit copper in the nanowells for 30 seconds and 60 seconds (Fig. 4.10 B). The extent of deposition was evaluated from cross-sections of typical AFM images (Figure 4.11). The copper deposits were observed to be single, spherical particles with average heights of 90 nm and 110 nm from 30 and 60 second depositions, respectfully.
Figure 4.11: AFM characterization of copper deposits. The 30 second deposition (A, B) produced particles with average heights of 90 nm. The 60 second deposition (C, D) produced average heights of 110 nm.

Figure 11 illustrates several challenges that remain in the method. While the copper formed within the nanowell has a consistent size for each deposition time, there are nanowells where copper deposition did not occur. This would indicate that the conductive domain at the bottom of the nanowell was not exposed, despite removal of the template. To improve reproducibility of copper deposition, both between the nanowells in a single sample and between samples, modification could be made to the sol to prevent excess silica formation or the spheres could be packed on the electrode prior to spin coating the silica film, to ensure that sol cannot get between the spheres and the electrode.
4.3.3 Conclusion

It was determined that the deposition time could be used to control the size of electrochemically deposited copper deposits at the bottom of silica nanowells on a glassy carbon electrode. Particles with average sizes of 110 nm and 90 nm were created by holding the potential at -0.2 V for 60 or 30 seconds, respectfully. In addition, a new blocking method was devised, where pinholes were filled in by the electro-generation of the hydroxide catalyst in the presence of silica precursors for short times.

4.4 Gold nanoparticles

The use of electrochemical plating methods for the incorporation of nanoparticles into silica thin films as described in section 4.3 is dependent upon the presence of a conductive substrate, and does not currently allow for alternative nanoparticle configurations or patterns within the nanowells. To provide an alternative nanowell/metal nanoparticle design, self-assembled monolayers (SAMs) and electroless deposition techniques were explored. It has been previously shown by Natan et. al that by modifying a flat glass substrate with a thiol functionalized silane, a single layer of gold nanoparticles could be formed. In a later publication, the layer was made conductive by electrolessly growing the particles. This general method was applied to macroporous silica thin films and allowed for the formation of a gold monolayer along the entire surface of the film. It was postulated that this technique could be coupled with an appropriate blocking method to restrict the nanoparticles to just the surface of the nanowell. The particles showed tunable growth based on their time in an electroless growth solution.
4.4.1 Methods

The silica films were developed using the same method as in section 4.4.1, with two exceptions. The films were cast onto a non-conducting glass substrate which, due to its surface characteristics after cleaning, was well wetted by the sol. Therefore, the SDS was not used. In some cases, after the film was cast and dried, blocking attempts were made to prevent the formation of the gold monolayer on the film surface outside of the cavities. The films were soaked in solutions of 5% n-octyltrimethoxysilane (OTMOS, Aldrich) or dimethyldimethoxysilane (DDMOS, Aldrich) in dry ethanol overnight to form the blocking layer. The templates were then removed by soaking the film in chloroform for 3 hours. The surface of the film was then modified with 3-mercaptopropyl trimethoxysilane (SHTMOS, Aldrich) by soaking the film in a 5% solution of SHTMOS and dry ethanol for 3 to 12 hours. Before each silane functionalization step, the films were cleaned in 1:1 HCl and ethanol, and then rinsed well. The SHTMOS layer was then used as a linker between the film surface and a monolayer of gold nanoparticle seeds. The size of the gold particles was increased by soaking in a 0.1% HAuCl₄ solution catalyzed with 0.45 mM NH₂OH·HCl for 5 and 10 minutes, and then characterized with AFM and scanning electron microscope (SEM, Hitachi SU-70). The procedure for patterning the film surface by selective functionalization is summarized in Figure 4.12.
Figure 4.12: Simplified schematic of the procedure used to form a gold nanoparticle monolayer on the silica film surface by using functionalized layers of silane. Before the templates are removed from the film, a layer of OTMOS is formed at the available silica surface. The templates are then removed and cleaned, then functionalized with STMOS, which serves as the link between the silica film and gold nanoparticles. After forming a monolayer of gold nanoparticles, the size of the gold can be increased by soaking the film in an electroless growth solution.

Gold nanoparticles were formed by the reduction of 1 mM HAuCl₄ by 38.8 mM sodium citrate in a round bottom flask during a 15 minute reflux.¹⁰⁸ After refluxing, the nanoparticles were removed from the heat source and continued to be stirred for another 10 minutes. To ensure cleanliness, all glassware used to make the gold nanoparticles were cleaned with aqua regia and dried before use. UV-vis was used to confirm the gold identity and size, and was used to evaluate monolayer quality.
4.4.2 Results and Discussion

Characterization of the spin coated films with the AFM showed no significant differences between films formed on glassy carbon or on glass slides (Fig. 6). The films on glass have average thicknesses of 250 nm and nanowell diameters of 400 nm, corresponding with the size of the template. It was not necessary to block pinholes/defects in the film as electrochemistry experiments were not undertaken. If, however, this method was transferred to a conducting surface for electrochemical experiments, the general methods outlined in the previous section for blocking defect sites should be followed.

Before attempts to pattern the surface were made, the formation of a gold monolayer on a non-templated silica film was studied. After the spin coated film was completely dry, the substrate was soaked in chloroform for 3 hours, leaving behind the nanowells in the film with the previously described dimensions. The newly available silica surface was then functionalized with SHTMOS to provide a platform for the assembly of gold nanoparticles. To prevent adsorption of impurities, the films, once rinsed, were immediately laid flat in a gold colloid suspension containing ~10-30 nm gold nanoparticles. The kinetics of gold deposition on a thiol surface is relatively fast, but to ensure maximum gold formation the films remained in the seeding suspension for 3-12 hours. No noticeable difference between these times was observed. Upon removal, successfully prepared films had a red color, as expected for gold particles of this size. Films from control experiments, with no SHTMOS layer, retained their original color. This was also seen in early experiments before optimum cleaning methods were determined. A very clean silica film surface is required for the formation of a quality SHTMOS layer. The cleaning method that was ultimately chosen was soaking the template film for 30 minutes in a solution of 1:1 concentrated hydrochloric acid and ethanol. This method is
attractive because the cleaning solution did not need to be heated, and because the additional ethanol helps dissolve organic impurities into solution leading to greater gold surface coverage compared to the silica coated films cleaned only in HCl.

Once dried, the films were characterized using the AFM and SEM. AFM images showed a single layer of gold particles with reasonable close packing over the surface of the film, which was confirmed by the SEM images (Figure 4.13).

**Figure 4.13:** AFM images of a gold coated film. Top view (A) and 3D view (B), $z = 700$ nm. SEM image of gold coated film (C).

The maximum surface coverage of an untreated gold monolayer on a planar surface was shown in the literature to be approximately $30\%$. This amount can be increased by treating the nanoparticles with adsorbents to lessen repulsion between the gold, but this was not deemed necessary for this work. Surface coverage has also been shown to double for areas of positive
curvature compared to flat surfaces due to an increase in relative surface area. Negative curvature, therefore, should have a corresponding increase in coverage. The exact extent of coverage this for these films, however, has not been determined.

UV-vis spectrophotometry was used to confirm the elemental identity of the gold particles and to evaluate the quality of the monolayer. The transparent glass slide allowed for the measurement of the absorbance of the gold nanoparticles by shining UV-Vis radiation though the slide, the film, and the gold monolayer. The resulting spectra (Figure 4.14) had an absorbance peak at 530 nm, which is characteristic for gold nanoparticles in this size regime (10-30 nm). In addition, it has been previously reported in the literature that aggregation of gold nanoparticles on a surface produces a broad peak between 600 and 800 nm. Therefore, it is believed that the films contained only a single, non-aggregated layer of particles. Aggregation can also be determined by eye after the film is removed from the gold seed suspension, as these films have a blue or metallic color.

**Figure 4.14:** The UV-vis spectrum of a gold nanoparticle monolayer on a silica nanowell templated film. The characteristic absorbance peak of gold nanoparticles at 530 nm can be seen. The peak arises due to surface plasmon resonance.
It has also been shown in the literature that immobilized gold particles can be grown larger by electroless deposition.\textsuperscript{109} In this process, Au\textsuperscript{3+} reduction occurs by way of a catalyst, \( \text{NH}_2\text{OH-HCl} \), forming solid gold at the surface of the particle. The degree of growth is dependent on the concentration of the gold salt (HAuCl\textsubscript{4}) and the length of time the film is exposed to the growth solution. For this work, time was used to control the size of the particles. To provide consistency, the films were immersed in the same growth solution, and removed at the desired times (5 and 10 minutes). They were then washed, dried and characterized using the AFM. The AFM images showed clear increases in particle size, both inside and outside the nanowells and the size of the largest particles were estimated to be about 100 nm in diameter (Figure 4.15).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{images.png}
\caption{AFM images of films soaked in the gold growth solution for 5 (A) and 10 (B) minutes. (z scale: A = 600 nm, B = 800 nm)}
\end{figure}

In the second part of this work, attempts were made to strategically confine the gold nanoparticles in the nanowells and not on the surrounding regions (see figure 4.12). Patterning attempts were carried out by using OTMOS and DDMOS as blocking agents. The first attempts at patterning used OTMOS. In this procedure, the silica film was soaked in a solution of 5% OTMOS and dry ethanol before the PS templates where removed. If OTMOS successfully
formed a closely packed arrangement, then the surface of the silica not blocked by the template would be the long eight carbon chain ligands. It has been shown that single layers of non-polar organosilanes can be achieved and that the quality of the monolayer is chain-length dependent, so it was hypothesized that length of the n-octyltriethoxysilane ligand would provide the order and coverage needed to prevent the further condensation at the film surface. When the patterned films were soaked in chloroform and treated with the SHTMOS, the gold monolayer was observed to still have formed on entire film surface and not just inside the nanowells (Figure 4.16). Therefore it was believed that the original blocking monolayer did not successfully form, leaving almost the entire surface to be covered with the SHTMOS.

![Figure 4.16: An AFM image of an unsuccessful patterning attempt. An area of poor packing was chosen to show the extent of gold nanoparticle layer formation on the silica surface. (z=800 nm)](image)

The OTMOS monolayer formation was attempted both under room conditions and under nitrogen, with the same results. Therefore, humidity was eliminated as a possible interferent. Several alternative methods were also explored, such as changing the solvent for the OTMOS as well as using a second blocking monolayer. It was noted that in the literature, OTMOS was typically dissolved in organic solvents such as toluene, but toluene also dissolves the PS
The solvent hexane, which has good solubility with OTMOS but does not dissolve PS, replaced EtOH in the procedure and the experiment repeated. In addition, the silane DDMOS, which has two methyl ligands, was testing in the place of OTMOS as blocking agent. Unfortunately, no noticeable change was observed in either case.

Upon further consideration, it was determined that the failure of the two-step surface functionalization method was due to the requirement for a second harsh cleaning step after template removal and before the addition of the SHTMOS layer. To confirm this, the process was simplified by attempting the blocking method on bare glass slides and the same trend was observed. In addition, in the case of bare glass, the hydrophobic nature of the OTMOS monolayer became more pronounced. This hydrophobicity, however, was lost after even the shortest HCl:EtOH cleaning. Attempts to produce quality gold nanoparticle layers without the extensive cleaning before the formation of the thiol SAM were also not successful.

4.4.3 Conclusion

Silica thin films template with PS spheres were successfully modified with a monolayer of gold nanoparticles (size 15 – 30 nm). An electroless gold bath was used to enlarge the gold particles to approximately 100 nm, with intermediate sizes formed with less exposure to the bath. Several attempts were made to control the location of the the gold nanoparticles by selective formation of functionalized silica layers on the film surface. The organosilanes OTMOS and DDMOS were used to coat the areas outside the nanowells. It was found, however, that these silanes could not survive the necessary cleaning needed to form a quality SHTMOS layer inside the nanowells. The original films, however, still have potential for electrode use. In future work, it is suggested that the electroless growth of the gold nanoparticles be controlled such that the surface gold layer becomes conductive, but remains porous to allow hydration of the
underlying film. By having the silica film sandwiched between the substrate and the electrode, loss of analyte due to leaching could be minimized, as the species would be required to pass through the porous electrode before reaching the bulk solution.

4.5 Conclusion

In this work, two methods for integrating metal nanoparticles into “nanowell” modified silica thin films were explored. In the first method, electrodeposition was used to produce copper particles at the bottom of the nanowells in the template silica films. Particles with heights of 90 nm and 110 nm were produced by varying the deposition time from 30 to 60 seconds respectfully. The deposition of copper was localized at the exposed nanowell surface by blocking defects in the film by way of electro-assisted silica deposition. In the second method, silica films template with PS spheres were used as substrates for the addition of a gold nanoparticle layer. The size and particle distance was successfully controlled through timed exposure to an electroless growth solution, increasing the gold particle size from approximately 15 nm to 100 nm.
Chapter 5: Size and Shape Control of Gold Nanodeposits in an Array of Silica Nanowells on a Gold Electrode

5.1 Introduction

The major objective of this study was to create macroporous silica thin film electrodes with gold nanoparticles of tunable size and shape at the bottom of each well. The nanoparticles’ effect on the electrochemical response through the film was studied, particularly with respect to charge. Portions of the material presented here have been published in the International Journal of Electrochemistry.

5.2 Background and Purpose

Patterned or structured electrodes have been shown to have considerable importance in many areas of science and technology, particularly electroanalytical applications. The development of strategies for the fabrication of such materials is needed as the desire to make smaller, more sensitive, and more selective devices becomes increasingly important. One means to create structured electrodes involves strategically combining sol-gel chemistry and templating together. As discussed in chapter one, a suitable template can be doped into a silica sol and cast on a surface such as an electrode. Upon subsequent removal of the template, voids remain in the microporous oxide network. In prior work described in chapter 4, we have shown how an array of silica nanowells can be formed on an electrode surface and how these structured electrodes can be used to controllably grow copper nanoparticles through electrochemical plating. The success of this method depends on the extent at which, upon removal of the latex sphere, the underlying electrode surface is exposed, enabling it to be used as a microelectrode. Providing there are no defects (pin holes) in the insulating silica surrounding the nanowells, the
electrochemistry only takes place in the nanowell, thus restricting growth to this area. The advantages of growing arrays of nanoparticles within a porous inorganic network using this approach are (a) the interparticle spacing between nanoparticles can be controlled by the size of the template used to form the nanowell, (b) the size and shape of the resultant nanoparticles/nanostructures can be controlled by the size and shape of the nanowell, and (c) the silica support helps prevent aggregation of the nanoparticles as they begin to grow larger.

From an electroanalytical point of view, enlarging the conductive domains located at the bottom of the nanowell also provide a means to potentially increase the sensitivity of the microelectrode array. The importance of nanoparticle arrays in electroanalytical chemistry has been well documented in the literature.

In this work we describe an alternative approach for expanding the conductive domain at the bottom of the porous nanowells that is less sensitive to defect sites (pin holes) in the silica framework and more amenable to different metals. A major challenge for electroplating metals into templated silica films that contain pinholes is that metal growth at the defects in the film is not consistent with the growth that occurs in the nanowells, sometimes leading to much larger deposits. While methods have been described both in the literature and in this dissertation for blocking pinholes, they involve the use of organosilanes that can change the chemistry of the silica surface or require the electro-assisted deposition of silica, a process that can add an extra day to electrode construction time. Therefore, the alternative method of electroless deposition was explored. The procedure involves the formation of the silica nanowells on a gold electrode using a colloidal crystal of PS latex spheres as the soluble endotemplate followed by the electroless growth of the gold microelectrode that is exposed when the template is removed. The height of the gold nanoparticles can be easily adjusted by changing the incubation time in the
electroless plating solution. In related work recently published, the silica nanowells were formed from the vapor deposition of dimethyldichlorosilane around an array of latex spheres formed on quartz. To form the gold nanoparticle array, the exposed surface (hydroxides) was immersed in a solution of tin ions, followed by silver ions, and then gold ions. In another report, shallow nanowells were formed on a silicon wafer via the vapor deposition of chlorosilanes around the latex sphere. The hydroxylated surface located at the bottom of the nanowells was then functionalized with mercaptopropyltrimethoxysilane and subsequently used to bind gold nanoparticles. In contrast to these reports, the current method is a one-step method that does not require multiple reaction steps or chemical modification. It utilizes the sol-gel process, which means various reagents can be entrapped into the microporous network to create a chemical sensor, and it is directly formed on an electrode surface and thus making it a structured electrode ideally suited for electroanalytical applications.

5.3 Methods

5.3.1 Spin cast method for colloidal crystal formation

Gold electrodes (EMF, Ithaca NY) were cut to ~ 1.5 cm x 1.5 cm, and then cleaned by successive sonications in ethanol, water, and water for 15 minutes each, followed by plasma cleaning at 10 W (Southbay PE-2000, DC bias of -100 V) to make the slides hydrophilic. The silica sol was prepared by stirring 0.25 mL tetramethoxysilane (TMOS, 99%, Acros), 1.20 mL methanol (MeOH), 1.15 mL water, and 0.015 mL 0.1 M HCl for 30 minutes, then aged for two days. Sodium dodecylsulfate (SDS) was added (5 mM) to the sol before it was mixed with 0.4 \( \mu \)m polystyrene latex spheres (PS, from Invitrogen, formally Interfacial Dynamics Company (IDC), sulfate stabilized, 8%) at a 1:1 (v/v%) ratio. The SDS was added as a wetting agent to improve the quality of the sphere packing. The solution was viciously mixed, then pipetted on
to the surface of a clean gold electrode and spin coated at 3000 rpm for 30 seconds. After the films were dried overnight on the bench top, they were submerged in chloroform for three hours to remove the PS spheres.

5.3.2 Evaporative method for colloidal crystal formation

Gold (Au) electrodes were cut into ~ 1.5 cm x 1.5 cm squares and cleaned by successive sonications in 2-propanol and water followed by boiling piranha solution (7:3) for 5 minutes. The electrodes were rinsed well with water and ethanol and soaked in a 5 mM cysteamine solution in ethanol for 24 hours. To form the colloidal crystal, a modified version of the vertical deposition method was used. In this method, the evaporation of the solvent lead to capillary forces forming at the liquid/vapor interface. A meniscus forms along the substrate as the solvent evaporates, resulting in the PS spheres moving up the thin layer of solvent and packing in close packing arrangement. In this work, the modified electrode was vertically placed in a glass vial and a mixture of ethanol and 0.5 μm spheres in a 33:1 V/V ratio added (figure 5.1).
Figure 5.1: Simplified schematic of the evaporative sphere packing method. Vials with cysteamine modified gold slides were submerged in a solution of ethanol and 0.5 µm spheres (33:1 V/V) heated to 50°C by a water bath. Spheres form a close-packed colloidal crystal due to interparticle capillary forces produced by the meniscus at the evaporating interface.

The solution was slowly evaporated at 50 °C by placing the vial in a thermostatted oven or a water bath. A closed water bath was preferred because it tended to minimize fluctuations in temperature and ambient humidity. Evaporation took approximately 24 hours and resulted in a well-packed, single layer (or near single layer) of spheres on the gold electrode.

To form the silica nanowells on the surface of the gold electrode, a silica sol (0.2 mL TMOS, 0.06 mL MTMOS (methyltrimethoxysilane, 97%, Acros), 0.1 mL MeOH, 0.3 mL water, 0.06 mL 0.1M HCl, stirred for 1 hour) was diluted with ethanol 1:100, and the diluted sol was
then spin coated over the packed spheres at 8000 or 6000 rpm for 60 seconds. To ensure the sol effectively penetrated the voids in the colloidal crystal, the substrates were first plasma cleaned for 2 minutes at 10 W (DC bias of -100 V) and the diluted sol also was allowed to rest on the substrate for one minute prior to electrode rotation. The films were dried overnight and the PS spheres were removed via soaking in chloroform to form the silica nanowells on the gold electrode. In some cases, to further hydrolyze the sol, 10 µL of 0.16 M KOH was added to the sol and stirred for an additional 30 minutes prior to spin coating.

5.3.3 Electroless gold deposition

To insure that all PS was removed from the film, the substrates were rinsed with fresh chloroform and plasma cleaned for 2 minutes at 15 W (DC bias of -150 V) prior to submerging in a 1:100 (v/v%) solution of hydrogen tetrachloroaurate (1 mM) and NH$_2$OH-HCl (0.45 mM) for varying time lengths. During deposition, the solution was placed on a shaker at 180 rpm. The solution was replaced with a fresh solution at 15 minute intervals. The films were rinsed with water then dried on the bench before further characterization.

5.3.4 Electrochemistry

Electrochemistry was performed in a three-electrode cell using a saturated Ag/AgCl electrode as a reference and a Pt wire as the auxiliary on a CH instruments potentiostat. The electrode area was defined by a quarter inch diameter hole punched into a piece of Teflon tape and copper tape was attached to the edge of the gold slide as a lead. Ferrocene methanol (1 mM) and potassium ferricyanide (1 mM) in 0.1 M KCl were used as the redox probes.

5.4 Results and Discussion

In the present work, two methods were used to form the silica nanowells. The first method (Figure 5.2, method 1) is the more traditional way to make sol-gel derived films that first
involves doping the silica sol with latex spheres and spin coating the composite sol on the electrode surface. In the second method (Figure 5.2, method 2), a near monolayer of spheres was formed first, followed by spin coating an undoped silica sol on this surface. These structured electrodes are then used as reaction vessels to electrolessly grow gold nanoparticles of varying height and width, defined in part by the size of the nanowell and the electroless growth conditions. It is known in the literature that exposure of gold nanoparticles to HAuCl4 in the presence of the reducing agent NH2OH, either in solution or immobilized on a substrate, results in particle growth.81 This method was specifically explored in chapter 4, section 4, where a HAuCl4 electroless growth solution was used to enlarge gold nanoparticles that had been attached as a monolayer to a silica thin film template with PS spheres. It was determined that the exposed gold electrode located at the bottom of the silica nanowell can be used as a reduction site for gold deposition and nanoparticles were not necessary to achieve this affect. This same method could be applied to any gold surface of limited dimensions such as the small area of gold exposed at the bottom of the nanowell upon template removal. The size/microstructure of the gold deposits can be controlled by the length of exposure time to the growth solution (Figure 5.2, bottom) and the area exposed to solution upon removal of the PS latex sphere. No prior modification of the surface is necessary.
5.4.1 Gold Nanoparticles Formed in Silica Nanowell Electrodes Prepared via Method 1

In this method, silica sols are doped with PS spheres and then spin cast on the electrode surface. The packing of the spheres on the surface of the electrode depends on many factors including surface charge (electrostatic repulsion), surface hydrophilicity, and surface cleanliness. Figure 5.3 A shows a tapping mode Atomic Force Microscope (AFM, Veeco Multimode SPM) image of the surface of a bare gold electrode. As can be seen, the bare electrode consists of a flat surface with small, random roughness. After spin coating the silica sol/latex sphere mixture on the gold electrode, localized regions of the surface show a hexagonally packed monolayer of the PS spheres (Fig. 5.3 B). After template removal, silica nanowells are formed on the surface as shown in Figure 5.3 C. The depth of the nanowell largely depends on the speed at which the sphere-doped sol is cast, the viscosity of the sol, and size of the latex sphere. At a spin speed of 3000 rpm and a sphere size of 400 µm, the
nanowells have an average dimension of 500 nm in diameter and a nanowell depth of 300 nm. These nanowells are open at the top (evident in the AFM images) and the bottom (evident from AFM section scans and gold growth (described below)) thus exposing the underlying nanostructured surface.

**Figure 5.3:** Tapping mode AFM images (5 µm x 5 µm) of (a) a bare gold electrode, (b) hexagonally packed PS spheres in a silica film coated gold electrode, (c) the nanowells formed after chemical removal of the PS spheres.

The nanowells, such as those shown in Figure 5.3 C, can be used as reaction vessels to electrolessly grow gold nanoparticles. In prior work, we utilized a similar electroless deposition procedure to grow nanostructured gold wires in micron size channels formed from bacteria. In that work, the bacteria/sol template system was cast onto a glass slide that has already been modified with a monolayer of gold nanoparticles. Upon removal of the bacteria, portions of the underlying gold monolayer became exposed and thus were available for electroless growth. It was hypothesized that the exposed gold electrode located at the bottom of the silica nanowell could be used as a reduction site for gold deposition and that nanoparticles would not be necessary to achieve this affect for the PS template/silica film system on a gold electrode.

Figure 5.4 A shows an area of the substrate not covered by packed spheres, which, due to the generally poor interaction between gold and silica, results in almost no film formation.
Exposure of the bare gold electrode surface to the gold growth solution resulted in increased roughness of the surface, with the occasional large asymmetrical gold deposit. The electroless deposition of gold within the nanowells, however, was found to be markedly different compared to that observed at a bare gold electrode, Figure 5.4 B and 5.4 C. Electroless deposition in the nanowells produced (near) sphere-like deposits of consistent size throughout the film. The growth of single particles in the nanowells is likely due to there being only a few exposed points of roughness from the underlying substrate. A single small growth is formed at those points, and then the particle increases in the same manner as an anchored, pre-generated nanoparticle formed in solution, free from competition and eventual merger with adjacent deposition sites as seen in the bare substrate. This growth progression is seen in the time dependent growth study. A one-minute exposure results in the formation of a deposit with an observable height of about ~20 nm (Fig. 5.4 B), which is similar to gold nanoparticles typically generated in solution. As the exposure time continues, the particle increases in size while retaining its basic shape (Fig. 5.4 C). There appeared to be a limit to this growth, however, as it was observed that growth would not continue past a height of ~150 nm (Fig. 5.4 D), even when left in the growth solution overnight. Figure 5.4 E shows an overlay of the cross sections of the nanowells before and after electroless deposition, ranging from particle formation to the growth limit. As can be seen, the conductive domain located at the bottom of the nanowell progressively increases as the incubation time in the growth solution increases.
Figure 5.4: 5 μm x 5 μm AFM images of gold deposited on (A) a bare gold electrode (electroless deposition for 6 minutes) and in silica nanowells grown by electroless deposition for (B) 1 minute, (C) 15 minute and (D) 3 hour exposure times. (E) Cross-section plots overlaid for clarity (blue = 1 min, red = 15 min, green = 3 hours)

5.4.2 Gold Nanoparticles Formed in Silica Nanowell Electrodes Prepared via Method 2

The spin coating method, while simple and easy to do, does not produce the nanowell arrays with significant long range order on gold electrodes that would likely be required for
electroanalytical applications. Part of the problem likely results from the surface of gold not being easily wetted by the silica sol, as well as the lack of available hydroxyl groups for the silica to bind with.\textsuperscript{129, 130} To address this short coming, the method used to pack the colloidal crystal on the electrode surface was separated from silica film formation. There have been many methods described in the literature for the formation of colloidal crystals on gold with long range order.\textsuperscript{35, 52, 128, 131} Many of these published methods are ideally suited for forming multilayer films, which would be more challenging in this study. In this work, the method with the greatest success for forming a monolayer or near-monolayer of PS spheres with long range order is a variant of the vertical deposition/solvent evaporation method.\textsuperscript{35, 126} As the solvent slowly evaporates, a compact layer of spheres remain on the surface due to capillary forces.\textsuperscript{126} In this work, the concentration of latex spheres in ethanol was kept relatively low (1:33 V/V PS spheres:EtOH) and evaporation took place at an elevated temperature (50 \degree C). In contrast to a room temperature based deposition, a packed monolayer (or near monolayer) of PS spheres can be formed in 24 hours. The system was originally placed in an oven, but it was observed that fluctuation in the environment, either due to the oven cycling between on and off to maintain a consistent temperature or due to fluctuations in ambient humidity resulted in strips in the sphere packing (Fig. 5.5).
Figure 5.5: Optical images of long range PS sphere packing on gold slides modified with cysteamine. Packing was accomplished by the evaporation method in an oven at 50°C. Environmental fluctuations produced stripped patterns of inconsistent packing. Darker areas correspond to multilayers of spheres, whereas the beige color corresponds to well-packed single layers. Finally, the light green area is produced by poorly packed spheres in a single layer.

Heating with a water bath minimizes both of these types of fluctuations by providing a more consistent temperature and saturating the humidity. This method produced a vastly superior colloidal crystal with long range packing of spheres, mostly in a single layer, compared to the spin coating method. Figure 5.6 shows representative 157 x 110 µm Scanning Electron Microscope (SEM, Hitachi FE-SEM SU-70, 5 kV, platinum/gold sputter to minimize charging effects) of a single (or near single layer) of PS spheres on a gold electrode formed by spin coating the sphere-doped sol on a gold electrode (Fig. 5.6 A) or via the vertical deposition method (Fig. 5.6 B). While the spin coated packed electrode shows good packing in localized areas, the packing is web-like over the entire surface, leaving a large amount of the substrate exposed. The vertical deposition method, however, exhibits good packing on both the
microscopic and macroscopic length scales (Fig. 5.6 B). In Figure 5.6 C, an SEM of the nanowells formed after template removal is shown.

![SEM images of typical sphere packing on a gold electrode using (A) the spin coating method and (B) the vertical deposition method. (C) SEM of the nanowells formed in a film prepared via the vertical deposition method. (Scale bar: A: 500 µm, B: 50 µm, C: 10 µm)](image)

**Figure 5.6:** SEM images of typical sphere packing on a gold electrode using (A) the spin coating method and (B) the vertical deposition method. (C) SEM of the nanowells formed in a film prepared via the vertical deposition method. (Scale bar: A: 500 µm, B: 50 µm, C: 10 µm)

Once the colloidal crystal was formed on the gold electrode, a silica sol could be spin cast directly over this layer of spheres to ultimately form the silica nanowells on the gold electrode (Fig. 5.6 C). The silica nanowells produced by this method have many similarities to that of the doping method (described above) in that dimensions of the nanowells are similar. One major difference is in the introduction of variation in the diameter of the underlying exposed electrode surface (the conductive domain), which has consequences for the electroless deposition of gold. The variables that will likely influence the diameter of the bottom of the nanowell include the degree at which the sol is hydrolyzed and condensed (its age), the viscosity of the sol (dilution factor), the time the sol is placed on the surface before the electrode is rotated, and the speed at
which the sol is cast over the packed spheres. Fresh silane precursors and faster spin speeds (8000 rpm) tend to produce wider bottoms, while aged silane (one day) and slower speeds (6000 rpm) produce narrower bottoms. Because speed influences film thickness, the original sol was diluted more when the spin speed was decreased to retain nearly the same nanowell depth. Figure 5.7 shows representative examples of the sizes of the conductive domain formed at the bottom of the nanowells on a gold electrode. The “wide bottom” nanowells expose a substrate area of about 70-80% that of the mouth of the nanowell, whereas the “narrow bottom” nanowells expose roughly 30-40%. The sides of the nanowell shown in Figure 5.7 A exhibit a more particle-like surface relative to that observed in the nanowell shown in Figure 5.7 B. These observed differences in the microstructure of the silica network are attributed to differences in the age of the silane precursors prior to making the sol. In Figure 5.7 B, the silane precursors were freshly removed from a nitrogen environment and immediately used to prepare the sol whereas in Figure 5.7 A, the silanes were partially hydrolyzed via exposure to air prior to use.

![Figure 5.7: SEM images of (A) a narrow and (B) a wide conductive domain located at bottom of the silica nanowells on a gold electrode. (Scale bar: A: 150 nm, B: 250 nm)](image-url)
Films that exhibited large conductive domains at the bottom of the nanowells produced gold deposits with asymmetric shapes and sizes (Fig 5.8 B inset). Films with smaller conductive domains produced deposits consistent with that observed with the doped films (Fig. 5.4), with a single sphere-like particle (Fig 5.8 A inset). The growth in the wide bottom appears to be a hybrid of the growth patterns on the bare gold surface and in the narrow bottom wells. The shape of the deposit reflects the natural roughness of the gold surface under the film, but is able to grow past the point commonly seen on the bare surface, similar to the nanowells with smaller conductive domains. It is believed that this is the result of the wider conductive domains having several initial growth sites within the nanowell that merge together at longer growth times. By combining the vertical deposition method of film formation with the gold growth method utilized in the spin coated slides, a large, well-packed array of nanowells containing gold particles of controllable size was formed (Figure 5.8).

![Figure 5.8: SEM images of (A) narrow bottom and (B) and wide bottom films. Insets display representative gold deposits within silica nanowells. (Scale bars: 20 µm, inset: 250 nm)](image)

### 5.4.3. Electrochemistry

The voltammetry of ferrocene methanol (FcCH$_2$OH) and potassium ferricyanide (Fe(CN)$_6^{3-}$) were examined at electrodes prepared via method 2. In Figure 5.9 A, cyclic
voltammograms (CVs) for FcCH$_2$OH at a bare gold electrode and a silica film/sphere coated electrode can be observed. As expected, at a bare gold electrode, the voltammogram has a diffusion controlled shape characteristic of a redox probe in solution transferring electrons at the surface of a large planar electrode. At the sphere coated electrode, different electrochemical responses were observed depending on the quality of the packing of the latex spheres (and the redox probe, described below). When the electrode contained closely spaced defects, such as those formed at surface dislocations and areas not coated with silica, and/or at pinholes between spheres, the CV of FcCH$_2$OH looks almost identical to that obtained at a bare electrode. In this case, the diffusion layers at the individual defect sites overlap and the surface appears as one big electrode.$^{8,132}$ In contrast, when the electrode is covered with a densely packed layer of spheres with few defects and better long-range packing, the oxidation of ferrocene methanol is hindered and the voltammetric curve is suppressed relative to that observed at a bare electrode. Upon removal of the spheres leaving behind a closely spaced array of nanowells, the voltammetry once again looks like that observed at a bare electrode because of the overlap of diffusion layers at the closely spaced nanowells, Figure 5.9 B.$^{102}$ Once the spheres are removed, the quality of the packing of the colloidal crystal (i.e., the presence of defects/pin holes) cannot be assessed from the voltammetry because the electrochemistry that takes place at a defect sites cannot be distinguished from the electrochemistry that takes place in the nanowell.$^{102}$ Further growth of the exposed gold electrode via electroless deposition for 45 min does not produce distinct changes: the voltammetry of FcCH$_2$OH looks identical to that observed at nanowell electrode.
Figure 5.9: CVs of ferrocene methanol (1 mM) in 0.1 M KCl at 0.1 V/s. Panel A: **Red**: bare gold, **Blue**: Silica film/sphere coated electrode with many defects in the colloidal crystal, **Black**: Silica film/sphere coated electrode with fewer defects in the colloidal crystal. Panel B: **Red**: Bare gold, **Blue**: after sphere removal via soaking in chloroform for 3 hrs, **Black**: after particle growth for 45 minutes.

Very different results were observed using Fe(CN)$_6^{3-}$ as the redox probe. Fe(CN)$_6^{3-}$ is very similar in size to FcCH$_2$OH, but is negatively charged. Thus, electrostatic interactions will be more important compared to the case for FcCH$_2$OH, which is initially neutral. Under near-netural pH conditions, the silica matrix will be negatively charged. Figure 5.10 shows the CVs at a bare electrode, a silica film/sphere coated electrode, the nanowell electrode, and the nanowell electrode with the conducting Au domains enlarged. In contrast to that observed using FcCH$_2$OH, a significantly diminished response is observed for Fe(CN)$_6^{3-}$ at the silica/sphere coated electrode. The voltammetric curve exhibits a sigmoidal shaped response indicative of the presence of pinholes/defects that are relatively far apart. After removal of the spheres, the
voltammetric shape remains sigmoidal-like but increases in size. The negatively charged silica matrix obviously hinders access of Fe(CN)$_6^{3-}$ to the underlying gold electrode relative to that observed for FeCH$_2$OH. By increasing the size of the Au conducting domain via electroless deposition, electrostatic repulsion between the redox probe and the silica framework is lessened and the CV of Fe(CN)$_6^{3-}$ more closely resembles that observed at the bare electrode.

![Figure 5.10](image)

Figure 5.10. CVs of potassium ferricyanide (1 mM) in 0.1 M KCl at 0.1 V/s. Red: bare gold, Blue: silica film/sphere coated electrode, Black: silica film after sphere removal via soaking in chloroform for 3 hrs, Green: silica film after gold particle growth for 45 minutes.

5.5 Conclusion

Nanostructured gold electrodes were created through the selective electroless deposition of gold into nanowells formed in a silica film on a gold electrode. The size and shape of the deposited particles was controlled via exposure time and changes in film characteristics. Method 1, which involved spin coating a doped sol on a gold electrode, was simple, easy, and yielded nanowells that all had similar size conductive domains. When used as a chemical reactor to electrolessly expand the conductive domain, uniform gold deposits were obtained. The nanowells, however, were not uniformly distributed/packed across the entire surface of the electrode, potentially limiting their application in electroanalytical chemistry. Method 2, while a more time consuming 2-step method, yielded a much more uniformly packed array of nanowells. The conductive domains located at the bottom of the nanowells, however, varied in size. Both
nanowells with large conductive domains and nanowells with small conductive domains were obtained by judiciously changing the sol-gel processing conditions. The size of the conductive domain significantly influenced the size and structure of the gold deposit electrolessly formed at the bottom of the well. Initial electrochemistry experiments using two different redox probes, ferrocene methanol and potassium ferricyanide, showed interesting results. Most significantly, the shape of the cyclic voltammetric curve and the magnitude of the Faradaic current were strongly dependent on the long-range packing and the presence of defects in the film and the redox probe in solution. For potassium ferricyanide, enlargement in the conductive domains lessens electrostatic repulsion effects observed from the silica network and results in a more traditional shaped voltammetric similar to that obtained a bare electrode.
Chapter 6: Electro-assisted Deposition of Silica Nanotubes and Nanopillars

6.1. Introduction

The objective of this work was to develop self-supported high-aspect ratio silica materials using electrochemically assisted deposition. This was accomplished by converting track-etched membranes into electrodes, submerging them in a sol, and applying a sufficiently negative potential. After the formation of the tubes, the membrane was removed, either entirely by dissolving with an organic solvent or partially with plasma etching. The resulting structures formed were hollow nanotubes, partially filled tubes or solid nanopillars depending on the experimental conditions. They were thoroughly characterized using atomic force microscopy and scanning electron microscopy.

Figure 6.1: Simplified schematic some of the high-aspect ratio silica materials produced in this work. After silica nanotubes were obtained, the track-etched membranes were either completely removed (solvent) or partially removed (plasma etching). Silica nanopillars were obtained by filling in the silica nanotubes partially or completely with additional silica.

6.2. Background

High-aspect ratio silica nanotubes and wires, with their easy functionalization, hydrophilicity, and mechanical stability, have considerable potential for applications in separations, catalysis, sensing and as nano-containers. As described in recent reviews and papers, many techniques have been introduced to create silica nanotubes and other high aspect ratio silica structures. Some techniques, such as the formation of 12 nm x 1 mm silica
nanowires from molten Ga by chemical vapor deposition (920 °C), 20 nm x 10 µm silica wires from the gold nanoparticle catalyzed reaction of SiCl₄ (1000 °C), and 50-200 nm x 8 µm self-supported silica nanotubes from the multi-step oxidation and etching of existing silicon wires (800-1000 °C), involve high temperatures.⁴⁶,¹³⁴-¹³⁶ By contrast, sol-gel techniques can be used to form silica nanotube and wires, but under bench-top conditions.¹³³

Sol-gel methods for creating high-aspect ratio silica materials have utilized templating methods to direct the condensation of silica into the desired form.⁴⁶, ⁴⁹, ¹³³ For example, silica nanotubes have been created using the reverse-microemulsion-mediated sol-gel method.¹³⁷ In this method, a surfactant was added to an apolar solvent mixed with TEOS, which then formed a tube by reacting at the reverse-micelle’s water-oil interface after the addition of water and FeCl₃. Carboxylic acids are other solution based templates for forming silica nanotubes of a variety of sizes.¹³⁸ Mixtures of DL-tartartic acid, TEOS, ammonia and water have been shown to form tubes with dimensions of 0.1-1µm x 200-300 µm and similar citric acid/TEOS/ammonia mixtures have produced 50-500 nm x 0.5-20 µm tubes.¹³⁹

Membrane templating coupled with sol-gel chemistry is another method that has been used to create silica nanostructures.⁴⁹, ¹⁴⁰ Two examples of nanopore membranes commercially available are (1) AAO membranes, which consist of membranes with thickness typically between 10 to 100 µm and ordered pores (density: 10¹¹ cm⁻²) and (2) track-etched membranes, which consist of membranes with thickness typically between 6 to 20 µm and randomly arranged pores (density: 10⁹ cm⁻²).⁴⁷ Track-etched membranes were used in this work and a cartoon of the top surface and side view of a track-etched membrane is given in Figure 6.2.
Figure 6.2: Simplified schematic of a track-etched membrane with randomly arranged pores. The side view shows how some pores may be at an angle and the top view show how some pores may overlap on the surface.

Typical methods for forming silica structures inside the pores of membranes such as polymer track-etched membrane or anodic aluminum oxide membranes (AAO) involved capillary action filling the membrane pores with the sol solution.\textsuperscript{49} If the pores are completely filled, then solid nanorods are formed and if the sol only wets the pore surface, nanotubes are formed. In the earliest form of this technique, AAO membranes with 200 nm pores was simply dipped into a sol (SiO\textsubscript{2} or TiO\textsubscript{2}) for 5 seconds to produce tubes with thin walls, 25 seconds for tubes with thick walls, or 60 seconds for solid rods.\textsuperscript{49} The method was further developed to gain better control over the thickness of the formed nanotube walls.\textsuperscript{141} In this process, known as the surface sol-gel method, an AAO membrane was submerged into a solution of SiCl\textsubscript{4} and chloroform, moved to a chloroform wash, and then water for tube formation.\textsuperscript{141} In the first step, some SiCl\textsubscript{4} adsorbed on the surface of the membrane while the unadsorbed silane was washed away in the chloroform wash, to leave just a thin layer to be hydrolyzed upon addition of water. These methods are very straightforward but have several drawbacks. Despite improvements made with the surface sol-gel method, the thickness of the tube can be hard to control.\textsuperscript{133} Also, the nanotubes are generally fragile and do not remain oriented after the AAO template is removed.\textsuperscript{142} Membrane templating for silica nanotubes does have a major advantage that makes it an attractive method for further development. Before the silica nanotubes are removed from
the membrane, there is an opportunity to chemically functionalize just the inside of the tube. Different chemical characteristics on the inside and outside of the nanotube could be used in sensing or separations applications.

A potential alternative method for forming silica nanotubes or pillars in porous membranes is by using electro-assisted silica deposition. In this process, water or oxygen are reduced at an electrode to produce hydroxide. The localized increase in pH drives the condensation of silica in the area around the electrode. Some work has been published on this general method. For example, metal oxide nanowires such as TiO$_2$ were electrodeposited into AAO membranes with diameters below 40 nm and lengths between 2 and 10 µm. They observed that the length of the nanowires could be control by increasing the deposition time. As described below, a very different result, however, was found in this work, which uses track-etched membranes with pore diameters of 100 nm to 400 nm, suggesting that the formation of silica in a tubular structure by electrochemical methods may be size dependent.

In this chapter, a method for the growth of silica nanotubes and solid pillars in polymer track-etched membranes by electro-assisted silica deposition was developed and evaluated. Unlike deposition in small diameter AAO membranes, the length of the formed silica tubes was found to be dependent of the thickness of the membrane. It was also found that after the formation of the silica nanotube, additional silica growth occurred lengthwise, and filled in the tube and resulting in a pillar structure. In addition, multiple depositions with fresh sols resulted in further silica growth within the nanotubes, suggesting that functionalized gradient pillars could be formed. The method also allowed for a large degree of physical and chemical variation and nanotubes with controllable exposed lengths, diameters, chemical functionality and porosity to be produced.
6.3 Methods

6.3.1 Electrode constructions and electrochemical cell

200 nm, 400 nm, and 100 nm pore track-etched polycarbonate membranes (Whatman) where coated with a 100 nm layer of gold by LGA films (Ca) via sputtering. AFM showed that the deposited gold layer covered the surface of the polymer completely and the pores only partially, resulting in the membrane being open on both sides (Fig. 6.3). From AFM images, the average pore opening was found to be ~170 nm in diameter.

Figure 6.3: Simplified schematic of a gold coated track-etched membrane pore (200 diameter). AFM was used to confirm that the membrane pores remained partially open (170 nm diameter) after the gold layer was deposited.

To construct the electrodes, the coated membranes were cut to 0.5 cm x 1 cm with a razor blade. The gold side of the membrane was then partially attached to a 3 inch piece of copper tape. Teflon tape (PTFE, CS Hyde) was used to completely cover the gold side of the membrane and enough of the uncoated side to completely cover the area around the copper tape (Fig. 6.4). The Teflon tape also was extended up the copper tape at least an additional inch to prevent any contact with the solution.
Figure 6.4: Simplified schematic of both sides of the membrane electrodes. Copper tape was attached to the gold side of the membrane and then both the copper and the gold were covered with Teflon tape. As a result, the only available surface for electrochemistry is the gold at the bottom of each membrane pore.

All electrochemical studies were carried out on a CH instruments potentiostat in a three electrode cell using the aforementioned electrode as the working electrode, a Ag/AgCl wire as reference and graphite rod as the counter. A Ag/AgCl wire was used instead of a traditional Ag/AgCl reference electrode to prevent clogging of the frit with silica. The three electrodes were immersed into the sol by a rubber stopper with three holes approximately 1 cm apart. This allowed for a consistent distance between the electrodes between experiments. The electrodes were immersed a distance of 4 cm from the bottom of the 7 dram glass shell vial that served as the cell. A 1.5 inch stir bar, just smaller than the diameter of the shell vial, was placed at the bottom of the sol prior to completing the deposition. To ensure consistent and precise stir speed, a digital stir plate (Scientific Industries, Inc.) was used. To minimize effects of heat from the stir plate during long deposition times, the sol was separated from the surface of the stir plate by a petri dish and a wooden cell holder. Figure 6.5 illustrates the electrochemical cell set up.
Figure 6.5: Simplified schematic of the 3 electrode electrochemical cell used in this work. A rubber stopper was used to hang the electrode 2 cm from the stir bar. In addition to the nanopore membrane electrode, the other electrodes used were a Ag/AgCl wire as reference and a graphite rod as counter.

6.3.2 Deposition of silica into 200 nm pore membrane electrode

Silica sols were prepared by stirring 1 or 0.5 mL TMOS, 5 mL ethanol, 4 mL water, and 1 mL 0.2 M KCl for 30 minutes or by mixing immediately before the experiment. Gold coated 200 nm track-etched membranes were used to create working electrodes as previously described and the electrodes were immersed in the solution. Potentials used for the amperometric deposition of silica ranged from -0.4 V to -1.2 V and deposition times ranged from 15 minutes to 2 hours. Some depositions were carried out multiple times, where the electrodes were removed and rinsed with water, dried with a stream of nitrogen, and then returned to the cell with a fresh sol. When depositions were complete, the membrane electrodes were removed from the sol, rinsed with water or ethanol and dried overnight on the bench.

After the electrodes were completely dried, the exposed membrane was cut from the electrode and two methods were used to remove the membrane. First, the membrane was partially removed by plasma etching (Southbay PE-2000, DC bias of -700 V) for 70 minutes, or 30 minutes in select experiments. There was some variation in the DC bias over the time period, so the bias was adjusted to keep it at -700 ± 30 V. If the membrane was etched from the side
with the gold electrode, the gold layer was first removed by peeling or a 20 second soak in aqua regia. The exposed silica was then imaged using scanning electron microscopy (SEM, Hitachi SU-70, platinum/gold sputter to minimize charging effects). In the second method, the membranes, once cut from the electrode, were soaked in chloroform for 10 minutes. The membrane was then transferred to a fresh volume of chloroform for several more minutes (~ 5). In some cases, the chloroform and membrane was centrifuged at 4000 rpm for 3 minutes during this step. The membrane was then dipped into fresh chloroform once more to ensure complete removal of the polymer and then allowed to dry on the bench. In control experiments, the previously described experimental procedures were repeated in entirety, except that a potential was not applied.

6.3.3 Further variation in the method

The following experiment uses the method described in 6.3.2 in its entirety except where otherwise indicated. A brief description of the specific experimental conditions is given. The diameter of the nanotubes were varied by using membranes with pore sizes of 100 nm and 400 nm in place of the 200 nm membranes in the procedure described in section 6.3.2, with the specific variables of TMOS: 1 mL, stir speed: 400 rpm, deposition potential: -0.6 V and deposition time: 2 hours.

Additional chemical functionality was introduced by modifying the sol prepared in section 6.3.2. The recipe used was 0.2 mL of 3-mercaptopropyl trimethoxysilane (SHTMOS, Aldrich), 0.5 mL of TMOS, 5 mL ethanol, 4 mL of water, and 1 mL 0.2 M KCl. Other specific experimental conditions were stir speed: 400 rpm, deposition potential: -0.6 V and deposition time: 2 hours.
Macropores were introduced to the tubes and pillars by PS sphere template integration. Aqueous suspensions of polystyrene microspheres functionalized by sulfate, amine or epoxy/sulfate with diameters ranging from 60 nm to 100 nm were obtained from Invitrogen (formally Interfacial Dynamics Corporation (IDC), 1.4 wt/v% for sulfate-PS, 2.0 wt/v% for amine-PS, and 3.8 wt/v% for PS-Epoxy/Sulfate). The pores of the membrane electrodes were filled with templates by evaporating 10 µL of either undiluted spheres or a solution of 1:1 v/v spheres to ethanol on the membrane surface. To increase wettability of the membranes, they were plasma etched for 2 minutes at 15 W (DC bias of -150 V). Excess spheres were blown off with a stream of high pressure nitrogen and in some cases the evaporation process was repeated after sonicating the membrane in ethanol for 30 seconds to remove excess spheres. Experimental conditions used in these studies were: TMOS volume: 1 mL, stir speed: 400 rpm, deposition potential: -0.6 V or -1.2 V and deposition time: 15 minutes or 2 hours.

6.4 Discussion

In the work presented below, the electrodeposition of silica in the pores of a gold coated track-etched membrane is described in three sections. In the first section, the general method for the electro-assisted deposition of silica is outlined using the 200 nm pore track-etched membrane electrode as a test case and the importance of several parameters on the growth of silica within the membrane pores is outlined. The parameters investigated were (1) the speed that the sol was stirred during silica electrodeposition; (2) the applied potential; (3) the time allowed for hydrolysis of the TMOS prior to electrochemical experiments (pre-hydrolysis); (4) the volume of TMOS in the sol; and (5) the time the reducing potential was applied. The time based studies allowed for further investigation of the growth of silica within the pores. In the second section, important control experiments are described to distinguish between silica formed by trapped
excess sol left within the pores after an experiment and silica formed over the course of the electrodeposition. In addition, an alternative method for obtaining silica nanopillar through short depositions is described. In the third section, variation in the tube characteristics was introduced by changes in the basic method. The characteristics that were controlled were the exposed tube length, tube diameter, tube chemical functionality, and tube porosity.

6.4.1 Nanotube Formation

The 200 nm diameter pore membrane electrodes were used as the template to electrochemically grow the nanostructures under a variety of experimental conditions. The resulting silica structures were imaged with the SEM. The silica nanotubes were formed by the electrogeneration of hydroxide ions at an applied potential between -0.4 V and -1.2 V via the reduction of oxygen and/or water.

\[
\begin{align*}
(6.1) \quad & O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \\
(6.2) \quad & 2H_2O + 2e^- \rightarrow 2OH^- + H_2
\end{align*}
\]

The first set of experimental conditions studied used a sol made by combining 1 mL TMOS, 5 mL ethanol, 4 mL water, and 1 mL 0.2 M KCl. The sol was stirred at 160 rpm during electrodeposition at an applied potential of -0.6 V for 45 minutes. In later experiments, the volume of the silane used to make the sol was changed while the volume of other components stayed the same. A typical cyclic voltammogram and amperometric curve for these conditions are presented in Figure 6.6 A and B, respectfully. The voltage -0.6 V was selected because it was thought that by using a less reducing potential, a smaller amount of OH⁻ would be produced, and thus help to prevent the formation of excess silica at the top of the membrane. This was later proved not to be the case.
Figure 6.6: Typical electrochemical data and resulting silica nanostructures. The CV (A) shows the reduction of oxygen and water to hydroxide at a membrane electrode. The amperometric curve (B), held at -0.6 V for 45 minutes, shows a typical current response for the first deposition of silica into the porous membrane electrode. C shows SEM images of the resulting silica nanotubes from the amperometric curve in B, etched from the membrane side of the electrode (“top”) and the gold side of the electrode (“bottom”) to show that tube formation is complete for the entire membrane pore.

Collectively, the two SEM images in Figure 6.6 C show that the silica nanotubes formed after application of -0.6 V for 45 minutes extend through the entire length of the membrane pore (10 µm). The nanotubes on the top and bottom sides of the membrane were exposed by cutting...
the membrane in half and then plasma etching the top and bottom (the gold was first removed by peeling) side. The formation of silica on a template/electrode system begins on the surface of both the template and the electrode itself. The hydroxide catalyst diffuses quickly through the pores in the membrane so that the pH increase occurs throughout the entire length of the pore (~10 μm). This results in the formation of hollow tubes that are similar over their entire lengths and have outer diameters equal to the diameter of the membrane pores, in this case 200 nm. Close inspection of the top side (membrane side) shows that the nanotubes are largely formed by the single layer aggregation of individual silica particles. This is consistent with established behavior of basic sols, where the addition of a salt, in this case the supporting electrolyte KCl, leads to decreased repulsion between the particles, allowing aggregation. Upon close inspection of the bottom side of the membrane (where the gold was), it can be seen that many of the pillars have what appears to be a ‘cap’. The cap forms because the gold side of the membrane, initially sealed by the Teflon tape, is closed. The cap on the nanotube has a slight indented ring around the top, showing where gold layer hung over the membrane pores. The formation of this cap likely causes the drop in current observed in the amperometric curve between 10 and 20 minutes (Fig 6.6 B). It is hypothesized that the drop in current is due to the silica cap partially impeding the direct diffusion to and from the electrode. This was later supported by the disappearance of the current drop in the amperometric curves for depositions in membranes that have already had a first deposition (not shown). Light sonication (~ 5 minutes) results in some of the nanotubes losing their caps, showing that the nanostructures are indeed hollow tubes (Fig. 6.7).
To fully understand the process that results in the formation of the silica nanotubes, the effect of several parameters were explored. First, the influence of the stirring speed of the sol during deposition was considered. When the electro-generated hydroxide diffuses out of the pores, the pH at the membrane surface will increase. The top of the membrane provides an additional surface for the deposition of silica, resulting in a thick film unless the electro-generated OH\(^-\) is swept away before silica condensation occurs. The pillars formed at the top membrane side of the electrode in Figure 6.4 represent an area of the film with little excess silica growth. This was not the case over the entire surface of the membrane when the sol was stirred at 160 rpm; an example of the overgrown area is shown in Figure 6.8 A. This area shows the formation of a thin layer of silica particles, similar to those that make up the tubes on the membrane side. Stirring the sol at this moderate speed does, however, decrease the amount of overgrowth compared to tubes formed in the membrane under no stirring (Fig. 6.8 B), which showed areas of very thick silica overgrowth. It should be noted that the tubes formed under conditions of no stirring were similar to those that were (Fig. 6.8 B inset), but the thick silica
layer was hard to control and could not be removed in a reproducible enough fashion for it to be considered a viable method. In attempt to further reduce the amount of silica coating the top surface, the stir speed was increased to 400 rpm. This much higher stirring rate was able to significantly decrease silica formation on the top surface by effectively sweeping away the excess hydroxide exiting the pores to the bulk sol. The majority of the film showed either separated tubes (Fig. 6.8 C) or areas where the tubes were connected by just a few silica strains made of individual particles (Fig. 6.8 D). This positive result lead to a stirring rate of 400 rpm being used for many of the experiments conducted. The prevention of excess silica formation was not complete, however, until the stirring rate was raised to 600 rpm. As seen in Figure 6.8 E and 6.8 F, the formation of excess silica has been virtually eliminated. The stir speed of 600 rpm, however, did necessitate careful placement of the electrodes within the cell because the sol formed a visible vortex at stir speeds of about 475-500 rpm. Despite this, experiments could still be conducted as long as each of the three electrodes (working, reference, and counter) was completely submerged in the sol.
Figure 6.8: SEM images the top side of the membrane after electrodeposition at -0.6 V at the following stirring speeds: (A) 160 rpm, (B) 0 rpm with inset of close up of tubes formed under the thick silica layer, (C) 400 rpm with completely separated tubes, (D) 400 rpm with loosely connected nanotubes, (E) 600 rpm, and (F) close up of nanotubes formed at 600 rpm.

The next parameter explored was potential. As discussed in chapter 4.4, when electrodepositing a metal at the surface of an electrode, choosing a potential just after the initial
increase in current on the CV gives greater control over the metal growth. To test the influence of potential on the formation of the silica nanotubes, the potential was varied while keeping all other variables the same (Fig. 6.9). The experimental conditions for these experiments were: stir speed: 400 rpm, 1 mL TMOS, 2 hours deposition time, no pre-hydrolysis, and constant potentials of either -0.4 V, -0.6 V, -0.9 V, or -1.2 V. Theses voltages were selected to represent each major area of the current response shown in the CV as seen in figure 6.4 (-0.4 V: initial increase, -0.6 V: moderate increase, -0.9 V: maximum current response, -1.2 V: maximum potential).

**Figure 6.9:** SEM image of the surface of the top of the membrane showing nanotubes formed at -0.4 V(A), -0.6 V(B), -0.9 V(C), and -1.2 V(D). A typical wall thickness is shown in figure B and the average was determined to be ~ 40 nm. Particles attached to the outside of the nanotubes ranged from 20 nm (C) to 60 nm (D). (Values determined in Image J software)
As can be seen in Figure 6.9, very little variation in the tubes formed at each potential was seen. The tubes had an average wall thickness of about 40 nm for each potential, which appears to be determined by the size of the individual particles making up the tubes. There was also not a noticeable difference in the silica overgrowth over this potential range. Upon further consideration, this trend was attributed to the fact that, even at low potentials, an excess of hydroxide ions are produced over the course of the 2-hour deposition time required for tube formation. Therefore, the continued increase in hydroxide concentration would have little effect on the system.

The next two parameters considered were the pre-hydrolysis time and the concentration of TMOS in the sol. Pre-hydrolysis is used in the sol-gel process to allow for the more complete hydrolysis of the silane precursors prior to gelation. In early studies, such as those seen in Figure 6.6, the sol was stirred for 30 minutes prior to the application of potential. This was determined not to be necessary, and this step was skipped for most experiments, such as those in Figure 6.9. Allowing the precursors extra time to hydrolyze and condense can be useful, especially in neutral or acidic systems where condensation rates are low due to partial hydrolysis; but in basic systems, the silanes are almost completely in their hydrolyzed form so no added benefit is gained in these experiments. Next, the sensitivity of tube formation to TMOS concentration was determined by cutting the volume of TMOS in half (1 mL TMOS to 0.5 mL TMOS). As shown in Figure 6.10, no changes in the tubes were observed.
Figure 6.10: SEM images of the top surface of the top of the membrane showing tubes formed with 0.5 mL and 1 mL TMOS at -0.6 V. Halving the TMOS concentration was not seen to produce a difference in the silica nanotubes.

The final parameter considered was deposition time and it was the parameter determined to have the greatest effect on the nanotube’s physical characteristics. As previously stated, the nanotubes in Figure 6.6 were formed with deposition times of 45 minutes. When this time was increased to 2 hours, it was observed that the tubes were no longer hollow at the bottom (electrode) side of the membrane. Figure 6.11 show the comparison of nanotubes formed at 45 minutes and 2 hours, each etched from the bottom side after the gold layer was removed. To clearly show the internal diameter of the nanotubes below the surface, each sample was crushed by applying pressure from a gloved finger. The silica nanotubes formed for 45 minutes are clearly hollow tubes and have wall thickness that are slightly thicker than found at the top of the membrane, approximately 50 nm. The increase in thickness is likely due to the addition of non-particulate silica to the nanotube, which is supported by the appearance of the inside of the nanotube walls. The internal walls of the tubes at the bottom side show slight bumps from large particles, but they have been significantly smoothed out compared to the internal walls of the tubes near the top of the membrane. The 2-hour deposition, by contrast, produced silica structures that were nearly solid at the new surface of the membrane the same etching times.
Figure 6.11: SEM images of silica deposition on the bottom (electrode) side of the membrane after 45 minutes (A) and 2 hours (B) ($E_{\text{applied}} = -0.6 \text{ V}$). After crushing the silica, it is seen that the 45 minute deposition produced nanotubes with wall thickness of ~ 50 nm, but the tubes were nearly filled at the bottom (electrode) side of the membrane after 2 hours. The two dark spots pointed out in B suggest that the silica nanotubes are being filled by thickening of the tube walls. (Values determined in ImageJ software)

The tubes produced from the 2 hour deposition have become completely solid for most of the structures in Figure 6.11 B, but two of the tubes show a central dark spot that suggest that the growth of the silica is from the sides of the walls near the bottom of membrane, rather than growth occurring from the “cap” of the tube next to the electrode. As will be later shown, the nanotubes have not been affected by this extra deposition of silica near the bottom of the pore, suggesting that the thickening of the tube walls occurs at a slope. The presence of tubes that have almost, but not quite, been completely filled in suggest the length that has been etched, which is about 1.55 µm, as seen from the measured broken silica tube (now a pillar), is the approximate distance that the nanotubes are solid.

An alternate means to fill in the silica tubes is sequentially through multiple depositions in fresh sols. To show that multiple depositions would result in further growth, electrodeposition was preformed at -0.6 V for 1 hour, and then the membrane electrode allowed to dry overnight. The membrane was cut in half and then one side was cut from the electrode completely, being
sure to keep the copper lead unaffected. The remaining half of the membrane was returned to the cell with a fresh sol and then held at -0.6 V for another 3 hours. The membranes were then etched from the bottom of the electrode side and then crushed in the same manner as previously described. Figure 6.12 A shows that after the first deposition, silica hollow tubes were formed. After the second deposition, however, the tubes had been filled in (Fig. 6.12 B), confirming that a multi-step deposition method could be used.

![A: 1st deposition](image1.png) ![B: 2nd deposition](image2.png)

**Figure 6.12:** SEM images of the surface of the bottom side of the membrane after one deposition for one hour at $E_{\text{applied}} = -0.6$ V (A) and a second deposition at $E_{\text{applied}} = -0.6$ V for three hours (B).

Based on these findings, multiple depositions were conducted in the track-etched membranes until the tubes had been completely filled from top to bottom. To determine the extent that the tubes had been filled in, the following samples were characterized by etching the top side of the membrane. The first multi-step experiment conducted used three deposition steps, each with the experimental conditions: stir speed: 400 rpm, potential -0.6 V, TMOS volume: 1 mL, deposition time: 2 hours. After crushing, the silica structures were still un-thickened tubes after etching from the top surface and crushing (not shown). It was determined that 5 depositions, for a total of 10 hours, resulted in the tubes in some areas that have been completely filled in (Fig 6.13 A) and in other areas have thickened walls (Fig. 6.13 B) when etched from the
top side and crushed. The walls of the silica nanotubes were less thick at the tube opening, (Fig. 6.13 C) and a sixth deposition resulted in the tubes being completely filled in all the way to the top (Fig. 6.13 D).

Figure 6.13: Figures A and B show typical SEM images at two areas of the surface of the top of the membrane after etching. The silica structures were produced by five 2- hour depositions, at -0.6 V. The membrane was crushed to see the cross section of the nanotubes and shows that silica has filled in almost completely through the pore. Figure C, however, shows that that top of the nanotubes remain somewhat hollow. After six depositions (D), the nanotubes appear to have filled in completely.

The process by which the nanotube form is interesting because it appears to merge the previously discussed growth pattern seen in silica nanotubes formed by the surface sol-gel method (from tube walls inward) with those seen in the growth of metal through a track-etched
membrane (from electrode up through the pore). The growth observed in this work is summarized in Figure 6.14. In the devised method, the formation of silica begins at the surface of the cylindrical pore walls, where hollow nanotubes are formed. After tube formation, the silica will grow up through the tube from the electrode towards the top of the membrane. Unlike with the growth of metals, however, silica is not formed as a flat surface up, but appears to form an inverse cone shape, where the walls thicken at a slope, eventually meeting in the center.

**Figure 6.14:** Simplified schematic for the growth of silica within the membrane pore over time. First, a silica nanotube with the length equal to the thickness of the track-etched membrane is formed. Then, the silica nanotube serves as a template for the further growth of silica from the bottom of the pore to the top. The growth occurs with an inverse cone shape, where the walls get thicker with a slope, meeting in the center to completely fill in the tube.

In this process, it appears that the initially formed silica nanotube serves as a template for the further growth of new silica. Based on the trends seen in base-catalyzed silica condensation,
the monomer-to-cluster growth model described in chapter 1 explains that, because a basic environment results in close to complete hydrolysis of silica, the most favorable reaction occurs between large silica structures and the individual precursors. This is because of the increased acidity that the results from the Si-O- ligand on the reactive silicon relative to HO- or RO-. In this system, that means that the TMOS added after the formation of the nanotube will mostly be in the form of monomer addition to the tube. A second layer of particles are not formed on the initial particulate tube during a second deposition because nucleation has been suppressed. The directional component of the second phase of growth may be due to a diffusion gradient formed by the directional introduction of the hydroxide catalyst. A summary of the effect of each parameter is given in Table 6.1.

**Table 6.1: Summary the effect of selected parameters for silica nanotube deposition**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>-0.4 V</th>
<th>-0.6 V</th>
<th>-0.9 V</th>
<th>-1.2 V</th>
<th>Little Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potential</td>
<td>-0.4  V</td>
<td>-0.6  V</td>
<td>-0.9  V</td>
<td>-1.2  V</td>
<td>Little Change</td>
</tr>
<tr>
<td>TMOS Volume</td>
<td>0.5 mL</td>
<td>1 mL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stir rate</td>
<td>0</td>
<td>160 rpm</td>
<td>400 rpm</td>
<td>600 rpm</td>
<td>Silica growth on surface of membrane decreases as sol stirring rate increased.</td>
</tr>
<tr>
<td>Deposition time</td>
<td>45 min</td>
<td>2 hrs</td>
<td>Additional hour depositions (up to 6).</td>
<td>2</td>
<td>Electrogenerated solid silica nanotubes at 45 mins, then tubes filled in from the electrode at longer times and further depositions.</td>
</tr>
</tbody>
</table>

6.4.2 Study of short times and controls

The previous discussion of the deposition time as a variable in the formation of silica nanostructures focused on increasing the time relative to that found to produce silica nanotubes. Shorter time scales were also studied, with unexpected results. When comparing silica formation
at -1.2 V for 2 hours vs 15 minutes (both with 1 mL TMOS, and stirred at 400 rpm), it was expected that at a 15 minute deposition there would either be no silica formation or the tube would have very thin walls. Instead, smooth silica pillars were observed (Fig. 6.15). These silica structures showed little of the particulate character found in tubes formed with long deposition times, where mostly solid (Fig. 6.13 C), and they also show no evidence of excess silica growth on the top surface of the membrane.

![Image of silica pillars](image)

**Figure 6.15:** SEM images of silica pillars formed after a -1.2 V deposition for 15 minutes after the top surface of the membrane was etched. Figure C shows that pillars are solid after being crushed.

Control experiments conducted concurrently produced similar results. In the control experiment, the membrane electrode was suspended in a sol (1 mL TMOS) stirred at 400 rpm for
2 hours with no applied potential. Smooth silica pillars were evident when the top side of the membrane was etched. Compared to those prepared via electrodeposition at -1.2 V for 15 minutes, however, the control pillars were far less consistent in quality and appearance in the membrane (Fig. 6.16 A, B, C). Some areas showed solid pillars where others showed very thin tubes (< 25 nm thickness). Similar control experiments were then carried out for the 15 minute deposition, such that all experimental conditions (TMOS: 1 mL, stir speed: 400 rpm, time in sol: 15 minutes) were kept constant; no potential was applied. These experiments still showed the production of some pillars, but the coverage and quality became worse; pillar formation mainly occurred at folds in the membrane resulting from it not lying flat on the underlying Teflon tape (Fig 6.16 D).
Figure 6.16: Comparison of SEM images of the top side of the membrane after etching. The membranes were soaked in sol; no potential applied. A, B, and C are different areas of the same membrane that was soaked in a stirred sol for 2 hours. The film had areas of high quality pillars, but also areas of low quality pillars or no pillar formation at all. C showed areas of very thin, partially formed tubes with thicknesses below 25 nm (calculated in ImageJ software). D shows an area of pillar formation for a membrane soaked in a stirred sol for 15 minutes. Most of the membrane had no pillar formation.

The similarities between the physical characteristics of the silica structures created at 15 minute depositions and the controls, such as the smoothness of the pillars and the lack of overgrowth on the top of the membranes, contrasted with those made at the long depositions times, suggests that there may also be similarities in their growth process. In previous work (appendix), we found that the solvent used to rinse the electrodeposited materials is important. When silica was electrodeposited in confined areas such as between latex spheres comprising a
colloidal crystal (appendix) or in nanopore electrodes, the partially hydrolyzed silica precursors can remain entrapped in confined environments. Upon drying, these precursors will condense to form a silica structure. Washing with a more miscible solvent such as ethanol will remove more of these precursors than by washing with water. Ethanol also plays a role in the reverse reaction of silica condensation and can dilute a sol without adding additional water to the hydrolysis reaction.

Figure 6.17 shows typical SEM images at two locations on a single membrane for the 15 minute and 2 hour controls with no applied potential and the 15 minute and 2 hour depositions at a potential of -1.2 V. In all cases, the membranes were rinsed with ethanol instead of water and were allowed to dry. The 2 hour, no potential experiment showed a decrease in the number of nanotubes formed. The tubes that were formed also showed decrease in quality as evidence by warping being present in most of the silica nanotubes. These nanotubes were similar to those observed for the 15 min, no potential deposition experiments that had been rinsed with water (Fig 6.17 A). The 15 minute, no potential experiment showed even less silica formation then previously seen for the membranes that were rinsed with water; only a few small areas with poor quality nanotubes were found (Fig 6.17 B). The membrane rinsed with ethanol following a 15 minute deposition at -1.2 V most notably, no longer had high quality pillars formed over the majority of the membrane. It now showed large areas of no silica formation and poor quality pillars formed in other areas (Fig. 6.17 C). By contrast, the 2 hour deposition at -1.2 V showed no change in its tube formation, with the high quality nanotubes covering the entire membrane.
Figure 6.17: SEM images of the surface of the top of the membrane rinsed with ethanol after etching. Controls with no applied potential (A: 2 hours, B: 15 minute), and the 15 minute deposition show a decrease in the formation of silica compared to when rinsed with water, but the 2 hour deposition was unaffected.
These results suggest that the smooth tubes formed at short deposition times and at long times with no applied potential (control) are due to the condensation of trapped silica precursors and clusters that remain within the tubes after rinsing, similar to the silica structures formed by dipping previously described in the literature. The similarity between the silica structures formed at -1.2 V for 15 minutes and no applied potential for 2 hours is likely because the electro-generated OH in the former promoted hydrolysis and condensation very quickly and for the latter, the sol had enough time to reach a hydrolyzed state ready for gelation under more neutral conditions. The increase in quality of the formed silica under the 15 minute electrodeposition conditions is likely due to the electrogeneration of the catalyst being evenly spread out over the membrane, resulting in more consistent sol conditions prior to drying. The fact that rinsing with ethanol had no effect on the 2 hour electrodeposition suggests that the silica tube formation was at or near completion when the membrane electrode was removed from the sol. Any excess, unreacted silica that remained within the pores would likely condense on the silica tube by the monomer-cluster model, allowing the tubes to keep their particulate nature. Because of the high quality of the nanostructures formed at -1.2 V for 15 minutes, they will continued to be considered for the study of the possible variation in silica nanostructure characteristics.

6.4.3 Variation in Nanotube Characteristics

Once the method for the formation of silica nanotubes through electro-assisted deposition was confirmed, attempts were made to introduce variation in their physical and chemical properties, so to take advantage of the tunablity often seen in the sol-gel process. The characteristics that were considered were: the length of the tube extending above the surface, nanotube tube diameter, chemical functionality and porosity.
In the previous discussion of nanotube formation, the membrane was partially etched in an oxygen plasma to expose the silica structures. The exposure time (70 minutes) and the DC bias (-700 V) of the plasma were kept constant, resulting in nanotubes of similar lengths being extending from the membrane surface each time. The goal of this portion of the work is to control the amount that the silica nanotubes have been exposed by partial or complete removal of the membrane. There are several methods in the literature to etch membranes. Polycarbonate membranes, like the ones used here, are soluble in chloro solvents and Zoski et al. showed that a solution of dichloromethane and ethanol (1:1) allowed for partial removal of a membrane, exposing electrolessly deposited gold wires after rubbing the membrane surface with a very small amount of that solvent. Martin et al. similarly, controlled the removal of polycarbonate membranes templates used for the formation of gold nanowires, but utilized oxygen plasma etching. In this work, oxygen plasma was used for the controlled removal of the membrane because of the ease of the procedure and because it doesn’t not require rubbing the membrane, which may damage the silica nanotubes. To show that the length of plasma etching time in our system could also control the amount of membrane etched away, the membrane was plasma etched for only 30 minutes and compared to the standard 70 minutes (Fig 6.18). There is a clear difference in the exposed lengths of the silica tubes, indicating that the amount of polymer removed from the 30 minute etching process was less than for 70 minutes.
Organic solvents can also be used to remove the entire membrane to yield self-supported nanotubes. This should result in the silica tubes remaining attached to the thin gold layer electrode, which is supported by the Teflon tape. The membranes were soaked in chloroform for 10 minutes, then transferred to another chloroform solution for 5 minutes, then finally rinsed with fresh chloroform. Figure 6.19 shows SEM images of the nanostructures formed after at 45 minute deposition at -0.6 V and a 15 minute deposition at -1.2 V. In general, the nanotubes were found to have good stability, and remained attached to the gold layer even after centrifuging in chloroform at 4000 rpm for 3 minutes. The nanotubes formed at long deposition times (45 minutes) appear to be less flexible than the pillars formed at short times (15 minutes), and are better able to withstand the capillary forces that result from the drying chloroform. The “bunching” or “clustering” effect seen in the SEM images is a common feature for self-supported high aspect ratio materials that have been immersed in a liquid.
Figure 6.19: SEM images of the nanostructures supported on gold following complete removal of the membrane with chloroform following a 45 minute deposition and a 15 minute deposition and rinsing with water.

The next element of variation in the tubes studied was nanotube diameter. Track-etched membranes with many different pore sizes are commercially available, thus the diameter of formed silica tubes can be changed by using a different size membrane. The alternate membranes used had either 100 nm or 400 nm pore sizes. These membranes were coated with gold in the same manner as the 200 nm pore membranes and were then used to make membrane electrodes. The experimental conditions of 1 mL TMOS, stir speed 400 rpm, potential -0.6 V and deposition time 2 hours, followed by a water rinse, were used to create silica tubes with
diameters of approximately 100 nm and 400 nm (Fig 6.20). The 400 nm membranes, in particular produced high quality tubes with little over growth of silica observed.

**Figure 6.20:** SEM images of silica nanotubes formed in 400 and 100 nm track-etched membranes etched from the top of the membrane (TMOS: 1 mL, stir speed: 400 rpm, potential: -0.6 V; time: 2 hours; water rinse). The diameter of the silica tubes was controlled by using a 400 nm and a 100 nm track-etch membranes. The resulting silica nanotubes had diameters similar to the pores size used in their formation.

As described in chapter 1, chemical functionality can be introduced into the silica structures through the addition of organosilane precursors to the sol. Since the desired ligand is attached directly to the silicon, it will not be hydrolyzed during the formation of the sol. In this experiment, the organosilane SHTMOS was selected for several reasons. First, the thiol functional group has been shown have useful properties, such as the ability to anchor
nanoparticles to a substrate. In addition, the thiol group does not influence the sol-gel process, so its addition to the sol should not require major modification to the method. To create the thiol functionalized silica nanostructures, a sol was prepared using 0.5 mL TMOS and 0.2 mL of SHTMOS, which was then deposited into the membrane at -0.6 V for 2 hours, stirred at 400 rpm and then rinsed with water. The sol did appear to be slightly more viscous than the TMOS only sol, but it did not appear to interfere with the silica formation. It may, however, have led to many of the silica tubes being capped at the top, suggesting that the codeposition of TMOS/SHTMOS may benefit from higher stir speeds. SEM-EDS was used to characterize the silica structures and an additional sulfur peak was found for the tubes formed with added SHTMOS, indicating that the integration of the SHTMOS was successful (Fig 6.21).
Figure 6.21: (A) Comparison of SEM-EDS studies on silica nanotubes formed from sols with TMOS only and with TMOS/SHTMOS. The presence of the sulfur peak suggests that the SHTMOS integration was successful. (B) SEM image of silica “cap” nanotubes formed from a TMOS/SHTMOS sol etched from the top side of the membrane after a 2 hour deposition at -0.6 V.

6.4.3.1 Nanotube/pillar porosity:

The final step in this work was to introduce of defined sizes into the silica nanostructures formed upon electrodeposition. In this study, polystyrene latex spheres were used as endotemplates. It has been shown in the literature that, by packing track-etched membranes
with PS spheres of a well-defined size, porous metal wires can be created by electrodeposition.\textsuperscript{45} Examples in the literature show that the pores of the track-etched membranes can be completely packed with the PS spheres using vacuum filtration to infiltrate the membrane with spheres.\textsuperscript{149} To prevent the spheres from passing completely through the membrane, a second membrane with pores smaller than the infiltrating spheres was placed between the membrane and the filtration system. Once the membranes were filled with the spheres, one side of the membrane was coated with gold, and then an electrode constructed. Early attempts to introduce porosity into the silica tubes used this method, but they were not successful. It was found that track-etched membranes that had been previously coated with gold did not fully adhere to a second membrane, preventing the formation of a vacuum.

As an alternative procedure to introduce the template into the nanopores of the track-etched membrane, a 10 µL drop of undiluted spheres was added to the top of a membrane electrode and allowed to evaporate. To improve wetting, the membrane electrode was exposed to a weak oxygen plasma (-100 V bias) for 2 minutes. After evaporation, a thick layer of spheres remained on the top of the membrane that could be blown off with a stream of nitrogen. The sphere filled membrane electrode was then used for silica deposition. Several types of spheres were used, both in size and functionalization. Larger spheres with sulfate or amine functionalized PS (>100 nm) resulted in silica forming around the spheres themselves, forming cages (Fig. 6.22). The sulfate sphere example shown had diameters of 100 nm and was deposited in a 200 nm membrane electrode at -0.6 V for 45 minutes, and then etched from the bottom (Fig. 6.22 A). The amino sphere example also had diameters of 100 nm, but was etched from the top after a 15 minute deposition at -1.2 V (Fig. 6.22 B).
Figure 6.22: SEM images of silica tubes formed with large PS sphere templates. Both sulfate and amine PS spheres had diameters of 100 nm and resulted in silica forming around the template. (Experimental conditions: Sulfate spheres - etched from bottom after 45 min deposition at -0.6 V; amine sphere - etched from top after a 15 min -1.2 V electrodeposition.)

Better results were found with smaller (60 nm) epoxy spheres, although there were still some challenges. Porous solid pillars were formed, but their formation was inconsistent over the entire film. When the bottom (gold coated side) of the membrane was etched, a combination of nanotubes with no added porosity, tubes with added porosity (Fig 6.23 A) and solid pillars with completely entrapped pores (Fig. 6.23 B) were found after a 45 minute, -0.6 V deposition. The inconsistency between the silica structures is likely due to inconsistent filling of the pores by the PS spheres. Etching from the top of the membrane showed areas of either no silica formation or solid porous silica pillars. Unlike the pillars found at the bottom side of the membrane, however, these pillars did have pores opened on the surface, they were not completely formed and showed gaps in the silica (Fig. 6.23 C).
Figure 6.23: SEM images of silica structures formed with the pores of a 200 nm track-etched membranes packed with undiluted epoxy spheres after electrodepoistion and plasma etching. A and B show examples of two types of porosity seen in tubes etched from the bottom (electrode) side due to the evaporation of undiluted epoxy spheres on the membrane surface prior to silica the 45 min deposition ($E_{\text{applied}} = -0.6\text{V}$). A shows an area where the spheres added pores on the outside of the tubes and B shows an area the spheres were closed-packed, but the pores did not completely open to the outside of the silica pillar. C shows silica pillars etched from the top of the membrane after a 2 hour deposition around spheres packed the same way as in A and B. Parts of the film showed no silica formation at all and areas that did often showed gaps in the pillar walls.

Porosity experiments were also conducted using the short deposition time method, with promising results. After using the same evaporation method to fill the pores with spheres, 200 nm and 400 nm membrane electrodes were electrodeposited with silica for 15 minutes at -1.2 V (1 mL TMOS, stir speed: 400 RPM) and etched from the top side. This resulted in the formation
of porous silica pillars that, unlike those seen after long depositions, had both exposed pores present on the surface of the pillar and were completely formed, with no gaps in the tubes (Fig 6.24 A, B). The close up image in Figure 2.24 C shows that the porous pillars are being formed by small silica particles (~ 20 nm) packing around the epoxy templates, which was similar to those found after a 2 hour deposition around packed spheres. It is hypothesized that the higher quality porous pillars found in the 15 minute deposition may be due to there being more excess unreacted silica remaining in the pores after the deposition that could fill in any gaps left by the silica formed during deposition. Consistency was still an issue with this method, however, and high quality porous pillars normally covered less than half of the membrane surface.
Figure 6.24: SEM images of examples of porosity seen in tubes (diameter: 200 nm (A) and 400 nm (B)) etched from the membrane side due electrodeposition of silica for 15 minutes into pores that has been packed with undiluted epoxy spheres by evaporation ($E_{applied} = -1.2$V). Pillars like these covered 30-50% of the membrane surface, with the rest either showing no pillars or very poorly formed porous pillars. (C) A close up of a 400 nm porous pillar, showing that the structure is made up of packed silica particles (~20 nm) fused together. (Values calculated with Image J software).

The method for filling the membrane pores was revisited, and instead of using an undiluted drop of sphere to evaporate on the surface, the epoxy spheres were diluted 1:1 with ethanol, a solvent that would better wet the membrane. The 10 µL drop of the sphere:ethanol solution was found to wet the surface of the membrane much better than the aqueous undiluted sphere solution. In addition, to fill the pores as completely as possible, spheres were evaporated
multiple times, sonicating the membrane for 30 seconds in ethanol between each time to remove excess spheres stuck to the surface. This resulted in improvement in pillar formation at the top side of the membrane and high quality porous pillars now covered the majority of the membrane surface (Fig. 6.25).

Figure 6.25: SEM images of porous silica pillars formed after the membrane side was etched following a 15 minute silica deposition ($E_{\text{applied}} = -1.2\,\text{V}$). The pores were packed by placing a drop of 1:1 epoxy spheres/ethanol on the membrane surface prior to silica deposition. Porous pillars were well formed (A) and covered most of the membrane surface (B).

6.5 Conclusion

Silica nanotubes and pillars were created by coupling templating methods with the electro-assisted condensation of silica. Gold coated track-etched membranes were used as the template whose nanopores gave the silica structures their dimensions (length: 10 $\mu$m, diameter: 100 nm, 200 nm, or 400 nm). It was determined that the silica formation was largely insensitive to the potential used for electrodeposition, as well as the range of silane concentrations studied. The rate at which the sol was stirred during deposition did not influence the physical properties of the silica nanostructures formed in the membrane pores themselves, but it was an important factor in the prevention of the over growth of silica on the top of the membrane exposed to solution. By using high stirring rates (400 rpm, 600 rpm), individual silica tubes remained after
membrane removal. The most important parameter determined was deposition time. It was found that silica tubes were formed first along the pore wall by aggregation of silica particles. As deposition time continued and multiple depositions carried out, however, the silica tubes would fill up, creating partially filled nanotubes or solid silica pillars. By contrast, very short deposition times did not result in silica formation during the time frame that the potential was held, but did lead to consistent sol conditions that created high quality smooth nanopillars from sol trapped in the pores after removal from the cell.

The growth pattern described for long deposition times does not agree with those found in the deposition of metal oxides (TiO$_2$ and SiO$_2$) in AAO membrane previously published, but the size difference between the track-etched membranes used here and the AAO membranes used in the published work is the likely reason for the difference. Xu at al found that the length of growth was dependent on the deposition time, but the diameters of the AAO membranes used were below 50 nm. The membranes used in this work had diameters between 100 nm and 400 nm and the particles that made up the initially formed nanotubes are of similar scale to the AAO pores. The size limitation of the AAO membrane likely did not allow for the formation of independent particles of sufficient size to form tubes throughout the entire length of the 2 to 10 µm membranes used.

The physical and chemical characteristics of the silica structures were also controlled by modifying the basic method. The length of the silica nanotubes extending from the surface of the membrane was controlled by varying the etching time or by completely dissolving the membrane with chloroform. The diameter of the silica nanotubes was changed by using membranes with a different pore diameter. The silica nanotubes were functionalized with thiol using an in-situ one-step method via addition of a mercapto-organosilane into the sol before
deposition. In addition, well-defined macropores were incorporated in the silica nanotubes formed at short deposition times via the use of a secondary template; in this case, epoxy functionalized latex spheres. Possible application for these silica structures include the formation of internal gradients by changing the character of the sol between depositions or as solid supports that can be functionalized selectively, either by functionalizing the inside of the tube before membrane removal or by modifying the outside of the tube between partial removal and complete removal of the membrane template. ¹³³
Chapter 7  Conclusion

Sol-gel chemistry was used as a method to obtain silica materials under bench top conditions. Specifically, methods for the fabrication of macroporous silica thin films and nanotubes/pillars were developed. For the developed silica thin films, macroporosity was introduced through the integration of templates, such as bacteria or spherical PS microparticles, into a spin cast film. The casting conditions resulted in the templates being only partially submerged in the film, so that after their removal, the silica films had large open macropores. In the case of silica films templated with bacteria, long trough-like pores, or microchannels, were produced, which had widths of 200 nm and lengths from 20 µm to over 60 µm. These films have a variety of potential applications, such as templates for the formation of high-aspect ratio nanomaterials.

PS microspheres were used to create “nanowells” within the silica film. The nanowell arrangement in silica thin film modified electrode has two major advantages in electrochemical applications. First, the amount of surface area that is directly exposed to solution increases, which can potentially decrease the time required for the hydration of the film prior to conducting experiments. Second, the removal of the PS sphere template results in a small amount of the electrode being exposed at the bottom of the nanowell, allowing for direct access to the underlying surface. The nanowell modified film configuration was first used to control the growth of copper through electrodeposition. Copper growth only occurred at areas of exposed electrode, either at the bottom of the nanowells or at defects in the film. To limit the copper growth to only the nanowells, electroassisted silica deposition was employed to deposit silica at the defect sites in the film before the PS spheres were removed. Once the defect sites were sufficiently blocked, copper nanoparticles were electrochemically deposited in the nanowells.
from a solution containing Cu$^{2+}$. It was determined that the length of the electrodeposition
could control the height that the copper particles in the nanowells, where 30 seconds resulted in
particles with heights of ~90 nm and 60 seconds resulted in particles with heights of ~110 nm. It
was observed, however, that copper deposition did not occur in all the nanowells, so future use
of this method requires further modification to prevent excess silica from forming beneath the
template. This could be accomplished by revisiting the sol recipe or by packing the spheres on
the electrode prior to casting the silica film.

The nanowell silica films were also modified with a monolayer of gold nanoparticles
over the entire surface of the film and the size of the particles was controlled by timed exposure
of the film to a gold electroless growth solution. It was found that the nanoparticle size could be
increased from approximately 20 nm to 100 nm. Attempts were made to pattern the film by
controlling the location of the gold monolayer through layers of functionalized silica, but they
were not successful. The original, un-patterned film, however, does have potential for further
development, which was explained in section 7.2.

In the final study conducted on the nanowell modified films, the method for film
formation and template ordering was reexamined. By separating template packing and film
formation from a one-step process to a two-step process, greater template order was obtained
over the electrode. An evaporative method was first used to pack the spheres into a high quality,
single-layer colloidal crystal, for which a silica sol could then be cast over with the top. Upon
template removal, an ensemble of closely packed nanowells over nearly the entire surface of the
electrode was obtained. The electrochemical properties of the films were studied and it was
found that the films were selective against positively charged redox probes. Growth of the gold
particles at the bottom of each nanowell by electroless deposition, however, resulted in marked
improvements in the electrochemical response of the negative redox probe. In addition, the two step film formation process allowed for the control of the size of the exposed conductive domain at the bottom of the nanowells. It was found that larger conductive domains create asymmetric gold particles, whereas a small conductive domain created smooth, spherical gold particles. The size of the particle could be controlled by changing the exposure time to the electroless solution.

Finally, sol-gel chemistry was used to obtain silica nanopillars with controllable physical and chemical properties. This was accomplished by using electroassisted silica deposition in track-etched membrane electrodes. It was determined that the major variable controlling the growth of silica in the track-etched membrane pores was the length of time for the deposition and that the method was insensitive to increases in the deposition potential. Depositions from 45 minutes to an hour resulted in the formation of silica nanotubes with dimensions determined by the track-etched membrane. Longer deposition times resulted in additional silica filling in the tube from the electrode to the top of the membrane to obtain partially or completely solid silica nanopillars. Short deposition times resulted in a smooth solid pillar forming, but through a different mechanism. It was determined that these silica structures resulted from trapped sol remaining in pores after removal from the electrochemical cell. The length of the tubes extending from the membrane was controlled by partially removing the membrane or fully removing it. Chemical functionality was added to the tubes through the addition of a thiol-functionalized organosilane. Finally, well-defined macropores were introduced into silica pillars by packing the pores with 60 nm sphere templates prior to silica deposition.
7.1 Future work

As briefly mentioned in chapter 4, the macroporous silica thin films modified with a gold monolayer could provide an interesting avenue for future development. Because the gold monolayer can be grown to be conductive, there is the potential to form a porous gold electrode on the surface of a silica thin film. This arrangement could prove to be advantageous when using probes or analytes that undergo leaching when entrapped within a silica film. Leaching can lead to the loss of over half of a redox specie to solution over the course on an experiment. By placing the doped silica underneath a porous electrode, however, any leaching specie would be required to travel through an additional barrier to escape, which is unlikely.

Figure 7.1: Simplified schematic of a silica thin film sandwiched between a glass slide and a porous electrode. For an analyte to leach out of the sandwiched design, it must travel through the electrode, whereas in the conventional design, leaching occurs away from the electrode, resulting in a loss of sensitivity.

A second area for future development is using the ability of the electroassisted silica nanotubes to be filled in by separate sols to obtain solid silica pillars with functionalized gradients, either vertically or radially. For example, a TMOS sol could be used to create the initial silica tube, and then a thiol functionalized alkoxy silane could be electrodeposited for additional growth (Fig. 7.2). Alternatively the tube could be filled half way with one sol, such as TMOS, and then the rest of the way with another, such as SHTMOS (Fig. 7.2). Tubular silica gradients could have applications in separations and electrochemistry.
Figure 7.2: Possible gradient tubes obtained by the electroassisted deposition of silica. Depending on when the sol is changed, either a solid pillar could have an outer “shell” with different functional groups, or a tube could be half-filled with one kind of precusor and half-filled with another.
Appendix

Early efforts on the combination of electroassisted formation of silica with templating were completed while attempting to create a high quality, closely packed silica macroporous nanowell systems desired in chapters 4 and 5. A study involving the electroassisted deposition of silica around a colloidal crystal of spheres was published and it was noted that silica formation was not restricted to the surface of the electrode, but occurred at the surface of the templates as well.\textsuperscript{150} This work, however, also showed that electroassisted deposition of silica around the polystyrene templates could be very uneven, as much of the interior of the resulting silica inverse opal was hollow or half-formed.\textsuperscript{150} Similar results were found in the present work, but three main aspects of the formation of silica around templates through electroassisted deposition were determined.

The first consideration is that it is important for the colloidal crystal be consistent both within itself and between samples, so that silica formation will occur in a reproducible manner. Because the silica forms from the template surface, any unevenness found in the packing or ordering of the template will be reflected in the final silica material. It can also result in the sol condensing differently between areas. Second, the complete removal of sol from within the template structure is not trivial, but is very important as it can condense during drying directly resulting in silica formation. Therefore, it is important to develop methods to either remove the excess sol or to be able to distinguish silica formation due to the application of a potential from that of formation from excess silica condensing during drying. Finally, silica formation attributed to only the applied potential occurred much more slowly than expected, resulting in only a very thin layer covering the electrode. Therefore, longer times for the silica deposition were used in future experiments.
Methods

Gold slides were cut into 2 cm x 2 cm squares, and then cleaned with piranha solution (7:3) for 5 minutes (caution: Dangerous). After copious rinsing, the slides were dried with a stream of nitrogen and soaked in a 5 mM cysteamine solution in ethanol for 24 hours. The slides were then rinsed well with ethanol and the spheres were packed on the slide by the evaporative method, similarly to the method described in chapter 5, section 3.2. The slides were placed upright in vials that contained 0.5 µm PS spheres in ethanol (1:16.5 v/v). Unlike in the previously described method, however, the sphere/ethanol solution was evaporated on the bench top, which could take 3-4 days.

Once packed, the sphere-covered slides were made into electrodes by attaching copper tape to an area of the gold slide where the spheres were removed with a Q-tip. A piece of teflon tape with a one quarter inch hole was placed on the side, covering all of the gold outside of the hole and the copper tape. Several recipes of sols was prepared in this work, but the two presented here were made by stirring 88-171 µL TMOS, 0-30 µL MTMOS with 2.0 ml EtOH and 2.0 ml 0.2 M KCl for 30 minutes prior to being added to the cell. All electrochemical studies were completed using a CH instruments potentiostat. The electrochemical cell consisted of the sphere-packed gold electrode immersed in the sol along with a silver/silver chloride (Ag/AgCl) wire reference, and a graphite carbon rod counter electrode. The Ag/AgCl wire was used to avoid silica clogging the frit of a traditional Ag/AgCl reference. The electrochemical generation of the hydroxide catalyst occurred by holding the potential at -0.5 or -0.6 V vs the Ag/AgCl wire for 5 minutes. Control experiments were also conducted; in these cases no potential was applied. After removal from the cell, the electrodes were rinsed with water, soaked
in water or ethanol for 5 minutes, or put straight into chloroform for 2 hours. For all but the latter, the films were allowed to dry and then soaked in chloroform for 2 hours. The formed silica structures were studied using scanning electron microscopy (SEM, Hitachi SU-70).

Discussion

The first relevant study conducted on the deposition of silica around a colloidal crystal of PS spheres were those done on slides that had a very well-packed, single layer of spheres. In this experiment, a sol of 88 μL TMOS, 2 mL EtOH, 2 mL 0.2 M KCl was used and deposited on the electrode at -0.6 V for 5 minutes. After removal from the cell, the slide was rinsed well with water. These results showed the formation of a very high quality silica thin film with closely packed nanowells (Fig. A.1 A). The challenge here, however, was reproducibility. The gold slide packed with the very high quality PS monolayer had been prepared several months before by another student, and within the time frame of the current experiments a similar colloidal crystal was not able to be reproduced. The sphere packing that did occur during this time period was very inconsistent, both within a sample and between them. The typical packing on a slide could range from areas with monolayers to other areas with 10 or more layers. In traditional electrodeposition of a metal, the number of packed layers is not as important, so long as the metal deposition remains below the level that inconsistency occurs. For silica, however, formation does not occur from the electrode surface and it was found that an inconsistently packed slide could result in some very high quality areas (Fig. A.1 B) not far from very poorly formed areas (Fig. A.1 C) (experimental conditions: 58 μL TMOS and 10 μL MTMOS, -0.5 V for 5 min). Therefore, it was determined that any templates that are coupled with the electrogeneration of silica should be very consistent over all of its dimensions.
Figure A.1: SEM images of a silica film obtained after the deposition of silica into a well-packed single layer colloidal crystal (A). It was determined that the reproducibility of this result was controlled by the quality of the single layer packing. In Figure B and C, the degree of variation in silica formation within a single sample is shown. Areas of well-packed spheres lead to a high quality silica material, but poorly packed spheres interfered with silica formation.

The second relevant study involved control experiments, where the electrode was exposed to the sol in the same manner as in the previous experimental procedure (58 µL TMOS, 10 µL MTMOS) but no potential was applied. In these experiments, the electrodes were soaked in the sol for 5 minutes, removed and then soaked in either water or ethanol for an additional minute in attempt to remove any excess sol that may have remained between the spheres after simple rinsing. Because of the thick layer of spheres, it is unlikely that much of the sol from within the colloidal crystal was removed by rinsing with water or even the one-minute soak,
resulting in enough sol left behind to form the silica structure. SEM images show that the slides soaked in water afterwards showed silica forming in the same inconsistent manner as those that had been formed under an applied potential (Fig. A.2 A). The film soaked in ethanol, however, only showed a few isolated areas of silica formation (Fig A.2 B). Ethanol was chosen as the second solvent for comparison because of its role as a secondary solvent in diluting sols as well as because of its involvement in the reverse reaction of condensation. These results suggest that the earlier films had been so inconsistently formed because, under these experimental conditions, the silica formation resulted from sol that had been trapped between the spheres, condensing as it dried.
Figure A.2: SEM images of control sample at various magnifications. The packed spheres were soaked in the sol for 5 minutes under no applied potential, then soaked in either water or ethanol. The sample soaked in water (A), showed silica formation similar to that found under an applied potential. The sample soaked in ethanol (B), however, showed little formation of silica. This suggests that the silica material previously found after the application of a potential was also at least partially due to trapped silica.
To further probe the formation of silica around the spheres, the drying step was removed completely from the experiment. In this case, a slide either was electrodeposited with silica at -0.6 V for 5 minutes or soaked in sol for 5 minutes. In both, the excess liquid was shook off, and then they were put directly into chloroform. SEM images show that a very thin layer of particulate silica remained for the slides held at the -0.6 V, but none remained for the slide where no potential was applied. This further indicated that, under the experimental conditions used here, a very small amount of silica was forming at the electrode, but the vast majority of the silica film seen after drying was due to trapped sol.

Figure A.3: SEM images of silica films formed on electrodes that were soaked in chloroform immediately after the deposition of silica or after being soaked in sol for an equal amount of time.
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