ABSTRACT OF DISSERTATION

Qingliu Wu

The Graduate School
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SYNTHESIS AND ENERGY APPLICATIONS OF ORIENTED METAL OXIDE 
NANOPOROUS FILMS

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A dissertation submitted in partial fulfillment of the 
requirements for the degree of Doctor of Philosophy in the 
College of Engineering 
at the University of Kentucky

By
Qingliu Wu
Lexington, KY

Director: Dr. Stephen E. Rankin, Professor of Chemical Engineering 
Lexington, Kentucky
2011

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SYNTHESIS AND ENERGY APPLICATIONS OF ORIENTED METAL OXIDE NANOPOROUS FILMS

This dissertation mainly addresses the synthesis of well-ordered mesoporous titania thin films by dip coating with PEO-PPO-PEO triblock copolymer surfactant template P123. Because P123 is composed of poly(ethylene oxide) [PEO] and poly(propylene oxide) [PPO] blocks, concentrations of ingredients are adjusted to tune the films’ wall thickness, pore size and mesophase. Structural changes are consistent with partitioning of species among PEO blocks, PPO blocks, and the PEO/PPO interface. Titanates localize near PEO and increase wall thickness (by 5 nm to 7 nm). Depending on aging temperature, PPG either swells the PPO cores (when it is hydrophobic) or introduces large (>200 nm) voids (when it is hydrophilic but phase separates during heating). 1-butanol localizes at the PEO/PPO interface to favor a 3D hexagonal mesostructure.

In another approach, anodizing Ti foils yields vertically aligned titania nanotubes arrays with exceptional stabilities as anodes in lithium ion batteries; they maintain capacities of 130-230 mAh$^{-1}$ over 200 cycles. No microstructural changes are induced by battery cycling and good electrical contact is maintained. A diffusion induced stress model suggests that thin-walled nanotubes arrays should be stable under testing conditions, and that ordered hexagonal columnar pore arrays should have both high charge/discharge rates and low stress development.

KEY WORDS: materials synthesis, porous, thin film, alternative energy, self-assembly
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Chapter 1. Overview of Titania Thin Films with Nanoporous Structures and their Applications

Titania is an attractive material due to a wide range of applications in numerous fields including medicine\(^1\), environmental remediation\(^2,3\), and energy storage and conversion\(^4,5\). It is also of a high level of interest because it is non-toxic, photoactive, and has unique optical, physical and chemical properties. For instance, titania microtubes implanted in the brain of a rat showed excellent biocompatibility without changing the structure in the surrounding brain tissue or perturbations to neighboring neurons over a period of six months, which makes it an ideal material for use as a drug host for controlled release over a long time interval\(^6\). Titania has outstanding photocatalytic performance\(^7\), and has been widely used in environmental and waste water applications for oxidation of a large variety of bacteria\(^8\), viruses\(^9\), fungi\(^10\), cancer cells\(^11\), and organics including methyl orange\(^12\), trimethylamine\(^13\) and acetone\(^14\). Photocatalytic oxidation by titania allows these compounds to be totally degraded and converted to CO\(_2\), H\(_2\)O and harmless inorganic anions. The mechanism for these applications involves the generation of reactive oxygen species such as H\(_2\)O\(_2\), O\(_2\)\(^-\) etc. by the redox reactions of water or oxygen with electron-hole pairs created by the irradiation of titania with near UV-light\(^15\).

Recently, the risk of climate change due to global temperature increase and depletion of fossil fuels have become worldwide concerns\(^16\)-\(^18\), and more and more attention has been focused on efficiently utilizing solar energy as a substitute for non-renewable resources\(^19\)-\(^21\). With advantages such as high efficiency, low cost, chemical inertness, and photostability, titania-based systems, especially those with anatase phase, are extremely attractive for such applications\(^22\)-\(^23\). As a n-type semiconductor, the valence and conduction bands of anatase titania are respectively +3.1 and -0.1 eV, thus giving a band gap of +3.2 eV. Therefore, titanium dioxide readily absorbs UV light with wavelength below 387 nm\(^24\)-\(^25\). The mechanisms that determine the photoelectrolysis, photocatalytic or photovoltaic activity, are related to structural features such as surface area, crystallinity, and morphology of titanium dioxide\(^26\). Another important potential application of titania is in the field of energy storage, such as in lithium ion batteries. As anode materials in lithium ion batteries, titania, especially with nanoporous structure, has
advantages including small volume expansion (~3%) during intercalation/extraction of Li⁺ ions²⁷, good cycling stability²⁸, and high discharge voltage plateau (~1.7 V)²⁹, and has attracted enormous attention³⁰-³².

It is well known that the intrinsic properties of titania strongly depend on the morphology and crystallite size of the material, which are determined by the method of synthesis³³. Many forms of titania have been known and applied for a long time, including powders³⁴, fibers³⁵, and bulk films³⁶. However, the preparation of nanoporous nanocrystalline anatase TiO₂ thin films creates significant opportunities for a number of technological applications such as photovoltaic cells³⁷, electrochemical devices³⁸-³⁹ and photocatalysis⁴⁰. For instance, by utilizing mesoporous titania based thin films as catalysts or catalyst supports, the flux of reactant molecules can be vastly improved owing to the continuous mesoporous network. This facilitates interactions between reactant molecules and catalytically active sites, resulting in an increasing reaction rate for catalytic reactions that are transport-limited rather than kinetically limited⁴¹. Furthermore, considerable work has been done by Zhao and co-workers to show that the photocatalytic activity depends on both the specific surface area and the crystallinity of nanostructured titania film⁴². The work of Tang et al. has shown that highly crystalline, ordered mesoporous TiO₂ thin films exhibit a 2.5% photoconversion efficiency for water photolysis at zero-bias and Xe lamp illumination of 40 mW cm⁻².⁴⁰ The incorporation of metallic nanoparticles within mesoporous TiO₂ thin film “hosts” has been explored, and shown to improve the electron migration from the TiO₂ surface to metals and to suppress electron-hole recombination, resulting in increased photocatalytic activity for oxidation of stearic acid⁴³-⁴⁴.

As for photovoltaic cells, it is well known that the substitution of TiO₂ nanocrystalline layers for TiO₂ microcrystalline layers improves light-to-electricity conversion efficiency, and the application of mesoporous thin films with nanocrystalline walls leads to even higher solar conversion efficiency than that of thin films comprised of nanocrystalline titania⁴⁴-⁵⁰. For instance, photovoltaic devices fabricated from mesoporous anatase TiO₂ thin films exhibit photon conversion efficiency up to 0.52%, which is comparable to that of nanocrystalline colloidal anatase TiO₂ films with larger
Furthermore, an increase of solar conversion efficiency by 50% has been obtained by using cells containing TiO2 mesoporous films with thickness of about 1 μm instead of a randomly oriented anatase nanocrystalline film with the same thickness53.

Ordered porous titania films are of interest for other applications where photoactive materials are required. Due to their well-organized mesopore structure and high surface area, which together provide an efficient pathway for electrolyte transport and a continuous solid network for fast electron transfer in their walls, electrochromic devices fabricated from mesoporous TiO2 had 3 times the coloration efficiency and considerably faster switching response compared to nanocrystalline films composed of 7 nm diameter nanoparticles38. The combination of mesoporous TiO2 with metallic nanoparticles can induce a “confinement effect”, which is able to increase selectivities, activities, and surface acidity of these supported catalysts. This has been shown to lead to high selectivity and turnover frequency for allylic nucleophilic substitution, even at low loading of metallic nanoparticles54. Mesoporous TiO2 thin films, which in some cases have been shown to exhibit a quantum confinement effect indicated by a blue shift in the onset of UV-Vis absorption, also have outstanding optical transparency, sometimes with transmittance higher than 85% in the visible wavelength range55. Given the large number of applications for mesoporous titania nanocrystalline films, a large number of approaches have been explored to obtain thin films with well-defined nanoporous structures in order to design materials to meet the requirements of various applications.

1.1. Mesoporous Thin Films by Surfactant Templating

Since the discovery of the hydrothermal route to preparing the MCM (Mobil Crystalline Material) family of periodic mesoporous (alumino) silicates was reported56-57, similar approaches have been extended to transitional metal (TM) based materials, including metal oxides, metal phosphates and metal sulfates, by utilizing a large variety of surfactants or larger amphiphilic macromolecules as templating agents58. Despite a large amount of effort to successfully synthesize mesoporous TM-based materials, however, there are still many obstacles on the pathway to synthesize mesostructured films by design, including the high reactivity of metallorganic precursors, the variety of their coordination numbers (which affects their interactions with templates), the types of
oxo-hydroxide clusters they form, and their crystallization behavior. The most important of these is the high reactivity of TM-based precursors towards hydrolysis and condensation. This can be addressed by adding complexing molecules or acids as stabilizing agents, which hinder rapid condensation reactions and thus avoid the formation of a dense inorganic network and the separation of organic and inorganic components, either of which would result in materials with a poorly defined mesopore structure. In addition, many other techniques have also been explored to overcome this complication. For instance, polar non-aqueous solvents have been utilized by several researchers, in which a small amount of water can be introduced from environmental moisture to assist the hydrolysis reactions, leading to slow hydrolysis and condensation rate of the metal ions.

A recently developed synthesis approach is the evaporation-induced-self-assembly (EISA) process, in which the inorganic precursor is initially present in a dilute sol (which reduces the condensation rate). Rapid evaporation of the solvent leads to the formation of a co-assembled liquid-crystal-like TM/surfactant mesostructure in which condensation is also controlled. Another advantage of EISA for the preparation of mesoporous transition metal based thin films is the ability to adjust the pH of the initial sol to favor a final material with desired properties. Starting with a highly acidic sol prevents uncontrolled condensation of TM precursors, thus allowing slow formation the inorganic network within the liquid crystal (LC) phase. Gradual elimination of the acid by evaporation provides a way to control the polymerization of the inorganic components while allowing a fully cured inorganic network to form.

The formation process of films with ordered mesophase via EISA was investigated by Crepaldi and co-workers and a rough formation pathway was presented. During the period of drying and aging of dip coated films, the evaporation process could be categorized into five stages when the freshly coated solution of ethanol, template and metal precursor is exposed to ambient air. The first stage is assigned to the evaporation primarily of ethanol rich vapor, which only last for about 20-30 seconds and is followed by a slower process in which the H₂O/HCl rich vapor departs the film. In the third stage, a worm-like phase appears and micelles with uniform size and random orientation form.
In the fourth stage, the micellar aggregates organize and align and, after the residual solvents depart from the film in the fifth stage, the disorder-to-order transition path is completed. Crepaldi et al. also showed that, beginning from the third stage, the humidity in the atmosphere is a crucial parameter controlling the formation of the ordered film\textsuperscript{59}, presumably because the humidity determines the amount of residual water remaining in the “dried” films.

Investigations of the details of the titanium hydrolysis process and the interactions between metal ions and organic templates were carried out by other researchers. The work done by Livage et al. showed that the hydrolysis reaction mechanism of the metal ions depends on the electron affinities, sizes and the charges of metal ions and alkoxy groups, as well as the size and number of the alkoxy groups\textsuperscript{62}. Kim and co-workers proposed that there is a transition state between titanium alkoxides and hydrolyzed products and that two kinds of mechanism are involved in the hydrolysis of titanium alkoxides. One is an associative mechanism in which the entering group attacks the metal site first to produce a detectable intermediate of expanded coordination. This mechanism is most appropriate to describe the hydrolysis of Ti(OEt)\textsubscript{4} and Ti(O\textsuperscript{3}Pr)\textsubscript{4}. The other mechanism is an interchange associative mechanism in which the transition state is reached through formation of the bond with the entering group, followed by weakening of the bond to the leaving group. This mechanism is appropriate for the hydrolysis of bulky titanium alkoxides including Ti(O\textsuperscript{6}Pr)\textsubscript{4} and Ti(O\textsuperscript{6}Bu)\textsubscript{4}\textsuperscript{66}. Sanchez and co-workers suggested that the interaction between PEO-based template and the metallic centers plays a central role in the process of forming mesostructured materials. Under anhydrous or low water conditions, strong chelation between the polar heads of template and the metallic centers hinders the assembly of the template, leading to a final wormlike structure, while a well-ordered mesostructure can be obtained with the addition of large quantities of water and acid, which weakens the coordination between the metallic centers and polar heads of templates\textsuperscript{67}. Using a model based on a point charge approximation of the density functional equation, the chemical reactivity of titanium alkoxides Ti(OR)\textsubscript{4}(R=Et, Pr\textsuperscript{3}, and Bu\textsuperscript{6}) before and after hydrolysis and condensation reaction with tris(hydroxymethy)nitromethane as template was analyzed by Weymann-Schildknecht and Henry. The results indicate that bridging OR groups are sites for
preferential attack during the substitution by OH and/or OX group, and that a Ti$_4$O$_{16}$ structure may be preserved upon hydrolysis to serve as a building unit for complexes of higher nuclearity$^{68}$.

In spite of many investigations of the synthesis mechanism of mesoporous titanium-based thin films, the reproducibility in obtaining high quality films is still a weak point. This is because the formation mechanism of mesoporous titania-based thin film is kinetically controlled and influenced by many factors, including atmospheric conditions of the lab and other factors difficult to quantify and control, such as mixing time while preparing the sol, aging time prior to deposition, and purity of the (hygroscopic) precursors. To prepare mesoporous titania-based thin films for various applications and to investigate the formation mechanism in depth, a number of approaches have been explored and many factors that influence the formation of the mesoporous films have been investigated. The choice of template and its ratio to the inorganic species are of utmost importance in controlling the final mesostructure$^{69-70}$. For instance, using titanium isopropoxide as inorganic precursor, thin films with an anisotropic and distorted 2D-hexagonal mesostructure are obtained under certain conditions when the Pluronic surfactant P123 from BASF (a block copolymer with average formula HO(CH$_2$CH$_2$O)$_{20}$(CHCH$_3$CH$_2$O)$_{70}$(CH$_2$CH$_2$O)$_{20}$H) is used as the template, while cubic mesostructured films are obtained with Pluronic F127 (HO(CH$_2$CH$_2$O)$_{106}$(CHCH$_3$CH$_2$O)$_{70}$(CH$_2$CH$_2$O)$_{106}$H)$^{71}$. On the other hand, with cetyltrimethylammonium chloride (CTAC) as the template and (NH$_4$)$_2$Ti(OH)$_2$(C$_3$H$_5$O$_3$)$_2$ as the inorganic precursor, lamellar phases are formed for molar ratios of CTAC/Ti greater than or equal to 0.49$^{72}$.

In terms of mechanism, it has been shown by Grosso et al. that the final mesostructure in block-copolymer-templated silica sol-gel films does not form until the ethanol and excess water used for prehydrolysis escape the film$^{73}$. Based on this observation and the phase diagram of nonionic surfactant templates in water$^{74-75}$, Alberius et al. proposed that the final mesophase is controlled by the volume fraction of surfactant ($\Phi$), which is defined as the ratio of the volume of copolymer in the dried film to the estimated volume of the nonvolatile components in the final film. Thus, they predicted
that the mesophase should be cubic, 2D hexagonal or lamellar for $\Phi$ in the ranges from 29%-36%, 38%-55% or 61%-75% respectively, for P123 as template and titanium teraethoxide as inorganic precursor.$^{69}$

Despite successful predictions of metal oxide film mesostructure based on surfactant phase behavior, this approach is rather simplistic in that it ignores other factors, such as relative humidity of the atmosphere,$^{59,76}$ the acidity of the sol$^{59}$ and the coating flow.$^{77}$ For instance, spin-coating at a low speed such as 600 rpm has been shown to generate cubic mesoporous TiO$_2$ thin films, whereas 2D hexagonal mesoporous thin films are formed at a high spin-coating speed of around 2000 rpm for 20 s, for F127 as template and titanium tetraisopropoxide as inorganic precursor$^{77}$. This could be due to a slower rate of evaporation of water in the former case. Considerable work accounting for the effects of relative humidity was done by Crepaldi et al. and their results indicate that different mesophases can form by varying the template/Ti ratio. However, Crepaldi et al. observe that P123-templated 2D-hexagonal and cubic mesostructures could not be stabilized, even at very low P123/Ti ratio(s), which differs from the results obtained by Alberius et al.$^{59}$

In addition to changing the type of mesophase that forms, changing the surfactant:precursor ratio or temperature (which strongly influences the critical micelle concentration, or CMC$^{78-79}$) also changes the amount of inorganic precursors incorporated with the hydrated PEO head groups and the number density of micelles after coating, which dictates the distance between micelles or the wall thickness of the films. Ryoo et al. clearly showed this by demonstrating that the wall thickness of mesoporous precipitated silica SBA-15 increases with increasing SiO$_2$/P123 ratio in the coating solution$^{80}$. On the other hand, pore size can be influenced by adjusting the size of the micelles themselves. To generate films with large pore size, Ti(OBu)$_4$ has been explored as an inorganic precursor. The hypothesis driving this approach is that the hydrophobic butanol released in situ should swell the surfactant template micelles during film formation, thus increasing the pore size with an increase of the amount of Ti(OBu)$_4$.$^{81}$ Also, because the CMC of P123 is lower in the presence of 1-butanol than in ethanol, the utilization of 1-butanol can favor the mesostructural organization at relatively low P123
concentrations. The effect of using 1-butanol as solvent has been investigated and the result indicates that titania thin films with thermally stable mesostructure up to 400 °C, in addition to swollen mesopores, can be obtained\textsuperscript{82}. The enhanced thermal stability of mesostructure is ascribed to the use of a low P123/Ti ratio with 1-butanol as solvent, which supplies more than sufficient amounts of inorganic building blocks that are compactly located in the P123 corona region. The final outcome of this strategy is a mesoporous titania thin film comprised of thick robust inorganic walls with high thermal stability\textsuperscript{82}. The influence of the substrate has also been investigated, and it has been shown that the mesostructure of films coated on hydrophobic substrates, such ITO glass, was prone to collapse at relatively low RH, while the structure of the films coated onto a hydrophilic substrate, such as a silicon wafer, was retained\textsuperscript{76}. While these are only several examples of results of changing process variables that have been reported, they illustrate the complexity of the surfactant templating process and the challenges associated with the design of a process to create a film with desired mesoporous structure. Some of these challenges in the context of titania thin film formation for energy application will be addressed in this dissertation, as described below.

1.2. Aligning Mesopores

In the work discussed so far, the focus has been on preparing mesoporous transition metal-based films with highly ordered pores, controlled pore size, and the high crystallinity of the inorganic phase. By focusing on these properties, different chemical and physical properties have been obtained to satisfy the needs of various applications, and a certain level of understanding about the synthesis mechanism has been achieved. However, when anisotropic 2D hexagonal films are prepared, the direction of the mesochannels in almost all mesoporous/mesostructured films is parallel to the substrate. The control of pore orientation is still a new area and advances in oriented mesoporous transitional-metal based materials continue to be made\textsuperscript{41}. If the direction of mesochannels is perpendicular to a substrate, we can expect a wide variety of potential applications including highly responsive chemical sensors, highly selective separations, ultra-high-density recording media, etc\textsuperscript{83}. The importance of pore accessibility is illustrated in the case of photocatalysis, for which cubic mesoporous titania films have been found to offer
higher photocatalytic efficiency than 2D hexagonal films since the mesopore channels of the 2D hexagonal mesophase are parallel to the substrate and therefore not accessible\textsuperscript{41}.

One important application area for the mesoporous titania based thin films is in photovoltaic materials. Because TiO\textsubscript{2} is an n-type semiconductor, infiltrating the pores with a p-type organic semiconductor has been proposed as a route to low-cost solar cells\textsuperscript{46}. However, having straight, non-intersecting, accessible pores is essential for high hole conductivity; for instance, poly-3-hexylthiophene (P3HT) loaded into perpendicular 2D hexagonal close-packed (HCP) channels conduct holes 5 orders of magnitude faster than in interconnected cubic channels\textsuperscript{37,46}.

Because of the technological promise of thin films with oriented cylindrical pores, the synthesis of this architecture has attracted the interest of several research groups. For instance, a combination of eutectic decomposition of amorphous films and subsequent chemical etching was utilized by Kondoh et al.\textsuperscript{84} to prepare mesoporous silica with channels perpendicular to the substrate, in which an amorphous silica matrix is embedded in a framework composed of a regular array of needlelike hematite crystals. Then, the pore space was liberated by removal of hematite crystals via chemical etching\textsuperscript{84}. However, the TEM images of the resulting films do not clearly indicate the degree of perfection and orientation of the pores. The use of ternary surfactant systems was also used to create particles with perpendicular pore orientation, in which bilayer lamellar structures of a fluorinated surfactant formed, and the Pluronic silicate nanocomposite of SBA-15 was aligned between the bilayers, although the products were flake-like particles\textsuperscript{85}. Perpendicularly arranged mesochannels have also been prepared by assembling surfactant-templated silica inside the columnar pores of anodic porous alumina\textsuperscript{86}. However, this approach cannot be used to obtain continuous films with homogeneous composition. High magnetic fields have been shown to orient the mesochannels of mesoporous silica films due to alignment of the lyotropic liquid crystal templates\textsuperscript{83}. However, extremely large magnetic fields (~30 T) are required to achieve complete alignment in thin films, making this approach challenging to scale up and out of the reach for most academic labs\textsuperscript{87}. Another type of external field that has been applied to orient mesostructure is a concentration gradient. Ordered mesoporous silica films with
mesochannels perpendicular to the substrates are obtained through the coassembly of poly(styrene-b-ethylene oxide) and oligomeric organosilicate precursor and annealing the films under chloroform and octane vapor after coating. Surface chemistry can also allow lyotropic phases to orient perpendicular to a substrate, and a dip coating method was reported using P123 as the surfactant and crosslinked PPO-PEO copolymers as surface modifier for deposition of perpendicular 2D HCP silica thin films. This method was then extended to titania, and in principle, to any substrate as recently reported by Koganti and Rankin. However, the films are fragile due to their thin walls and small pores. This makes it difficult to crystallize the titania without loss of long-range pore order, and makes the films susceptible to damage. Manipulation of the pore size also is of interest for loading of conductive polymers into the pores. Therefore, mesoporous titania films with channels normal to the substrate, thicker walls and larger pores are in demand.

1.3. Titania Nanotube Arrays

An alternative method to achieve nanoporous titania thin films with channels perpendicular to the substrates is to fabricate titania nanotube arrays. Various approaches have been explored to prepare titania nanotubes and nanotube arrays, including template-assisted methods, the sol-gel process, seeded growth and hydrothermal treatment. For instance, by using porous aluminum oxide, crown-appended cholesterol-based organic gelator or ZnO nanorods as templates, titania nanotubes can be obtained. Kasuga and co-workers showed that needle shaped titania with tube structure can be synthesized from a titania based powder derived from the sol-gel method followed with treatment in concentrated (5-10M) NaOH aqueous solution. By employing TiO₂ nanoparticles as seeds, Tian and co-workers successfully grew titania nanotubes on titanium foil which was treated in 10 M NaOH solution at 160 °C. The details of the fabrication of titania nanotubes through hydrothermal treatment, including formation mechanism, effect of temperature, time, precursors, acid washing, and post-synthesis treatments, are discussed by Ou. However, all of the above methods can only generate titania powders with separated tubular structures, or arrays of tubes with random alignment, which limits the further applications of these materials.
By far, electrochemical anodic oxidation is the most attractive approach to synthesize highly ordered titania nanotube arrays demonstrating remarkable properties. This strategy, based on the anodization of titanium foil in fluoride-based baths, has several advantages including desirability for large scale production, feasibility for many different types of applications, and easily controllability for ordered alignment by tailoring electrochemical conditions\textsuperscript{7,90}. Zwilling and co-workers\textsuperscript{96} first reported in 1991 the formation of a porous surface on titania films by anodizing titanium and titanium alloys in the presence of an electrolyte containing chromic acid and hydrofluoric acid. However, the more detailed work on the fabrication of titania nanotube arrays through electrochemical anodic oxidation was done by Grimes and co-workers. In 2001, Grimes and co-workers first reported the successful growth of uniform titania nanotube arrays after anodizing titanium metal sheets at voltages between 10 and 40 V in dilute (0.5-1.5 wt\%) aqueous HF solutions\textsuperscript{97}. It was found that nanotubes ranging in diameter from 25 nm to 65 nm could be prepared, and that the diameter increased with an increase of the applied voltage, while the final length of the tubes was independent of the anodization time. They also found that, as the bath temperature decreased from 50 °C to 5 °C while anodizing titanium in electrolytes containing HF and acetic acid mixtures, the wall thickness of tubes increased from 9 nm to 34 nm, while the pore diameter remained constant at \~22 nm\textsuperscript{98}. Thus, the temperature, voltage, and time can all be adjusted to create titania nanotubes arrays with a desired set of structural characteristics.

However, because the dissolution speed of titanium oxide in aqueous fluoride solutions is very high, Grimes’ group found that it is impossible to create nanotube arrays with length greater than 500 nm by using electrolyte solutions containing hydrofluoric acid\textsuperscript{99}. Later, this same research group reported that the pH value of the electrolytes plays a big role in determining the length of the tubes, and successfully grew titania nanotube arrays with length up to 4.4 µm in an electrolyte with pH value of 4.5. In this procedure, they substituted KF or NaF for HF in electrolyte solutions and adjusted the pH value of the electrolytes solution with additives such as sulfuric acid, sodium hydroxide, and sodium hydrogen sulfate.\textsuperscript{100} Subsequently, considerable investigations about the impacts of various salts and solvents on titania nanotube length were carried out by various researchers. Schmuki and co-workers reported that using neutral fluoride solutions
comprised of \((\text{NH}_4)_2\text{SO}_4\) (1 M) and \(\text{NH}_4\text{F}\) (0.5 wt\%) as the electrolyte solution can generate titania nanotube arrays with lengths up to micrometers. Furthermore, by using electrolyte solution containing 0.5 wt\% \(\text{NH}_4\text{F}\) in glycerol with a dynamic viscosity of 1350 mPa at 20 °C, they achieved titania nanotubes with excellent properties including 40 nm pore diameter, 7 \(\mu\)m length, and extremely smooth homogeneous walls. This strategy successfully takes advantage of highly viscous glycerol based electrolyte solutions to control the acidification at the pore tips by suppressing pH bursts and damping local concentration fluctuations during anodization.

Compared to the aqueous solution, organic solvents are less corrosive and can reduce the dissolution rate of TiO\(_2\), and have also been used in the anodic fabrications of titania nanotube arrays with lengths up to hundreds of micrometers. For instance, self-organized titania nanotube arrays with a length of 180 \(\mu\)m can be grown from titanium sheets in a 2-propanol-water system containing \(\text{NH}_4\text{F}\) when the water volume percent is lower than 16\%. The length of titania nanotube can be tailored and increased up to 1000 \(\mu\)m by using nonaqueous organic polar electrolytes including dimethyl sulfoxide, formamide, ethylene glycol and N-methylformamide combined with fluoride ions. In general, the average pore diameters of nanotubes derived from nonaqueous electrolyte solutions are almost always above 50 nm and wall thicknesses are usually above 15 nm.

Various approaches and theories have been developed to understand the formation mechanism of titania nanotube arrays, and most researchers consider field-assisted dissolution to be the predominant mechanism of titania tubular structure formation. The point defect model, proposed by Grimes and co-workers based on the observation of the evolution of nanotube structures, is the most widely accepted approach to describe the formation process of titania nanotube arrays. In this mechanism, at a constant anodization voltage, the localized dissolution at defects on the surface is thought to generate the initial pits, thus making the barrier layer at the bottom of pits relatively thin. In turn, this thinner oxide layer increases the electric field intensity across the remaining barrier layer, resulting in further pore growth. Unanodized metallic portions also initially exist between the pores, and, as the pores grow, voids are formed and grow in these interpore regions by the field assisted oxidation and dissolution. Thereafter, the
growth of voids in equilibrium with the pores finally yields a tubular structure. However, the creation of voids finally leading to the separated, individual tubes could not be predicted by this model. Raja and co-workers proposed that perturbation analysis could be employed to determine the necessary conditions for generating instability of the anodized oxide layer and formation of self-ordered structures. They suggested that the perturbation of the metal sheet surface can lead to adsorption of fluoride anions at the valleys which eventually develop into porous structures, whereas separation of individual nanotubes of titania layers from the inter-connected nanopores could be attributed to the repulsion forces of the cation vacancies, which are generated by accelerated dissolution of the titania.

1.4. Mechanical Properties of Titania Thin Films with Mesoporous Architectures

As discussed previously, nanoporous titania is an extremely promising material for utilization as an electrode material in lithium ion batteries. However, only certain structures of porous titania films have been shown to exhibit long cycling life, while other structures exhibit a fast decay of capacity. Therefore, it is important to understand the effect of the pore structure on the electrochemical performances of nanoporous titania electrodes in lithium ion batteries. Mechanical fracture has been considered one of key factors causing the fading of battery capacity and hindering the growth in lithium ion battery technology, and a good deal of fracture mechanics analysis has been applied to better understand the mechanical degradation of lithium alloy electrodes. It has gradually been accepted that the fracture and degeneration of these electrodes are caused by diffusion-induced stresses (DIS), which arises from the dimensional changes due to variations in composition, and mathematical models have been explored for DIS. For instance, Prussin initially modeled the transverse stresses developed in a thin nonporous plate during mass transfer by using an analogy between thermal stress and DIS. This method was developed and extended by subsequent researchers to model electrodes with various porous structures. For example, Garcia and co-workers developed a two-dimensional finite element model to calculate stresses and tensions profiles in electrodes with geometrical two dimensional arrangements of particles. Golmon and co-workers used a fully-coupled diffusion-elasticity model with Butler-Volmer surface kinetics to simulate the evolution of stresses.
in electrodes with spherical silicon particles\textsuperscript{124}. Renganathan and co-workers used a quasi-2D porous electrode model for LiCoO\textsubscript{2}/graphite cells to evaluate stresses by combining the effect of changes in the lattice volume due to intercalation, and phase transformation which occurs during the charge/discharge process\textsuperscript{125}.

In all of the above models, the porosity of the electrodes is treated as the result of aggregation of nonporous particles with randomly arranged pores, and the porous structure contributes only to the improvement of electrolyte diffusion in the electrodes. However, in situations where the particles composing the electrodes also have porous structures, the mechanical properties of electrodes will be also be influenced by the pore architecture. In fact, this has been reported by several researchers. For instance, the work done by Lee and co-workers indicates that the stresses distributions in hollow cylinders are different from those in solid cylinders, in addition to the faster electrolyte diffusion found in hollow cylinders\textsuperscript{126-128}. In hollow cylinders, the radial stress component is tensile in the region near the outer surface and compressive near the inner surface\textsuperscript{126}, while it is tensile throughout the entire body of a solid cylinder\textsuperscript{129}. The tangential component of the stress is compressive in the region near both surfaces and tensile in the center of a hollow cylinder\textsuperscript{126}, while it switches from tensile at the center to compressive at the outer surface of solid cylinder\textsuperscript{129}. Furthermore, the ratio of outer radius to inner radius of hollow cylinders also has strong effect on the concentration and stress profiles, which are independent of specimen size in thin slab, solid cylinder and solid spheres after suitable normalization of length and time\textsuperscript{126}. Most recently, Harris and co-workers proposed that the presence of mesopores in an electrode can reduce the dimensionless strain energy to a little more than half of that found in a homogeneous solid electrode, assuming that the mesopore is cylindrical\textsuperscript{130}. Even a single mesopore present in an electrode has a significant effect on the lithium ion diffusion and fracture strength of the particle which affects the stress intensity factor in complex ways. Therefore, it can be imagined that the utilization of thin films electrodes with well ordered porous structure over a large area should have a significant effect on the reduction of strain energy and will open new opportunities for the development of electrode materials with outstanding electrochemical performance. However, all models considered to date treat only electrodes composed of agglomerated nonporous particles or
isolated particles with only a single pore. Electrodes composed of well ordered mesoporous structures present opportunities not only to increase electrolyte transport into the solid framework, but also to enhance the mechanical stability through the interconnected inorganic framework. Thus, there is a need to begin developing and testing a DIS model of ordered mesoporous thin film batteries, which will be a part of this dissertation work.

1.5. Characterization of Titania Thin Films

1.5.1. Diffraction

Another important aspect of the work being conducted for this dissertation is characterization of films with ordered and oriented mesopores. Until recently, 1D x-ray diffraction (XRD) was the most widely accepted technique to assess the structure of the mesoporous thin films due to its widespread availability. Because the pore spacings are on the order of a few nanometers, the diffracted reflections appear at low angles. The geometry used to obtain 1-D XRD patterns is known as the Bragg-Brentano geometry, where both the incident beam and the detector move simultaneously to develop the XRD pattern of the film. According to Bragg’s law, constructive wave interference, and hence the appearance of diffraction peaks occurs when the following equation is satisfied:

\[ n\lambda = 2d \sin \theta \] (1.1)

Where \( \lambda \) is the wavelength of the x-rays, \( n \) is an integer, \( d \) is the spacing between planes of objects (in this case pores), and \( \theta \) is the angle between the incident beam and the detector. Depending on the pore symmetry, we will observe peaks from different planes in the ordered structure. Based on the relationship between the d-spacings of these peaks, the pore symmetry and unit cell parameter can be determined. For instance, the 2D hexagonal phase (p6mm symmetry group) of nanoporous material is identified by well resolved Bragg reflections with the ratio of 1/d-spacing 1:√3:2:√7:3:… that can be indexed to the (100), (110), (210), (300) … reflections, respectively.

However, 1D XRD in the Bragg-Brentano geometry is not sufficient to determine the symmetry of all phases, especially when mesophases are oriented with respect to the substrate. Because of the weak diffraction occurring from mesophases, only a few
reflections can be observed even for what are well-ordered samples. Therefore, even for phases that are not intentionally aligned, preferential orientation with respect to the substrate can lead to an even small number of reflections that are difficult to assign. Fortunately, the work of Hillhouse et al.\textsuperscript{131} describes an alternate way to verify the orientation of HCP channels by observing films in several x-ray diffraction (XRD) modes. In the usual Bragg-Brentano reflection mode typically used for powder XRD, ordered HCP mesoporous films that are oriented with the (100) plane parallel to the substrate are indicated by the presence of (100) and (200) reflections, but the absence of the (110) reflection (Fig. 1.1b). When the pores are perpendicular or inclined to the substrate, no reflections should be observed by XRD in this mode (Fig. 1.1a). The combination of TEM of pieces of film scraped from substrates (to confirm ordering) with XRD will be shown to be a powerful tool to assess the orientation of mesochannels through chapter 2 to chapter 4. In this dissertation, most samples were characterized by the 1D XRD technique by employing a Bruker D8 diffractometer with an x-ray source with a wavelength of 1.54 Å.

Grazing incidence SAXS (GISAXS) is also a suitable technique to characterize the structure of thin mesoporous films since the angle of incidence of the x-ray beam can be adjusted to provide scattering information near the top surface of the film or across the entire film. Using GISAXS, information about the orientation, the anisotropy of the mesostructure and the coexistence of several mesophases can be determined. These techniques also typically employ a 2D CCD detector, thus providing more information about the full symmetry and geometry of a film. GISAXS experiments with high-intensity x-ray sources are also widely used for in-situ studies of the mesostructure formation mechanism and mesophase transformation in thin films (e.g. uniaxial contraction and/or crystallization of inorganic walls)\textsuperscript{132-136}. This technique is well suited to directly determining the orientation of mesopores in thin ceramic films. The diffraction patterns measured by GISAXS are composed of complicated reflection and refraction scattering effects at the air-film and film-substrate interfaces, and provide bulk average information about lattice parameters of 2D structures in thin films. To analyze these effects, programs have been developed based on the distorted wave Born approximation (DWBA) and are usually required to unambiguously assign the spots in
the resulting pattern\textsuperscript{137-142}. Therefore, in this dissertation, the GISAXS technique was performed on a limited subset of experimental samples to determine the orientation and mesophase within thin films. GISAXS data were obtained at the Advanced Photon Source at Argonne National Labs on beamline 8-ID. Details of the measurement and equipment set up described in chapter 5.

1.5.2. Electron Microscopy

Based on the length scale of the channels in the thin films studied here, the natural tool for direct examination of pore structure should be electron microscopy, especially transmission electron microscopy (TEM), which is a powerful imaging technique to image features down to the nanometer size scale. In this work, we use a JEOL-2010F high-resolution transmission electron microscope (HRTEM) with field emission at 200kV. Unlike in SEM, samples for TEM must be thin enough to directly transmit electrons. However, almost all samples prepared in this work are titania thin films deposited onto glass slides with thickness of \( \sim 1 \) mm, which are so thick that they can be considered to be opaque to electrons. Therefore, typical sample preparation for TEM observation in this work is as follows. First, films to be examined were scraped off of the substrate and the resulting powder dispersed in anhydrous ethanol. Two or three drops of this mixture containing ethanol and titania powders were then transferred onto copper TEM grids. After drying at room temperature overnight, all ethanol evaporated and only the titania samples were left on the Cu grid, which was then observed in the microscope. This sample preparation technique prevented us from being able to obtain information about the orientation of mesochannels because the pieces of film removed by scraping are randomly oriented on the grid. However, by combing TEM with the 1D XRD technique discussed above, it is possible to assess the orientation of mesochannels, as will be discussed in Chapters 2 to 4.

Additionally, Scanning Electron Microscopy (SEM) provides direct information about the surface of films. Unlike TEM, this technique does not require scraping samples from substrates, which makes this an ideal technique to obtain orientation information because the mesochannel structure is undisturbed by sample preparation. The sample is placed on the SEM sample stage and then is scanned with electron beam. The scattering
of electrons from the surface is measured to obtain the image. However, because of the poor electrical conductivity of a semiconductor such as titania, the accumulation of charge on the surface of samples always results in the deterioration of image quality. Therefore, to improve the electrical conductivity, titania thin films for SEM analysis were deposited on ITO-coated glass slides and were fractured and mounted onto SEM stubs for observation (Chapter 3). Depositing a layer of Au/Pd on the top of the sample surface with using argon as carrier gas is also used to improve the electrical conductivity of samples. Using SEM we could characterize the uniformity of the films down to a size scale of approximately 10-20 nm. We presently think that the Au/Pd layer used in the sample preparation is making it difficult to see features that are smaller than 100 nm. To improve the electrical conductivity of without covering pore features with different sizes, we control the thickness of deposited Au/Pd through adjusting the sputtering time. In Chapter 5, the bigger pores size of the final products is above 100 nm, and films were coated with a layer of Au/Pt alloy with a thickness ~ 15 nm using a sputtering process for 1 minute. Scanning Electron Microscope (SEM) images were subsequently collected with a Hitachi S-4300 microscope at 3kV for plan-view imaging of the pore accessibility. In Chapter 4, because the pore size of fabricated samples is smaller than 12 nm, films were left intact and coated with a layer of mixed Au and Pt with thickness ~5 nm. Scanning Electron Microscope (SEM) images were collected with a Hitachi S-900 microscope at 3kV for plan-view imaging of the pore accessibility.

1.5.3. Nitrogen Sorption Analysis

One of the characteristic properties of a sol-gel material prepared with or without surfactant templating is its pore structure. Nitrogen adsorption/desorption isothermal data were used in the experiments conducted as part of this dissertation to obtain information about specific surface area and pore structure parameters of the synthesized materials. Isotherms were measured at 77K with a Micromeritics Tristar 3000 automated nitrogen adsorption instrument using static volumetric determination technique. To obtain enough samples for the measurement, dozens of calcined films were scraped from glass slides. Before measurements, all samples were outgassed at an elevated temperature for several hours under flowing nitrogen. Specific surface areas of final products were evaluated using the standard Brunauer-Emmett-Teller (BET) multilayer
adsorption model\textsuperscript{143}, which is calculated by fitting the experimental adsorption data to the linearized form of the BET equation in the range of relative pressures from 0.05 to 0.2\textsuperscript{144}:

\[
\frac{x}{v_{m}(1-x)} = \frac{1}{v_{m}c} + \frac{c-1}{v_{m}c}x
\]

(1.2)

Where \(v_{m}\) is the volume of gas adsorbed when the entire adsorbent surface is covered with a complete unimolecular layer, \(v_{n}\) is the volume of nitrogen absorbed onto the material at any relative pressure \(x = p/p_{0}\), and \(c\) is a constant related to the heat of adsorption in the first layer. Monolayer capacity is obtained from the values of slope \((= (c-1)/(v_{m}c))\) and intercept \((=1/(v_{m}c))\) of the linear BET plot. The monolayer capacity thus obtained was multiplied by the cross sectional area of the adsorbed N\(_{2}\) (assumed to be 0.162 nm\(^2\) based on hexagonal close packing of nitrogen) to estimate the specific surface area of the material\textsuperscript{144}.

Because the Barrett-Joyner-Halenda (BJH) method in its original form underestimates pore sizes of mesoporous silica by about 20-25\%\textsuperscript{145}, pore size distribution and the average pore size were calculated by the modified BJH method of Kruk, Jaroniec and Sayari (the KJS method) based on the data obtained from nitrogen adsorption branch of isotherms assuming cylindrical pore shapes for all samples\textsuperscript{146-147}. It has been suggested by Kruk and Jaroniec that adsorption rather than desorption data should be employed to evaluate the pore size distribution of ordered porous materials\textsuperscript{146}. The reason for this is that pore network effects can cause delayed capillary evaporation. These network effects probably arise from the nonuniformity in pore diameter, and cause a situation where wider pore regions cannot be emptied of condensed nitrogen until the narrower pore sections are emptied or the relative pressure approaches the lower limit of adsorption/desorption hysteresis\textsuperscript{148}. In the BJH model, the Kelvin equation is used to evaluate the curvature radius of the meniscus formed at the interface between adsorbate and adsorbent at a given relative pressure. This curvature radius is known as the core radius which is confined by the adsorbed film on the pore walls. However, the pore sizes are underestimated by this model, especially as it is applied to materials with small pores that interact strongly with nitrogen\textsuperscript{149-150}. Therefore, the KJS method is used in this work.
and a correction for the statistical film thickness on pore walls is incorporated with the Kelvin equation. In this KJS model, the actual pore radius instead of core radius is used to evaluate the pore size distribution by means of BJH method with modified form of Kelvin equation to calculate pore radius\textsuperscript{147},

\[
    r = -\frac{2\gamma V_L}{RT \ln\left(\frac{P}{P_0}\right)} + t_n \left(\frac{P}{P_0}\right) + 0.3 n
\]  

(1.3)

Where \(V_L\) is the molar volume of the liquid nitrogen, \(\gamma\) is the surface tension of liquid nitrogen, \(R\) is the universal gas constant, and \(T\) is the absolute temperature (\(\gamma = 8.88 \times 10^{-3}\) N/m, \(V_L = 34.68\) cm\(^3\)/mol, and \(R = 8.314\) J/(mol\(\cdot\)K))\textsuperscript{147,151}. The film thickness was calculated for a particular relative pressure from the Harkins-Jura thickness equation with following form\textsuperscript{147},

\[
    t_n = 0.1 \left[\frac{60.65}{0.03071 - \ln\left(\frac{P}{P_0}\right)}\right]^{0.03968}
\]

(1.4)

1.5.4. Ultraviolet-Visible (UV-vis) Spectroscopy

In this work, UV-visible spectra were collected with an Ocean Optics Jaz Spectrometer in transmission mode to measure the optical properties of the final products. We assume all titania films prepares here are semiconductors with an indirect band gap\textsuperscript{152-153}. The indirect optical band gap (\(E_g\)) can be evaluated by the optical transmittance method through the following formula:\textsuperscript{153}

\[
    \alpha_{ab} = -\frac{1}{L} \ln(T_r) \approx A^* (h\nu_f - E_g)^2
\]

(1.5)

Where \(\alpha_{ab}\) is the absorption coefficient, \(L\) is the film thickness, \(T_r\) is the transmission (%), \(A^*\) is the constant that does not depend on \(h\nu_f\), \(h\) is the Planck’s constant (it is \(4.135 \times 10^{-15}\) eV.s), and \(\nu_f\) is the frequency. As we plot \(\alpha_{ab}^{1/2}\) on the ordinate against \(h\nu\) on the abscissa, the band gap can be estimated from the intercept of the tangent to the absorption edge with the abscissa.
1.6. Dissertation Outline

This dissertation is organized as follows. Chapter 2 will begin to describe the tuning of the structure of mesoporous titania films by examining the relationship between the wall thickness of titania thin film and the molar ratio of inorganic precursor (titanium ethoxide) to surfactant template (the tri-block copolymer P123). Chapter 3 will demonstrate the behavior of polypropylene glycol (PPG) when it is added to swell the pores of P123-templated titania films. The temperature/composition behavior of PPG of molecular weight $M_n = 3500$ in aqueous solution will be measured and correlated with its effects on the pore size of mesoporous titania thin films. In Chapter 4, conditions will be used where PPG undergoes phase separation from the matrix of P123-templated titania films to fabricate titania thin films with hierarchical meso-/macro-porous structures. In Chapter 5, a different additive will be explored (1-butanol), and it will be shown that 3D hexagonal (space group R-3m) mesoporous titania thin films with high transparency in visible light can be produced over a wide range of butanol concentrations. In Chapter 6, the preparation of amorphous TiO$_2$ nanotubes arrays by anodization at various voltages as potential anode materials for Lithium-ion batteries will be described, and their excellent capacity retention will be discussed. Furthermore, the impact of mesopore architecture including pore geometries, pore sizes and wall thicknesses, on the mechanical properties of titania thin films will be computationally explored, as they are utilized in lithium ion battery. Chapter 7 will include a summary of the dissertation and recommendations for future work.

This dissertation primarily focuses on understanding a few limited aspects of the formation and use of nanoporous titania thin films, especially the tuning of surfactant-templated sol-gel thin films formed using the EISA process. The formation of micellar lyotropic liquid crystal assemblies during the sol-gel approach with surfactant templating is explicitly elaborated, and has been fundamentally corroborated by the ability to design mesostructured titania thin films with expected porous architectures. The application of these ceramic films in the energy storage field as electrodes for lithium ion batteries is also demonstrated. The most significant impacts of this dissertation are expected to be: i) guidance in methods to investigate the lyotropic liquid crystal formation and phase separation behavior of polymers, and use this information for their application in
materials design; ii) new design ideas for the fabrication of nanoporous thin films; iii) 
development and application of methods to characterize materials with nanoporous 
features; and iv) demonstration of the potential for application of these titania thin films 
in energy storage. In addition to the significance of the findings reported here for titania 
thin film formation, the methods developed can also be used to develop future studies of 
surfactant template titania thin films and their applications.
Figure 1.1. Orientations of a \( p\text{6mm hexagonal mesophase} \) (above) and the corresponding predicted diffraction patterns (below). Adapted from Hillhouse et al.\textsuperscript{131} (a) mesophase with channels perpendicular to the substrate, (b) channels parallel to substrate and 100 face parallel to the surface.
Chapter 2. Tuning the Wall Thickness and Pore Orientation in Mesoporous Titania Films Prepared with Low–Temperature Aging


2.1. Summary

Porous titania thin films with well-ordered mesostructures are prepared by using Pluronic surfactant P123 (a poly(ethylene oxide) / poly(propylene oxide) triblock copolymer with average structure (PEO)₂₀(PPO)₇₀(PEO)₂₀) as the pore template and aging the films immediately after deposition in a high-humidity environment at -6 ºC. These structures are stable enough to undergo calcination at 400 ºC to generate nanocrystalline TiO₂ walls with retention of mesoporosity. Under the aging conditions used, the films have well-ordered mesostructures even as the molar ratio of P123 to titanium (R) decreases to as little as 0.006. Because the P123 micelle diameter remains constant across a range of compositions, the pore diameter also remains fixed but the wall thickness of the titania thin films increases as the P123 concentration decreases without decreasing the long-range order of the products. Furthermore, mesoporous titania thin films with hexagonal close-packed channels oriented perpendicular to the substrate can be obtained even with R values as small as 0.008 by sandwiching the as-prepared films between glass slides modified with crosslinked P123. Analysis of the mesophase obtained here indicates that a transition from films containing significant 2D hexagonal channels to 3D hexagonal structure occurs below P123/Ti = 0.008, but this does not correspond well to the volume fraction for phase transitions of the P123/water system. This suggests that a more detailed model would need to be developed to predict mesophases behavior at temperatures below the freezing point of water.

2.2. Introduction

Titania thin films are of considerable interest due to their unique electronic and optical properties, and have wide-ranging applications, including as components of dye sensitized solar cells⁴⁹,⁵²,¹⁵⁵, as photocatalysts¹⁵⁶-¹⁵⁷, as optoelectronic sensors¹⁵⁸-¹⁵⁹ and in fuel cells¹⁶⁰-¹⁶³. These applications require materials possessing a high density of
accessible active sites and efficient transport of charge carriers without recombination, and mesoporous crystalline titania with large surface area, accessible pores and controlled crystallinity represents a promising candidate for these applications. The continuous mesoporous network within thin films facilitates the flux of reactant molecules, while electron transport in the mesoporous TiO$_2$ thin films can be enhanced by promoting the formation of TiO$_2$ walls with suitable crystal phase, connectivity and crystallinity. Therefore, the performance of mesoporous nanocrystalline titania thin films for all of these applications can be significantly improved by developing synthesis methods to control all aspects of the structure of the material.

Many specific examples showing the importance of titania thin film structure control have been reported in the literature. Zhao et al. have shown that the efficiency of photon-energy conversion in nanostructured titania films depends on their specific surface area and crystallinity. The work of Tang et al. has shown that highly crystalline and ordered mesoporous TiO$_2$ thin films exhibit a 2.5% photoconversion efficiency for the photolysis of water at zero bias under Xe lamp illumination of 40 mW cm$^{-2}$. For photovoltaic cell applications, nanocrystalline TiO$_2$ layers exhibit improved light-to-electricity conversion efficiency compared to microcrystalline layers, and the solar conversion efficiency of nanocrystalline mesoporous TiO$_2$ is even higher than that of nanocrystalline thin films. As potential thermal insulating materials for infrared sensors, it has been shown that the effective thermal conductivity of crystalline mesoporous TiO$_2$ thin films is 2-3 times larger than that of the amorphous mesoporous thin films of similar porosity derived from the sol-gel approach using KLE (PHB-PEO block copolymers $H(CH_2CH_2CH(CH_3)CH_3)_{66}(OCH_2CH_2)_{86}H$) as templates. These applications illustrate the need to simultaneously control crystallinity and mesopore structure in TiO$_2$ thin films to optimize their performance.

Among the methods available to fabricate mesoporous thin films, the evaporation-induced self-assembly (EISA) process is perhaps the most versatile and facile. This approach to preparing thin films by surfactant templating was first reported to synthesize nanoporous silicon-based films and was later extended to non-silicon based materials. The wall structure initially formed in materials derived by this approach is
amorphous, and thermal treatment (calcination) is a common method used to simultaneously generate the pore space by removing templates and develop the metal oxide framework by dehydration, condensation, and crystallization of the metal oxide\textsuperscript{41,169}. However, because most EISA synthesis methods are based on avoiding the fast and full condensation of the inorganic phase to enable assembly of the as-synthesized mesostructured films, calcination of the materials are often unsuccessful, resulting in either poorly ordered materials or dense, fully collapsed structures\textsuperscript{170}. This problem is particularly acute in transition metal oxides because variability of their valence state makes them susceptible to redox reactions, and they have a propensity toward excessive crystal/grain growth during heating\textsuperscript{41,82,171-172}.

There are several approaches to resolving the crystallization problem. Calcination for a short time at high temperature can produce titania thin films with highly crystalline walls accompanied by minimal loss of mesoporous structure\textsuperscript{173}. By introducing so called delayed rapid crystallization (DRC) thermal treatments, Grosso and co-workers showed that the mesoporous structures could be well preserved in nanocrystalline titania thin films even up to a calcination temperature of 700 °C. In this strategy, a slow progressive heating process followed by long residence time at a temperature just below the point at which anatase forms (about 400 °C) was utilized to pre-consolidating the inorganic network of as-synthesized films before being calcined at higher temperature\textsuperscript{135,172}. Changing the conditions of sol polymerization to obtain better interlinked amorphous titania structure in the as-synthesized films can also favor controlled crystal nucleation. Ozin et al. proposed that, by substituting the more hydrophobic butanol for ethanol as a solvent, a more highly condensed inorganic framework in the as-synthesized films could be formed, which led to a thermally stable (up to 400 °C) titania mesostructure containing large anatase crystallites in the channel walls\textsuperscript{82}. However, the application of these approaches does not always completely avoid degrading the mesostructure of the thin films caused by over-growth of crystallites that are larger than the initial wall dimensions, especially when walls of the as-synthesized films are thin\textsuperscript{172}.

The preparation of mesoporous as-synthesized thin films with thicker and better interlinked walls provides a promising alternative means to stabilize an inorganic porous
matrix. By using the new template KLE, robust gel structures containing large micelles have been obtained which resulted in mesostructured films with a pore size of about 10 nm and wall thickness above 5 nm\textsuperscript{167,174}. However, this strategy still involves the formation of mesoporous thin films, for which the precise pathway to obtain a given mesostructured as-synthesized thin film is difficult to elucidate and hard to control for the reasons outlined above\textsuperscript{82}.

It is accepted by most researchers that partial hydration of PEO head groups of Pluronic surfactants occurs during the surfactant templated sol-gel process\textsuperscript{175-178}, and that the wall thickness of the porous films derived from these surfactants is on the same length scale as the size of the hydrated PEO headgroup\textsuperscript{176,179}. It has been reported that the hydrated PEO head groups interact directly with inorganic precursors\textsuperscript{67,179} (presumably through hydrogen bonding or complexation), thus promoting the formation of surfactant micelles at concentrations below the critical micelle concentration of the surfactant alone\textsuperscript{61,180-182}. Therefore, it is possible to increase the distance between adjacent micelles to increase the wall thickness in the final material by raising the amount of inorganic precursors incorporated with the hydrated PEO head groups. The work done by Ryoo et al. has proven the feasibility of this strategy by showing that in SBA-15 synthesis, decreasing the ratio of template P123 (a block copolymer with average formula \textit{HO(\textit{CH}_2\textit{CH}_2\textit{O})_{20}(\textit{CHCH}_3\textit{CH}_2\textit{O})_{70}(\textit{CH}_2\textit{CH}_2\textit{O})_{20}\text{H}}) to silica produces mesoporous products with 2D hexagonal symmetry and thicker walls\textsuperscript{80}. The increase of wall thickness was ascribed to incorporation of a larger amount of silicate species with the hydrated PEO chains of P123. However, this study was performed for precipitated silica particles and it is still unknown whether a similar strategy can be used to tune wall thickness in mesoporous titania thin films. The formation of transition metal based mesoporous thin films is a more complicated process, and the understanding of its formation mechanism is hindered because of sensitivity of the final product structure to a variety of process parameters, including the composition of initial precursors and templates, environmental temperature, humidity etc.\textsuperscript{69,82,170,183}.

Crepaldi and co-workers investigated the formation process of mesostructured films via EISA and presented an overview of the formation pathway\textsuperscript{59}. Mesophas
formation is heavily influenced by the evaporation process, which occurs during the drying and aging period. Low molecular weight species in the vapor phase (esp. water, ethanol and volatile acids or bases) readily exchange material with the films, so the humidity in the atmosphere is a crucial parameter controlling the formation of the ordered film\textsuperscript{59}. Another important concept in the design of a surfactant templating process proposed by Alberius et al.\textsuperscript{69} is the volume fraction model (VFM). In this model, it is hypothesized that the mesostructure of an oxide/surfactant material can be predicted by replacing the volume of water in an aqueous lyotropic liquid crystal with the equivalent volume of hydrolyzed metal precursor\textsuperscript{69}. Alberius et al. showed that titania thin films with lamellar, hexagonal and cubic symmetry can be achieved with calculated P123 volume percentages of 61-75\%, 38-55\% and 29-36\% respectively. These ranges are roughly equivalent to the volume fractions at which the lyotropic liquid crystals form at room temperature in the aqueous P123 system.\textsuperscript{69}

The VFM concept narrows down the range of the synthesis parameters that need to be explored to get a desired mesophase, but it has the known disadvantage of not directly accounting for the effects of the processing conditions used for materials synthesis on micelle interface curvature (and therefore final mesostructure)\textsuperscript{82,183-184}. For example, it has been confirmed by many research groups that high humidity during the initial aging period favors highly ordered mesostructures in titania thin films\textsuperscript{76-77,82,170,185-188}. However, that humidity level influences the degree of hydration of the surfactant, which may shift the surfactant composition boundaries for different mesophases. Urade et al. explicitly investigated this effect in silica films templated with a nonionic PEO-based surfactant and found that the film mesophases is heavily influence by relative humidity during aging\textsuperscript{189}. This effect is not inconsistent with the VFM, but the presence of free water in the film and its influence on the precursor condensation reactions needs to be accounted to have a truly predictive model.

Perhaps the greatest drawback of the VFM model is that it is based on the surfactant-water phase diagrams, which are not always available at the aging temperature of the film (especially if it is below 0 °C)\textsuperscript{74-75,190}. It is well accepted that the ideal conditions to make highly ordered mesostructures should allow the condensation reaction
of metal alkoxides to occur after the formation of liquid crystals. It is obvious that a low temperature can slow the rate of hydrolysis and condensation reactions of metal alkoxides and favor the formation of highly ordered lyotropic liquid crystals, as long as precipitation or crystallization of a solid phase does not occur. This concept has been verified by previous work in our group showing that mesoporous titania thin films with 2D hexagonal symmetry can be synthesized when the as-synthesized films are aged at low temperature (~4 °C) under high relative humidity (~93%) for only 2 hours. Oveisi et al. and Wu et al. also presented similar results indicating that highly ordered mesostructured titania thin films with cubic or 3D hexagonal symmetry could be formed by aging the as-synthesized films at extremely low temperature (-20 °C).

With these considerations in mind, the hypothesis is further tested here that aging as-synthesized titania-based P123-templated films at a low temperature with high relative humidity will lead to mesoporous titania thin films with well ordered pores by slowing down the condensation reaction of titanium species and favoring the formation of lyotropic liquid crystals. Also, under this aging condition, we will explore the range of conditions under which well organized mesostructures can be obtained from initial sol-gel solutions and test the hypothesis that decreasing of volume fraction of P123 will result in more titanium interacting with hydrated PEO head groups, eventually leading to thicker walls in the mesoporous TiO₂ thin films.

2.3. Experimental Section

2.3.1. Preparation of Thin Films

The procedure to prepare thin films is the same as that reported by Koganti et al. except for the aging temperature of the as-synthesized films. Commercially available glass slides (Gold seal micro slides, 3×1”) were first cleaned using Nochromix, and modified by dip coating with a P123 cross-linking solution. This solution was prepared by adding to a solution of 0.696 mmol/L P123 in acetone with a drop of glycerol to act as a cross-linker. An equimolar amount of 1,6-diisocyanatohexane (DH) was then added dropwise to this mixture under constant stirring. The resulting solution was dip coated onto the glass slides and then the slides were aged at 120 °C overnight to drive the isocyanate-hydroxyl cross-linking reaction to completion.
The titania sols were prepared by adding 2.1 g of titanium(IV) ethoxide to 1.53 g of concentrated HCl (36 wt%). After stirring this mixture for 10 minutes, a solution containing a variable amount of P123 dissolved in 6 g of ethanol was added. The molar ratio of P123 to titanium ($R$) was varied from 0.006 to 0.0122 in different films. Films were dip coated from this sol onto P123 modified glass slides and then were aged in a high humidity environment ($\text{RH} \approx 93\%$) in a refrigerator ($T \approx -6\, ^{\circ}\text{C}$) for 2 hours. To get a high relative humidity, glass slides coated with titanium sols were kept inside a sealed chamber with two beakers containing saturated KNO$_3$ aqueous solutions. As-synthesized titania films were then calcined by increasing the temperature in a muffle furnace in air at 25 °C/min to 400 °C and holding for 10 minutes before cooling back to room temperature rapidly. The calcination processes were carried out immediately after as-synthesized films were transferred to the muffle furnace to avoid uncontrolled condensation at the surface of films. In some cases, the films on P123 modified slides were sandwiched with an identically modified slide before starting the aging treatment, in order to orient the entire thickness of the film (these will be called “sandwiched films”).

2.3.2. Characterization

X-ray diffraction (XRD) analysis using Cu Kα ($\lambda=1.5406\, \text{Å}$) radiation was employed to determine the titania film structure. Measurements were conducted directly on the thin films in Bragg-Brentano geometry using a Bruker D8 Advance diffractometer. A Tristar 3000 (Micromeritics Instrument Corporation) automatic gas sorption analyzer was used to determine the structural characteristics of titania including Brunauer, Emmett, and Teller (BET) surface area. To obtain enough samples for the measurement, approximately 40 calcined films were scraped from about 20 slides to obtain ~0.015 g of powder for each sample and the resulting powder was outgassed for 4 hours at 120 °C under flowing nitrogen. It is known that the Barrett-Joyner-Halenda (BJH) method underestimates pore sizes by as much as 20-25%, and therefore the pore size distribution and the average pore size were calculated using the modified BJH method of Kruk, Jaroniec and Sayari (the KJS method) based on the data obtained from nitrogen adsorption branch of isotherms and assuming a cylindrical pore shapes for all samples$^{146-147}$. To determine the film mesostructure, films were scraped off of the glass slides and placed onto copper grids, and analyzed with a JEM-2010F (JEOL) high resolution
transmission electron microscope (TEM) with field emission voltage of 200 kV. UV-visible spectra were collected with an Ocean Optics Jaz Spectrometer in transmission mode. Glass slides coated with thin films were vertically positioned so that the spectrophotometer beam passed through the film and glass slide in sequence. For comparison, the UV-vis spectrum of a blank glass slide without coating was also measured.

2.3.3 Materials

P123 (H(OC₂H₅)₂₀(OC₃H₇)₇₀(OC₂H₅)₂₀OH, Mᵣ ~ 5800, BASF), titanium(IV) ethoxide (tech grade, Sigma-Aldrich), anhydrous ethanol (99.5+%, Acros), acetone (histological grade, Fisher), glycerol (99+%, Aldrich), DH (98%, Aldrich), and concentrated HCl (GR grade, EMD chemicals) were all used as received.

2.4. Results and Discussion

After aging at low temperature (~ -6 °C) for 2 hours, as-synthesized films with varying molar ratios of P123 to titanium (R) were calcined, and all of the resulting porous films were observed to be transparent and crack-free upon visual inspection. To quantify the optical characteristics of the films, Figure 2.1 presents the UV-visible light spectra of the titania thin films on glass slides as a function of R. All films have high visible light transparence with transmittance above 65%, consistent with defect-free transparent films regardless of Rs. The broad, weak oscillations in the spectra are interference patterns that arise from the thickness of films. The sharp decay that begins with an offset at about 380 nm is due to the UV light absorption caused by the excitation of electrons from the valence band to the conduction band of TiO₂. This corresponds to a band gap of ~3.4 eV, which is consistent with the reported band gap of mesoporous TiO₂ films 194-196.

To narrow the range of parameters to be explored, films deposited on modified glass slides with R = 0.0122 were investigated initially. The low angle XRD pattern obtained from a representative calcined film is shown in Figure 2.2, which displays only one reflection with strong intensity at 2θ = 2.26° (Fig. 2.2a) when as-synthesized films are exposed to ambient air during the aging process. Based on the characterization results to be discussed below, this peak is assigned to the (200) reflection of a 2D hexagonal close-packed (HCP) phase. This shows that, after aging at a low temperature
of -6 °C, a well-organized P123/titania composite mesostructured forms which can be preserved in the thin films during subsequent heating and removal of the template.

For “sandwiched films”, only one broad, weak reflection is observable at a similar position in the pattern (Fig. 2.2b). Hillhouse et al.\textsuperscript{131} has described that, for ordered HCP mesoporous films, reflections corresponding to (100) and (200) lattice planes can be observed in the powder XRD mode when there is mesostructure oriented with the (100) plane parallel to the substrate. However, no reflections should be observed by XRD in the Bragg-Brentano scanning mode when the pores are oriented perpendicular or inclined to the substrate. Conditions for fabricating the two types of films in Figure 2.2 are almost same, except that one was exposed to ambient air during aging, and the other was exposed to a slide modified with crosslinked P123 during the aging process. Therefore, the difference of reflections in the XRD patterns should be due to reorientation of the pores within “sandwiched films” perpendicular, or more precisely, orthogonally tilted with respect to the substrate. The presence of a weak reflection suggests that the pores are not completely reoriented but that the majority is orthogonal to the substrate. Using similar conditions except for aging the as-synthesized films at 4 °C, similar results were also observed by Koganti et al., who also confirmed by SEM that “sandwiched films” have channels perpendicular to the substrates\textsuperscript{191}. Therefore, we conclude based on prior work (and TEM characterization to be discussed below) that for films prepared with $R = 0.0122$, porous titania thin films synthesized with aging at low temperature (-6 °C) have well organized mesostructures, and the pores within these thin films are oriented orthogonal to the substrate when the as-synthesized films are placed in contact with a slide modified with crosslinked P123 during the aging period.

At such low temperature (-6 °C), the hydrolysis and condensation reactions of titanium alkoxides are expected to be slower than at 4 °C, and, as more inorganic precursors are added, more titanium species are expected to be incorporated with the hydrated PEO head groups of P123 during the aging period, leading to thicker walls in the final titania materials. This effect can be observed by XRD measurements. The XRD patterns obtained from mesoporous titania thin films with various molar ratios of P123 to titanium ($R$) are shown in Figure 2.3, which indicates that for films exposed to air during
aging, each sample has one reflection which decreases in position as $R$ increases. The
intensity of this peak remains almost the same as $R$ decreases from 0.0122 to 0.006,
suggesting that the mesoporous structure is maintained in the calcined films across the
composition range examined. However, the d-spacing of this reflection increases from
7.8 nm to 9.8 nm as $R$ decreases from 0.0122 to 0.006.

Given that unit cell parameters of P123-templated films are typically above 10 nm,
the reflection observed in the XRD patterns of all samples is indexed as the high-order
(200) peak of the 2D hexagonal phase, following the work of Kirsch et al. This
assignment is also consistent with our TEM images (see below) and indicates that the
films are, indeed, well ordered. The (100) reflection corresponding to this plane of atoms
cannot be distinguished from background scattering using our x-ray diffractometer. In
the case that $R$ equal to 0.0122, Koganti et al. have confirmed by SEM that films have a
2D hexagonal structure when the as-synthesized films are aged at 4 °C. Therefore, it is
likely that the films obtained here also have a 2D hexagonal structure when $R = 0.0122$,
and for the moment we assume that all of the films obtained with other $R$ values have the
same hexagonal structure. For the 2D hexagonal phase, the unit cell parameter parameter
is given by $a_H = 2d_{100}/\sqrt{3}$. The calculated values of $a_H$ for the films as a function of $R$ are
listed in Table 2.1, and the trend is the same as that of d spacing; $a_H$ increases as $R$
decreases. The increase in d-spacing could be caused by increase in either pore size or
wall thickness, but the average pore sizes estimated by nitrogen sorption (see below)
shows that an increase in wall thickness is responsible, and that the wall thickness
increases from 4.5 nm at $R = 0.0122$ to 6.9 nm at $R = 0.006$, while the pore size remains
nearly unchanged at about 4.5 nm (Fig. 2.4). In summary, low angle XRD suggests that
the variation of $R$ has no effect on the mesostructure of thin P123-templated titania films
except for changing the wall thickness, which changes the d-spacing of the structure.
However, a more complete understanding can be gained by examining samples by TEM.

Additional evidence that well organized mesostructures are still obtained in the films
as the molar ratio ($R$) decreases is provided by N$_2$ adsorption analysis. Figure 2.5 shows
nitrogen adsorption/desorption isotherms and the Kruk, Jaroniec and Sayari (KJS) pore
size distribution plots of calcined samples. Irrespective of the molar ratio of P123:Ti, all
samples exhibit a type IV isotherm, which is typical of ordered mesoporous solids. All isotherms have H2 hysteresis loops, which indicate the presence of ink-bottle-shaped or cage-type pores in the materials. The KJS pore size distributions of all samples here (Fig. 2.5B) are narrow, which is consistent with an ordered pore structure. Therefore, of the more likely interpretation of the type H2 hysteresis loop is that it arises from pore diameter nonuniformity along the pore axis rather than literal ink bottle pore shapes.

KJS pore size analysis performed on the adsorption branch of the isotherms shows that the average pore size of all samples remains almost constant at about 4.5 nm, even as the molar ratio ($R$) changes from 0.0122 to 0.006. However, the specific surface area of the samples, calculated by the multi-point Brunauer-Emmett-Teller (BET) method, decreases from about 151 m$^2$/g to about 99 m$^2$/g with $R$ decreasing from 0.0122 to 0.006 (Table 2.1 and Fig. 2.4). This makes sense because decreasing $R$ increases the distance between adjacent micelles and decreases the number of P123 micelles per area, which leads to the decrease in the number of mesopores per mass of titanium after calcination, rather than changing the size of the P123 micelles. This is consistent with an increase in wall thickness inferred from XRD and pore size data. We assume that the pore size can be independently controlled by adjusting post-synthesis treatment temperature and solvents. It can be confirmed from Figure 2.5 that the volume of N$_2$ adsorbed at low pressure is not large, showing that the surface area comes primarily from the mesopores and that increasing the number of mesopores has a positive effect on the surface area.

The finding that a well-defined mesoporous structure can be preserved while adjusting the molar ratio of P123 to titanium ($R$) is corroborated by the TEM micrographs in Figure 2.6, which show representative images of the mesostructures. Two samples with the highest $R$ (0.0122) and the lowest $R$ (0.006) were chosen for TEM. The presence of well ordered mesostructure features (Figs. 2.6a-d) in both films provides good evidence that films with well-organized mesostructures are obtained after template removal via calcination, even at the lowest $R$ value in the experimental range. From the TEM micrographs, the distance between pores is measured for $R = 0.006$ (Figs. 2.6c, and 2.6d) to be about 12 nm, which is larger than that of the films obtained with $R$ equal to 0.0122 (about 9 nm, Figs. 2.6a and 2.6b). While there is some numerical disagreement,
this is consistent with the calculated value of unit cell parameter \((a_h)\) obtained from 1D XRD (Table 2.1). Furthermore, the wall thickness can be carefully measured to be about 6.5 nm (Fig. 2.6c) and 4.2 nm (Fig. 2.6a) for \(R = 0.006\) and 0.0122 respectively, which also agrees well with the values calculated from XRD and nitrogen adsorption results. Selected area electron diffraction patterns recorded on the mesoporous TiO\(_2\) show that the walls of these materials are comprised of nanocrystalline oxides with powder-like diffuse electron diffraction rings (Figs. 2.7a and 2.7b inset), even though the films are x-ray amorphous at wide angles (suggesting that the walls are nanocrystalline). From the TEM micrographs, it is concluded that the mesoporous structures were well preserved in the films after template removal via calcination, and that the matrix between the mesopores contains titania crystallites.

However, the structure of the sample prepared with \(R=0.006\) is not necessarily the same as that of the sample prepared with \(R = 0.012\). Figs. 2.6a and 2.6b are both consistent with 2D columnar pore structure, while some of the projections in Figs. 2.6c and 2.6d seem to be more consistent with a mesophase formed by close-packed globular micelles. This could be a Pm3n cubic or 3D hexagonal phase, and careful indexing will be required to establish this clearly, accompanied with more XRD studies of detached films.

In the VFM of Alberius and coworkers, which was developed to predict the mesophase of materials, the volume fraction of block copolymer (\(\Phi\)) is defined as\(^{69}\)

\[
\Phi = \frac{V_{pol}}{V_{pol} + V_{inorg}} \tag{2.1}
\]

Where \(V_{pol}\) is the volume of the block copolymer and \(V_{inorg}\) is the volume of the nonvolatile components in the solutions. The polymer used here is P123, and in the case of titania, the calculation of \(V_{inorg}\) should include the volume of hydrochloric acid and is expressed as

\[
V_{inorg} = \frac{m_{Ti(OH)4}}{\rho_{Ti(OH)4}} + \frac{m_{HCl}}{\rho_{HCl}} \tag{2.2}
\]
where \( m_{\text{Ti(OH)\textsubscript{4}}} \), \( m_{\text{HCl}} \), \( \rho_{\text{Ti(OH)\textsubscript{4}}} \) and \( \rho_{\text{HCl}} \) are mass of Ti(OH)\textsubscript{4}, mass of HCl, density of Ti(OH)\textsubscript{4}, and density of HCl respectively. Here, the density of Ti(OH)\textsubscript{4} is considered as 1.8 g/cm\textsuperscript{3}, while that of HCl is 1.7 g/cm\textsuperscript{3}.

The calculated volume fraction of P123 (\( \Phi \)) corresponding to molar ratios (\( R \)) employed here is shown in Figure 2.8. As \( R \) decreases from 0.0122 to 0.006, the corresponding \( \Phi \) value decreases from 41\% to 26\%. According to the prediction presented by Alberius et al.\textsuperscript{69} and the P123-water phase diagram\textsuperscript{74}, the mesophase of as-synthesized films should vary from 2D hexagonal, to a cubic mesophase of undefined symmetry, to a disordered micellar solution sequentially, as the molar ratio (\( R \)) decreases from 0.0122 to 0.01, 0.008 and 0.006. However, the results obtained here indicate that even for a P123 to Ti ratio as low as 0.006, a stable well-ordered mesostructure is still obtained, which is similar to the results obtained by Crepaldi et al.\textsuperscript{170}. This may be due to the fact that the predictions based on the phase behavior of the surfactant are overly simplified, and the formation mechanism of the mesoporous titania-based thin films is influenced by many factors besides the templates and precursor volume fractions, including aging temperature, aging time, relative humidity of atmosphere, the acidity of the solution etc. Most importantly, this method is based on the phase diagram of P123 in water which is measured at a temperature well above 0 °C. Despite the quantitative disagreement with the boundaries predicted from the VFM using room-temperature P123/water phase behavior, the TEM observations here (Fig. 2.6-2.7) suggest that the structure may have undergone a transition from hexagonal to cubic as \( R \) decreases, which is consistent with the sequence of phases observed as the P123 content in water decreases\textsuperscript{74-75}.

A transition from hexagonal to cubic as \( R \) decreases can be further supported by observations of the ability to realign the pores by sandwiching them between P123-modified glass slides. As reported by Koganti et al., sandwiching films with 2D HCP structure should induce the alignment of the pores orthogonal to the substrate\textsuperscript{191}. Since 3D hexagonal and cubic phases always will have a crystal plane oriented parallel to the substrate (even if there is preferential alignment in some direction), this loss of intensity is not expected. When the molar ratio (\( R \)) is 0.0122, one strong reflection appears in the
patterns obtained from the films coated on a modified slide and exposed to air, but the low angle XRD patterns obtained from sandwiched films indicate only a very weak reflection (Fig. 2.9d). This indicates good realignment of a 2D HCP due to confinement between walls that are equally attractive to the PEO and PPO blocks. As the molar ratio \((R)\) decreases to 0.008, the intensity of the reflections on films sandwiched between modified surfaces is still weak (Figs. 2.9b and 2.9c). However, when the molar ratio \((R)\) is 0.006, the intensity becomes stronger (Fig. 2.9a), but still weaker than the intensity of the same sol cast onto a modified slide. The appearance of low intensity in the sandwiched films implies that the films obtained from films with a molar ratio as small as 0.008 have the same mesostructure as the films with molar ratio 0.0122. An ordered mesostructure may still be retained for the films with the molar ratio of 0.006 when the films are sandwiched, but retention of intensity of the peak suggests that it is composed a globular, rather than columnar, phase. The intensity observed for sandwiched films with \(R = 0.006\) may be due to the presence of an isotropic phase that still diffracts x-rays when oriented, or due to a weaker alignment effect for films containing less P123. In summary, the results observed here suggest that aging the P123/titania films below 0 °C expands the composition range of surfactants to form well organized 2D HCP mesophases, although the system still progresses to a globular cubic or 3D hexagonal phase at lower P123 content.

2.5. Conclusions

Here we have presented a method to synthesize mesoporous titania-based thin films with controllable wall thickness by varying the ratio of template P123 to titanium in the initial solution and aging at a temperature below 0 °C. The results obtained from XRD and TEM indicated that ordered mesostructures formed and were preserved upon calcination with P123:Ti ratios as small as 0.006. The results obtained from \(N_2\) absorption showed that even though the molar ratios were different among the series of films prepared, the pore size distribution of films were essentially unchanged and gave an average pore diameter of about 4.5 nm. Thus, the thickness of the walls in the films was increased by decreasing the P123:Ti ratio in the coating sol. While the temperature used to age the film was less than 0 °C, the results also indicate that films with 2D HCP mesostructured could be vertically aligned by sandwiching them with a second slide.
modified with crosslinked P123. The range of P123 contents used to prepare ordered mesoporous materials was expanded relative to films aged at higher temperatures, and the transition from 2D HCP to a globular mesophases occurred at a lower volume fraction of P123 than at higher temperatures. These results illustrate how the interplay of aging temperature after film formation and P123 concentration can be used to tune film mesostructured.

This method should be of general use for preparing the mesoporous transition metal-based thin films with tunable wall thickness and has promise for synthesizing titania films with large crystallites when it is combined with a pretreatment procedure or a thermal treatment schedule that will better retain mesoporosity during extended high-temperature heating. The data obtained here also provide insight into the mesophases of the P123-titania system at temperatures below the freezing point of water. However, further investigation of the symmetry of films formed with R = 0.006 will need to be performed before a complete understanding of this system is reached.
Figure 2.1. UV-visible transmittance spectra of TiO$_2$ thin films supported on glass slides obtained with various molar ratios of P123 to titanium ($R$) after calcination at 400 ºC.
Figure 2.2. Low angle XRD patterns obtained after calcination from (a) unsandwiched and (b) sandwiched P123-templated titania films with $R=0.0122$ cast onto crosslinked P123-modified glass slides.
Figure 2.3. Low angle XRD patterns of calcined unsandwiched titania thin films obtained with various molar ratios of P123 to titanium, $R = (a) 0.006$, (b) 0.008, (c) 0.010, or (d) 0.0122.
**Figure 2.4.** The dependence of surface area and calculated wall thickness on the molar ratio of P123 to titanium($R$) in calcined titania films prepared without sandwiching.
Figure 2.5. N$_2$ adsorption/desorption isotherm plots (A) and pore size distribution plots (B, calculated using the KJS method from the adsorption branches) measured for calcined mesoporous titania films with various ratios of P123 to titanium, $R = (a) 0.006, (b) 0.008, (c) 0.010, \text{ or } (d) 0.0122.$
**Figure 2.6.** Representative TEM images of calcined mesoporous titania thin films obtained using various molar ratios of P123 to titanium, $R = (a, b) 0.0122$ or $(c, d) 0.006$. All images have 100 nm scale bars. All of the films were coated on modified slides and exposed to air during aging.
Figure 2.7. Representative TEM images (both with 100 nm scale bars) with selected area electron diffraction patterns (inset, both have 5 nm$^{-1}$ scale bars) of calcined mesoporous titania thin films obtained using various molar ratios of P123 to titanium, $R = (a) 0.0122$ or (b) 0.006. All of the films were coated on modified slides and exposed to air during aging.
Figure 2.8. Calculated P123 volume percentage ($\Phi$) of water/P123 mixtures corresponding to materials prepared with various molar ratios of P123 to titanium ($R$).
Figure 2.9. Low angle X-ray diffraction patterns of calcined mesoporous titania films coated on modified slides and sandwiched with a second modified slide during aging. The molar ratio of P123 to titanium, $R = (a) 0.006$, (b) 0.008, (c) 0.010, or (d) 0.0122.
Table 2.1. Structural properties of calcined mesporous titania films prepared with P123 and cast onto modified glass slides.

<table>
<thead>
<tr>
<th>Molar ratio of P123/Ti</th>
<th>XRD reflection 2θ (°)</th>
<th>d-spacing (nm)</th>
<th>Unit cell parameter (nm)</th>
<th>Average Pore diameter (nm)</th>
<th>S\textsubscript{BET} (m\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.006</td>
<td>1.80</td>
<td>4.90</td>
<td>11.3</td>
<td>4.41</td>
<td>98.8</td>
</tr>
<tr>
<td>0.008</td>
<td>2.06</td>
<td>4.29</td>
<td>9.90</td>
<td>4.35</td>
<td>95.6</td>
</tr>
<tr>
<td>0.010</td>
<td>2.12</td>
<td>4.16</td>
<td>9.61</td>
<td>4.91</td>
<td>139</td>
</tr>
<tr>
<td>0.0122</td>
<td>2.26</td>
<td>3.90</td>
<td>9.01</td>
<td>4.54</td>
<td>151</td>
</tr>
</tbody>
</table>

a) Calculated assuming that the pores have 2D hexagonal columnar symmetry. b) Average pore diameter from the KJS pore size distribution. c) S\textsubscript{BET} = BET surface area.
Chapter 3. Tuning the Mesopore Size of Titania Thin Films Using a Polymeric Swelling Agent


3.1. Summary

A method is reported to generate mesoporous titania thin films with large pores and large surface areas by adding poly(propylene glycol), PPG, to the coating sol of films prepared by templating with Pluronic surfactant P123. Because P123 has average structure \((\text{PEO})_{20}(\text{PPO})_{70}(\text{PEO})_{20}\) where PEO is a poly(ethylene oxide) unit and PPO is a poly(propylene oxide) unit, the hypothesis underlying this work is that PPG segregates to the PPO domains to induce swelling of the template micelles. With the introduction of PPG, the final calcined films are observed to have well defined mesoporous structures, although the degree of long-range order diminishes with added PPG. The mesopore size of the films increases with increasing amounts of PPG, but PPG also introduces smaller mesopores into the films under our synthesis conditions to generate a bimodal pore size distribution. The size of these smaller pores remains nearly constant at \(\sim 2.4\) nm over a large range of PPG:P123 mass ratios, even as the larger mesopores size continues to increase. To understand the effect of PPG on mesostructured titania, the behavior in aqueous solution of the PPG polymer used for swelling is investigated and modeled with Flory-Huggins theory to estimate the full two-phase envelope. The phase diagram reveals that PPG \((M_n \sim 3500)\) and water have a lower consolute temperature of about \(-9\) °C, so at the temperature used for aging of the films immediately after coating \((4\) °C), the composition is well within the two-phase region. Therefore, repulsion between PPG molecules and polar species is expected to drive PPG into the hydrophobic cores of P123 micelles, thus leading to final products with large pore size. However because of partitioning of some PPG into the polar phase, a bimodal pore size distribution and decreasing long-range pore order are observed as the amount of PPG increases.
3.2. Introduction

Due to their unique electronic and optical properties, mesoporous titania thin films are attractive materials that have been used in a wide range of fields including solar cells\textsuperscript{49,52,155}, photocatalysts\textsuperscript{156-157} and optoelectronic sensors\textsuperscript{158-159}. Expansion of these applications to high molecular weight reactants, analytes and photoactive components requires facile methods of synthesizing large-pore mesostructured titania film. For instance, titania based thin films having cylindrical pores with a diameter of about 10 nm are hypothesized to be favorable for the fabrication of photovoltaic cells\textsuperscript{37,198}. However, infiltration of hole-conducting polymers into the pores of these materials carries a large conformational entropy barrier which can be reduced by expanding the pores.\textsuperscript{47} For the degradation of dyes such as rhodamine-6G, titania loaded SBA-15 with large pores (~ 7.2 nm) has higher photocatalytic activity than a comparable material with smaller pores (~3.7 nm) due to the better accessibility of large organic compounds to the pore surface\textsuperscript{199}; similar effects are expected for mesoporous titania films. As another particulate example, mesoporous anatase powder with an average pore size of 30 nm has been shown to have higher photocatalytic activity for degradation of formaldehyde under UV illumination than powders with pores size less than 10 nm\textsuperscript{200}. Even though formaldehyde is a small molecule, this illustrates the need for large pore diameters to achieve adequate transport for photocatalysis.

Among the approaches reported to prepare porous titania thin films, the Evaporation Induced Self Assembly (EISA) process is the simplest and most versatile. EISA was first developed and optimized to rapidly synthesize ordered mesoporous silicon-based films,\textsuperscript{168} and was later extended to non-silicon oxide materials\textsuperscript{58}. This process begins with dilute precursor / surfactant solutions prepared under conditions in which the hydrolysis and condensation reactions are slow. Drying of the solution drives the co-assembly of surfactant micelles and inorganic components whose gradual polycondensation leads to an ordered organic-inorganic hybrid material\textsuperscript{64}. The porous structures of the final inorganic framework derived from this approach can be controlled by employing different templates, varying the ratio of inorganic and organic components, and tuning the process parameters including time, humidity, temperature, etc.\textsuperscript{82}. 

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It is well accepted by most researchers that the pore size of thin films derived by templating PEO-based block copolymer surfactants such as PEO-PPO-PEO (PEO = poly(ethylene oxide) and PPO = poly(propylene oxide)) is determined by the length of the hydrophobic (PPO) block\textsuperscript{74,201}, while the wall thickness is on the same length scale as the PEO head groups\textsuperscript{176,179}. Based on this concept, two strategies can be used for pore expansion. One is to increase the molecular weight of the block copolymer template (and therefore the micelle radius). For instance, Grosso et al. showed that by employing high-molecular weight poly (ethylene-co-butylene)-b-PEO (KLE) and poly(isobutylene)-b-PEO (PIB-b-PEO) as templates, titania mesoporous thin films with pore sizes up to 10 nm could be produced\textsuperscript{41,174}. However, due to the lack of data on the phase behavior of these novel synthetic polymeric surfactants, it is difficult to predictively synthesize thin films with desired mesostructures. Adjusting block size as a method of pore tuning also has the disadvantage of requiring a new custom polymer synthesis each time a new pore size is required.

An alternative and more facile strategy to synthesize films with enlarged pores is the introduction of swelling agents to expand the size of the template micelles. Swelling agents introduced to the EISA process with PEO-PPO-PEO surfactants can swell micelles by localization either at the PEO-PPO interface (which would tend to stretch the surfactant, thus expanding the micelle), or in the core of the micelles. Both mechanisms may be operative for certain swelling agents. For instance, 1,3,5-trimethylbenzene (TMB) has been shown to increase the pore radius of SBA-15 (with Pluronic surfactant P123 of average structure (PEO)\textsubscript{20}(PPO)\textsubscript{70}(PEO)\textsubscript{20} as template) from 3.7 nm to 7.2 nm\textsuperscript{199}. Similarly, the pores of titanium oxophosphates were reported to expand from the micropore to mesopore range (with 3-4 nm pores) by swelling hexadecyltrimethylammonium bromide (CTAB) template micelles with 1-octanol\textsuperscript{202}. P123-templated titania thin films with pore size exceeding 10 nm can be achieved by using butanol as swelling agent, either by releasing the butanol from the titanium precursor in-situ\textsuperscript{81} or utilizing it as a solvent.\textsuperscript{203} However, because of butanol’s volatility and potential to change micelle curvature due to its location at the PEO-PPO block interface, it is beneficial to consider alternative swelling agents more selective for the PPO block.
Recently, high molecular weight poly(ethylene glycol) (PEG) has been shown to have the ability to expand micelles in solution. For instance, in the presence of low-molecular weight PEG (MW ~ 400 Da), the size of sodium dodecylsulphate (SDS) can be increased from about 14 nm to 16.7 nm, and it can be increased further with higher molecular weight PEG\textsuperscript{204}. The swelling effect is the result of aggregation of large clusters\textsuperscript{204} by intermolecular hydrogen bonding due to the large number of hydroxyl groups\textsuperscript{205}, although it is unclear whether these clusters localize at the corona or cores of micelles.

Poly(propylene glycol) (PPG) is structurally similar to PEG but it is a more hydrophobic polyether with a wide range of applications in biomedical areas due to its excellent biocompatibility\textsuperscript{206}. Because it is hydrophobic, nonvolatile and chemically identical to PPO blocks, PPG has significant potential as a swelling agent for P123-template
templated films. Cui and co-workers showed that, with the assistance of PPG (molecular weight ~2000 to ~2700 Da), the average pore size of P123-templated SBA-15 particles precipitated in solution can be increased to as much as 6.2 nm\textsuperscript{207}. PPG with high molecular weight is more effective for this purpose\textsuperscript{207}. Recently, Malfatti and co-workers also demonstrated pore expansion in titania thin films by the introduction of PPG with molecular weight ~4000 into coating sols containing F127 as template and a mixture of THF and butanol as co-solvents. A bimodal distribution of pores, with small pores 13-18 nm in diameter and large pores 20-150 nm, were observed in the final products\textsuperscript{208}.

The strategy of Malfatti and coworkers required cosolvents and a long room temperature aging period followed by two aging steps at 60 °C and 130 °C. However, it has been shown that porous titania thin films with well-organized mesostructures can be obtained by aging as-synthesized films at low temperature for a short time, since low temperature hinders the condensation reaction of titanium precursors and favors the formation of highly ordered liquid crystals derived from PEO/PPO copolymeric surfactants\textsuperscript{41,192,193}. Furthermore, previous work in our group indicates that mesoporous titania thin films with 2D hexagonal symmetry can be achieved when the as-synthesized films are aged at low temperature (~4 °C) under high relative humidity (~93%) for only 2 hours\textsuperscript{191}. However, the phase behavior of PPG strongly depends on the temperature as
well as its molecular weight. Here, we investigate the feasibility of utilizing PPG as a P123 swelling agent to fabricate titania thin films with large pores using only a short low-temperature aging step to promote long-range order.

Low molecular weight PPG is water-soluble and acts essentially hydrophilic (perhaps because of terminal hydroxyl groups), while high molecular weight PPG is more hydrophobic\textsuperscript{209}. The combination of hydrophilic (ether and hydroxyl) and hydrophobic (propyl) groups in PPG makes it soluble in a broad range of solvents, ranging from n-hexane to water\textsuperscript{210}. Furthermore, increasing the relative molecular weight of PPG from 400 to 1000 decreases the lower consolute temperature (LCST) in an aqueous system from above 50 °C to near 0 °C\textsuperscript{211}. The LCST of PPG with molecular weight above 2000 would be expected to be below 0 °C, although phase diagrams of aqueous PPG at these temperatures are rarely reported. The hypothesis tested here is that, at a temperature between ambient temperature and 0 °C, PPG with molecular weight ~ 3500 can be considered to be a tunable hydrophobic swelling agent for P123 micelles. As such, adding PPG to a P123-templated sol-gel process with ethanol as coating solvent is hypothesized to generate well-ordered mesoporous titania thin films with large pores after a short, low temperature aging period.

In order to substantiate the effects of PPG on materials synthesis to be discussed, the phase behavior in aqueous solution of PPG (M\textsubscript{n} ~3500 Da) will also be reported. The phase behavior will be fit using the Flory-Huggins activity coefficient model with temperature-dependent interaction parameter. While this is a straightforward measurement, such data could not be found in existing literature for 3500 Da PPG.

3.3. Experimental

3.3.1. Thin Film Preparation

The titania sols were prepared by adding 2.1 g of titanium (IV) ethoxide to 1.53 g of conc. aqueous HCl (36.5 ~ 38wt.%). After stirring this mixture for 10 minutes, a homogeneous solution containing various amounts of PPG and 0.65 g of P123 dissolved in 6 g of ethanol was added. The mass ratio of PPG to P123 (M) varied from 0 to 1. Films were dip coated from this sol onto commercially available glass slides (Gold seal
micro slides, 3×1”, cleaned in Nochromix dissolved in concentrated H₂SO₄ before coating), and then were aged in a moderate humidity environment (RH=53 ± 3.5%) in a refrigerator (T = 4 ± 1 °C) for 2 hours. The humidity was adjusted by placing the films in a closed container which also contained two beakers of saturated Mg(NO₃)₂ aqueous solution. After aging in the refrigerator, the as-synthesized titania films were calcined in air by increasing the temperature in a muffle furnace at 25 °C/min to 400 °C and holding for 10 minutes before cooling rapidly back to room temperature. In contrast to prior reported synthesis procedures that took as many as several days of aging, the total time required for film synthesis by this method is about 4 hours.

3.3.2. Film Characterization

Low-angle x-ray diffraction (XRD) analysis was performed on a Bruker D8 Advance diffractometer using Cu Kα (λ=1.5406Å) radiation to determine the titania mesostructure. Films were scanned at 0.5 °/min in 2θ increments of 0.02° from 1° to 4°. A Tristar 3000 (Micromeritics Instrument Corporation) automatic gas sorption analyzer was used to determine the structural characteristics of titania including Brunauer, Emmett, and Teller (BET) surface area. Samples for sorption analysis were prepared by scraping approximately 40-50 calcined films from their support slides and outgassing the resulting powder for 4 hours at 120 °C under flowing nitrogen. It is known that the Barrett-Joyner-Halenda (BJH) method underestimates pore sizes by as much as 20-25%, and therefore the pore size distribution and the average pore size were calculated using the modified BJH method of Kruk, Jaroniec and Sayari (the KJS method) based on the data obtained from nitrogen adsorption branch of isotherms and assuming a cylindrical pore shapes for all samples. To directly examine the film pore morphology, films were scraped from the glass slides and placed onto copper TEM grids. Transmission electron microscopy (TEM) was performed at 200 kV with a JEM-2010F (JEOL) high resolution transmission electron microscope with field emission. Scanning Electron Microscopy (SEM) images were collected with a Hitachi S-900 microscope. To improve the electrical conductivity, titania thin films for SEM analysis were deposited on ITO-coated glass slides and were fractured and mounted onto SEM stubs for observation. UV-visible spectra were collected with an Ocean Optics Jaz Spectrometer in transmission mode.
Glass slides coated with thin films were vertically positioned so that the spectrophotometer beam passed through the film and glass slide in sequence. For comparison, the UV-vis spectrum of a blank glass slide without coating was also measured.

### 3.3.3. Phase Diagram of the PPG-H₂O System

To develop the phase diagram of PPG in water, various amounts of PPG and DI water were placed in 15 ml conical centrifuge tubes (BD Falcon polypropylene tubes) and sealed to avoid the evaporation of water. To adequately mix PPG and DI water, the tubes were mounted on a vortex mixer and vortexed for 2 hours following by being kept at a fixed temperature for 24 hours (these were called once-aged mixtures). After centrifuging the once-aged mixtures at 1000 rpm for 5 minutes, an interface between two phases was clearly apparent in the tubes. The upper (water rich phase) and bottom (PPG rich phase) mixtures were carefully separated and collected, weighted, and then kept at room temperature for one week (at which point they are referred to as twice-aged mixtures). After a week of room temperature aging, the twice-aged mixtures were centrifuged again at 1000 rpm for 5 min and the phases separated to separately determine the masses of water and PPG. Because the solubility in water of the PPG used here < 0.01% (w/w) at room temperature, centrifuging the twice-aged mixtures gives a final upper phase composed of PPG-free water and a bottom phase of PPG. Thus, the mass fraction of PPG in both phases formed during the first aging step (at fixed temperature) was determined from the masses measured after the second aging step.

### 3.3.4. Materials

P123 (Mₙ 5800 Da, from BASF), PPG (Mₙ 3500, Aldrich), titanium (IV) ethoxide (tech grade, Aldrich), anhydrous ethanol (99.5+%, Acros), and concentrated HCl (GR grade, EMD chemicals) were all used as received.

### 3.4. Results and Discussion

After aging at low temperature (~4 °C) for 2 hours, as-synthesized films with various mass ratios of PPG to P123 (denoted as M) were calcined, and all of the resulting porous films, except that with M = 1, were observed to be transparent and crack-free under visual inspection. To quantify the optical characteristics of the films, Figure 3.1
presents the UV-visible spectra of the titania thin films on glass slides as a function of $M$. All films have high visible light transparence, as indicated by transmittance above 75% over the visible wavelength range, consistent with defect-free transparent films with up to $M = 0.5$ PPG / P123. The broad, weak oscillations in the spectra are interference patterns that arise due to the partial reflection and interference of the spectrophotometer beam with the thin titania films. The sharp decay that begins with an offset at about 380 nm for the titania films corresponds to a band gap of ~3.4 eV, which is consistent with the reported band gap of mesoporous TiO$_2$ films$^{194-196}$. However, the films obtained with $M = 1$ are observed to be opaque. Consistent with this, in the UV-visible light spectra, the sharp decay caused by the band gap of the titania is replaced by a gradually decreasing slope from a maximum transmittance (which is below 50%) at a wavelength of 800 nm to zero at 400 nm. The low light transmittance may be ascribed to light scattering due to the presence of cracks or macropores within films obtained with high $M$ (see below).

The effect of the mass ratio of PPG to P123 ($M$) on the mesostructures of the porous titania thin films is revealed by the low angle XRD patterns shown in Figure 3.2. In the absence of PPG, only one strong diffraction peak corresponding to a d-spacing of 4.5 nm is observed on the pattern (Fig. 3.2a), which implies that the long-range order of the mesostructure is preserved after calcination. Given the d-spacing and relatively intensity of the observed reflection, it is indexed to the (200) planes of a film having hexagonal symmetry, following the work of Kirsch et al$^{173}$. This indexing is consistent with the TEM and SEM observations (see below) and also in agreement with results reported by other researchers for P123-based films$^{70,212}$. In the presence of PPG, a broad peak with relatively weak intensity is observed for all films. This indicates that the long range order of mesostructure is partially lost or that the films have a broadened pore size distribution. It is also clear from the XRD measurements that the d-spacing values increase significantly from 4.5 nm ($M = 0$) up to 6.4 nm ($M = 0.5$) (Fig. 3.2b to 3.2d), but that the d-spacing increases only slightly (by about 0.7 nm) as $M$ increases from 0.5 to 1 (Fig. 3.2d and 3.2e). The increase of d-spacing values is possibly the result of pore expansion caused by swelling of P123 micelles by PPG, while the weak and broad reflections comes from the partial loss of long range mesopore order. Observations from UV-visible spectra and XRD suggest that mesopore expansion may occur in titania thin films with
the addition of PPG, but that there is a limit to the amount of PPG that can be incorporated into the micelles ($M \sim 0.5$) without disturbing the integrity of the films. The effect of PPG on the mesostructures can be further elaborated by observations from nitrogen absorption/desorption measurement, SEM and TEM.

Nitrogen absorption/desorption analysis of the calcined titania film samples is shown in Figure 3.3A. Type-IV isotherms with a hysteresis loop are clearly observable for all samples regardless of $M$, which is a characteristic of mesoporous solids. In the absence of PPG, a type H2 hysteresis loop is observed, which starts and ends at $p/p_0 = 0.43$ and 0.7 respectively (Fig. 3.3A-a). In general, an H2 hysteresis loop indicates the presence of ink-bottle-shaped or cage-type pores in a material, although variation in pore diameter along the length of the pore or short pore length may contribute to the appearance of this hysteresis loop. In the presence of a low mass ratio of PPG to P123 ($M = 0.1$) the area of hysteresis loop increases and it ends at a slightly higher relative pressure of 0.75 (Fig. 3.3A-b). This suggests that the sample possesses larger or more nonuniform pores due to swelling of P123 micelles upon the introduction of PPG. As $M$ increases further, the area of hysteresis loop increases gradually and it ends at higher relative pressures until it finally reaches all the way to $p/p_0 = 0.95$ with $M = 1$ (Fig. 3.3A-e). It is also apparent that, as $M$ increases, a transition of the type of hysteresis loops can be observed from H2 (Fig. 3.3A-a to 3.3A-c) to H3 (Fig. 3.3A-d and 3.3A-e), which is characteristic of the presence of larger mesopores embedded in a matrix with pores of much smaller size.

Modified BJH pore size analysis performed on the adsorption branch of the isotherm of the sample without PPG shows that a unimodal, narrow distribution of pores is found with a maximum at 3.4 nm (Fig. 3.3B-a). However, two distinct peaks, one below 3 nm and the other above 4 nm, are observable for samples obtained in the presence of PPG (Fig. 3.3B-b to 3.3B-e). In addition, the peak corresponding to the small pores remains at about 2.4 nm irrespective of the PPG content, while the one corresponding to large pores increases from 4.7 nm to 6.5 nm as $M$ increases from 0.1 to 0.5. However, both the small and large sized pores decrease in diameter slightly to 2.2 nm and 5.8 nm, respectively, as $M$ increases to 1. Table 3.1 summarizes the pore structure properties of this series of
mesoporous thin films including surface areas, average pore sizes and d-spacing values. The specific surface area of the sample, calculated by the multi-point Brunauer-Emmett-Teller (BET) method, increases from 88 m²/g to 157 m²/g as $M$ increases from 0 to 0.5 (Fig. 3.4). However, as $M$ increases from 0.5 to 1, the surface area decreases to 128 m²/g. The large surface area of the samples results from the emergence of small pores in the films; otherwise, the increase in the diameter of the larger pores would be expected to induce a reduction in specific surface area.

Additional direct evidence that the introduction of PPG in the films results in tuning of the pore size is found by electron microscopy. Representative SEM images of films after calcination with and without PPG are shown in Figure 3.5. In the absence of PPG, very uniform accessible mesopores with hexagonal symmetry are observed at the surface of the films. The distance between adjacent pores in the SEM image is about 10 nm (Fig. 3.5a), consistent with the size of the unit cell calculated from the XRD results assuming that the symmetry of mesostructure is hexagonal (Table 3.1). In the presence of PPG, an array of accessible pores at the surface of film is observed, without significant cracks, even for $M$ as large as 0.5 (Fig. 3.5b). However, the pores are not uniform and small pores (< 4 nm) as well as large pores (>10 nm) are observed on the surface of the calcined films. Although in isolated regions well-organized pores exhibit hexagonal symmetry, long range order of the pores is not evident, which confirms that the broadening and decrease in intensity of the XRD peak (Fig. 3.2) is due to a loss of uniformly spaced pores and broadening of the pore size distribution.

The tuning of pore size by varying the mass ratio of P123 to PPG ($M$) is further corroborated by TEM (Fig. 3.6 and 3.7). Without PPG, well ordered uniform mesopores with hexagonal symmetry are observed (Fig. 3.6a). The pore size is ~ 4 nm and the distance between adjacent pores is ~ 10 nm (Fig. 3.7a), in agreement with observations from nitrogen sorption isotherms and the calculated unit cell parameter from XRD. In the presence of PPG, a reduction of long-range pore ordering is readily apparent from the images, although pores with hexagonal symmetry are observed in local regions (Fig. 3.6b to 3.6d). Furthermore, uniformity of pores decreases as PPG is added. Both small pores with size below 3 nm and large pores with size above 10 nm are observed in the samples.
prepared with PPG (Fig. 3.7b to 3.7d). The size of the largest pores increases steadily as $M$ increases and reaches about 20 nm with $M = 0.5$ (Fig. 3.7d), while the wall thickness remains constant at ~5 nm. From the TEM and SEM observations, it is concluded that mesoporous titania thin films with tunable pore size can be prepared by introducing PPG into the initial coating solution, but the distribution of the PPG between P123 micelles and small-molecule aggregates broadens the pore size distribution and expands the larger pores in the films, thus decreasing long-range order in the final materials.

As noted above, the likely explanation for the bimodal distribution of small mesopores and tunable large pores is the distribution of different molecular weight components of PPG inside and outside of the P123 micelles. We can assume that at the molecular weight reported by the supplier, PPG acts as a hydrophobic compound, but its hydrophobicity can be assumed to decrease with decreasing molecular weight. The PPG is initially dissolved in ethanol with P123 and titanium precursors. Upon evaporation of ethanol (which happens rapidly in these coating processes$^{216-218}$), the high molecular weight PPG fraction is likely to be attracted to the PPO block of P123, leading to swelling of the micelles, which increases in proportion to the amount of PPG incorporated. Pore enlargement in the final films is consistently observed from nitrogen isotherms, SEM and TEM. However, from a thermodynamic view, the driving force for PPG molecules interacting with the hydrophobic blocks of P123 may not be strong enough to drive all PPG into micelles, and some of the PPG (most likely the lower molecular weight fraction) remains outside of the molecules and dispersed in the titania matrix. Because they still have a mildly hydrophobic character, these external PPG molecules form small aggregates in the polar titanium precursor environment with a uniform small size. As more PPG is added, more of these small aggregates form and give rise to the small mesopores (<3 nm in diameter) after calcination of the films. Consistent with the pore volume observations in Figure3B, the number of these small PPG aggregates increases with an increasing amount of PPG, thus giving films with increasing surface area and volume of pores below 3 nm in diameter. However, when an excessive amount of PPG is added to the P123 template (in this case, greater than $M = 0.5$), the large pores derived from swollen P123 and the small pores derived from PPG connect with each other in a poorly ordered mesostructure to generate macropores or cracks (as
indicated by the increase in opacity of the films), leading to a decrease of specific surface area and uniformity.

To corroborate the assumption that PPG behaves as a hydrophobic solute that is partially miscible with polar compounds under the experimental conditions used here, the bimodal curve of PPG in aqueous solution was measured and fit with the Flory-Huggins (FH) lattice model. In the FH model, the Gibbs free energy change of mixing is composed of terms due to the combinatorial entropy change of mixing and the enthalpy change expressed in terms of a temperature-dependent interaction parameter $\chi$, as stated in equation (3.1).

$$
\Delta G_{\text{mix}} = kT(N_1 \ln \phi_1 + N_2 \ln \phi_2 + \chi \phi_1 \phi_2 (N_1 r_1 + N_2 r_2))
$$

where $k$ is Boltzmann’s constant, $T$ is the absolute temperature, $N_1$ and $N_2$ are the numbers of molecules of the solvent and polymer respectively, and $r_1$ and $r_2$ are the numbers of lattice sites occupied by the solvent and polymer respectively. Here, the solvent is water and the polymer is PPG. $\phi_i$ the volume fraction of a species in the lattice model, is defined as

$$
\phi_i = \frac{N_i r_i}{N_1 r_1 + N_2 r_2}
$$

Although several researchers have considered a concentration-dependent interaction parameter $\chi$, we only consider a temperature-dependent interaction parameter represented by the following expression.

$$
\chi = a + \frac{b}{T}
$$

The coexistence curve (binodal curve) is found by equating the chemical potential changes of mixing for each species ($i$) between two coexisting phases, where:

$$
\Delta \mu_i = (\frac{\partial \Delta G_{\text{mix}}}{\partial N_i})_{T, P, N_{j \neq i}} \quad i = 1,2
$$

Differentiating equation (3.1) with respect to $N_i$ and $N_2$ and equating the resulting expressions for phases $\alpha$ and $\beta$ leads to:
\[ \ln \frac{\phi_1^{\alpha}}{\phi_1^{\beta}} + \left(1 - \frac{r_1}{r_2}\right) \left(\phi_2^{\alpha} - \phi_2^{\beta}\right) + r_1 \chi (\phi_2^{\alpha^2} - \phi_2^{\beta^2}) = 0 \]  

(3.5)

\[ \ln \frac{\phi_2^{\alpha}}{\phi_2^{\beta}} + \left(1 - \frac{r_2}{r_1}\right) \left(\phi_1^{\alpha} - \phi_1^{\beta}\right) + r_2 \chi (\phi_1^{\alpha^2} - \phi_1^{\beta^2}) = 0 \]  

(3.6)

To get the binodal curve, equations 3.5 and 3.6 are solved simultaneously for a series of different temperatures. Generally, \( r_1 \) is set to 1 for the solvent (water) and \( r_2 \) is considered to be the numbers of segments of the polymer or the specific volume of the polymer. However, when calculating chemical potentials using the volume fraction based on the number of actual segments in the polymer, the combinatorial contributions are sometimes overestimated, especially in aqueous polymer systems\(^{227-229}\). This is especially true when solvation of the polymer can occur. Therefore, \( r_2 \) needs to be treated as an adjustable parameter to account for possible changes to the effective segment number due to solvation.

The best fit of the binodal curve to the experimental coexistence compositions was found by adjusting the interaction parameter coefficients (\( a \) and \( b \)) and the value of \( r_2 \) until the best fit was obtained. The values found for \( r_2, a \) and \( b \) are 31.5, 4.02 and -879 K respectively, and a good fit of the Flory-Huggins model to the experimental data is obtained with these parameters (Fig. 3.8). Based on the binodal curve, the Flory-Huggins model predicts a lower consolute temperature of -9 °C, below which PPG and water are miscible in all proportions. Above this temperature, the two-phase region expands rapidly so that compositions in a broad range of PPG composition separate into two phases. At 4 °C, the solubility of PPG in water is significantly less than 3.8 wt% (the equivalent composition to the amount used in preparation of the films, assuming that water is replaced with an equivalent volume of polar titania phase) which implies that the PPG is hydrophobic and that some of it should partition into the PPO regions of the P123 micelles. As more PPG is added, more would be expected to partition into the micelles (leading to the observed swelling) while a portion remains in contact with the polar phase (leading to the small mesopores). Note also that the binodal curve in Figure 3.8 can be used to further tune the outcome of the film synthesis process. Lowering the temperature to -7 °C would cause PPG and water to be miscible over most of the composition range.
used for film preparation, which would be expected to prevent PPG from partitioning into the P123 micelles. We will show in a separate contribution that, consistent with this phase diagram, this leads to large-scale phase separation of PPG to generate a hierarchical macroporous / mesoporous film.

3.5. Conclusions

Based on the measured phase diagram of PPG in water, at 4 °C (the temperature used to age the titania films) PPG can indeed be considered to be a hydrophobic organic compound. This hydrophobic character allows PPG to penetrate into the hydrophobic core of P123 micelles to act as a swelling agent. Thus, titania based thin films with expanded mesopores were synthesized by introducing PPG into P123-based titania sols, and the pore size could be tuned in the range from 3.4 to 6.5 nm. The results also indicate that the addition of PPG introduced small mesopores (less than 3 nm in diameter), most likely due to the aggregation of the (possibly lower molecular weight) fraction of PPG that partitions into the polar phase during synthesis. The low temperature aging step used for synthesis allows this tuning to occur in a synthetic process that takes approximately 4 hours in the lab to process a batch of films. This swelling is accompanied by a loss of long-range mesopores order, and the use of excessive PPG (a 1:1 ratio by weight of PPG to P123) leads to nonuniform films, perhaps because the capacity of P123 micelles to solubilize PPG is exceeded. The principle demonstrated here of using aqueous solution behavior to find conditions for micelle swelling should be of general use for tuning the pore size in mesoporous transition metal-based thin films, and provides new possibilities for creating high surface area materials, especially catalysts and adsorbents.
Figure 3.1. UV-visible transmittance spectra of TiO$_2$ thin films supported on glass slides obtained with various mass ratios of PPG to P123 ($M$) after calcination at 400 °C. Most film are optically transparent save for interference fringes except for the film with $M=1$, which scatters significant amounts of visible light.
Figure 3.2. XRD patterns for the series of calcined films with mass ratio of PPG to P123, $M = (a) 0$, (b) 0.1, (c) 0.3, (d) 0.5, or (e) 1. The primary visible reflection is labeled with its corresponding d-spacing.
Figure 3.3. Nitrogen sorption isotherm plots (A) and pore size distributions (B) of the series of titania thin film samples, calculated using the KJS method from the adsorption branch of the isotherm assuming a cylindrical pore shape. The mass ratio of PPG to P123, $M = (a) 0, (b) 0.1, (c) 0.3, (d) 0.5, (e) 1$. The pore size at each peak in the pore size distributions is indicated.
Figure 3.4. The dependence of average pore size and surface area of titania thin films on the mass ratio of PPG to P123 ($M$).
Figure 3.5. Plan view SEM images of mesoporous titania thin films prepared with mass ratio of PPG to P123, $M = (a)$ 0 and $(b)$ 0.5. The brightness and contrast of figure (a) were digitally increased to enhance the visibility of the pores. The length of the scale bars are (a) 200 nm and (b) 60 nm.
Figure 3.6. Representative TEM images of mesoporous titania thin films collected at low magnification showing gradual loss of long-range order as PPG is introduced into the films. The mass ratios of PPG to P123, $M = \begin{cases} (a) \ 0, & (b) \ 0.1, & (c) \ 0.3, & (d) \ 0.5 \end{cases}$. All images have 200 nm scale bars.
Figure 3.6 (Continued). Representative TEM images of mesoporous titania thin films collected at low magnification showing gradual loss of long-range order as PPG is introduced into the films. The mass ratios of PPG to P123, $M = (a)$ 0, (b) 0.1, (c) 0.3, (d) 0.5. All images have 200 nm scale bars.
Figure 3.7. Representative TEM images of mesoporous titania thin films collected at high magnification illustrating the expansion of pores and adoption of a foam-like structure as PPG is introduced. The mass ratios of PPG to P123, $M =$ (a) 0, (b) 0.1, (c) 0.3, (d) 0.5. All images have 40 nm scale bars.
Figure 3.7 (Continued). Representative TEM images of mesoporous titania thin films collected at high magnification illustrating the expansion of pores and adoption of a foam-like structure as PPG is introduced. The mass ratios of PPG to P123, $M = (a) \ 0$, (b) 0.1, (c) 0.3, (d) 0.5. All images have 40 nm scale bars.
Figure 3.8. Phase diagram of the PPG / water system showing the binodal curve. Points are experimental data and the curve is the Flory-Huggins model fit to the data by adjusting the interaction parameter coefficients (a and b) and the average number of segments of PPG. Concentrations corresponding to the titania thin films are in the range between the two dash lines.
Table 3.1. Structure parameters of the titania thin films.

<table>
<thead>
<tr>
<th>Mass ratio $M$ ($W_{PPG}/W_{P123}$)</th>
<th>d-spacing (nm)</th>
<th>Unit cell parameter $^a$ (nm)</th>
<th>Average Pore diameter $^b$ (nm)</th>
<th>$S_{BET}^c$ ($m^2/g$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.46</td>
<td>10.3</td>
<td>4.48</td>
<td>88.4</td>
</tr>
<tr>
<td>0.1</td>
<td>5.01</td>
<td>11.7</td>
<td>4.75</td>
<td>109</td>
</tr>
<tr>
<td>0.3</td>
<td>5.88</td>
<td>13.6</td>
<td>5.09</td>
<td>121</td>
</tr>
<tr>
<td>0.5</td>
<td>6.39</td>
<td>14.9</td>
<td>7.34</td>
<td>157</td>
</tr>
<tr>
<td>1</td>
<td>7.12</td>
<td>16.4</td>
<td>6.56</td>
<td>128</td>
</tr>
</tbody>
</table>

$^a$ Calculated assuming that the pores have 2D hexagonal symmetry. $^b$ Average pore diameter from the KJS pore size distribution. $^c$ $S_{BET} = $ BET surface area.
Chapter 4. Hierarchically Porous Titania Thin Film prepared by Controlled Phase Separation and Surfactant Templating


4.1. Summary

Poly(propylene glycol) (PPG) of moderately high molecular weight (Mₐ = 3500, Da) exhibits amphibious behavior in aqueous solution in that it is hydrophilic at low temperature but hydrophobic at high temperature. This property is utilized to generate porous titania thin films with a hierarchical structure consisting of macroporous voids / cracks in films with mesoporous walls. The smaller mesopores result from the self-assembly of the Pluronic block copolymer P123 to form micellar templates in well-ordered arrays with hexagonal symmetry. The larger pores are generated from the phase separation of PPG during aging of the films. The PPG acts to a limited degree as a swelling agent for the P123 micelles, but because the films are aged at a low temperature where PPG is hydrophilic, much of the PPG remains in the polar titania phase. Upon heating, the PPG phase separates to form randomly dispersed, large pores throughout the film while retaining the ordered mesoporous P123-templated structure in the matrix of the material. TEM and SEM imaging confirm that calcined titania thin films have interconnected hierarchical porous structures consisting of ordered mesopores of size 4-12 nm in diameter, and macroporous voids >100 nm in size. The density and size of the voids increase as more PPG is added to the films.

4.2. Introduction

Materials with hierarchical pore architectures have attracted tremendous attention in recent years due to advances in understanding of the physical chemistry of their formation, and because of their remarkable potential to provide rapid mass transport to surfaces for a wide variety of applications such as catalysts, high-performance liquid chromatography (HPLC) separation, electrode materials for fuel cells, and biomaterials for drug delivery devices. Such materials combine rapid diffusion from a continuous phase into the pore matrix with the high degree of size and shape selectivity to guest species provided by mesopores or micropores. For
instance, silica based materials with hierarchical pore structures present new opportunities for design of efficient HPLC columns because the presence of macropores promotes rapid mass transport of solutes while mesopores provide high surface area and selectivity\textsuperscript{236}. In a fuel cell context, a cathode catalyst consisting of platinum supported on an ordered hierarchical carbon support has been shown to give a 53-88\% increase in power density compared with Pt loaded on carbon black\textsuperscript{239}. This enhancement is attributed to the unique hierarchical pore structure, which provides a large surface area and mesopore volume for uniform deposition of Pt nanoparticles, and a fast transport pathway to the active sites through an interconnected open macropore network. The catalytic reaction and reagent diffusion are both significantly enhanced at locations where the mesopore channels with large pore volume open to macropores\textsuperscript{239}.

Among various metal oxides being targeted for hierarchical pore design, titania thin films are promising multifunctional materials due to their high photo- and redox activity in applications including water purification\textsuperscript{12-14}, photovoltaic cells\textsuperscript{49,52,155}, and gas sensors\textsuperscript{158-159}. All of these applications employ the photoelectrochemical properties of titania, but the efficiency in these types of processes is limited by the rate of electron/hole pair generation at the active surface of the titania, and by possible recombination of these charge carriers. In addition to doping with other transition metals\textsuperscript{244-245} or anions\textsuperscript{246-250} to tune the band gap, the photovoltaic performance of titania can be improved by the introduction of a mesoporous structure to provide abundant pores and large surface area\textsuperscript{157,196,251-252}. Furthermore, the incorporation of macropores in mesoporous materials to form a hierarchical pore structure, has the potential to further the efficiency of titania for photoelectrochemical reactions since the macroporous channels could permit rapid transport of reactants or redox couples to the high surface area provided by the mesopores. The work done by Wang et al. and Yu et al. has demonstrated that hierarchical meso/macroporous titania materials enhance photocatalytic activity due to increased photoabsorption efficiency and rapid diffusion of molecules through the macropore network\textsuperscript{253-254}. These results suggest that developing methods of preparing titania with hierarchical pore structure will be of considerable scientific and practical interest. However, relatively few methods of preparing titania thin films with multiscale
hierarchical porosity have been reported relative to their broad potential applications\(^{208,253-255}\).

In the synthesis of hierarchical mesoporous-macroporous inorganic oxide-based materials, self-assembled surfactants or block copolymers are generally employed as mesopore templates while larger templates are used to generate macropores\(^{256-258}\). Much progress has been made in the tuning of surfactant-templated mesoporous titania in recent years, so there are tremendous opportunities for tuning that aspect of a hierarchical material. For instance, by varying the volume fraction of surfactant templates or utilizing different copolymers, titania thin films with cubic, hexagonal or lamellar mesophases have been obtained\(^{60,69,212}\); by incorporating swelling agents, the mesopore size can be tuned over a wide range\(^{81}\). The alignment of pores can also be controlled by functionalizing the surface of the coating substrate to adjust the interaction between surfactant templates and the surface\(^{191}\).

In hierarchical materials, large templates such as colloidal particles, microspheres and emulsions are used to create macroporosity at length scales ranging from sub-micron to millimeters. For instance, hierarchically porous silica, niobia and titania with tunable length scales ranging from 10 nm to several \(\mu\)m have been obtained by combining latex sphere templating with amphiphilic triblock copolymer templating\(^{255}\). Due to the ability of emulsion droplets to accommodate stresses arising upon shrinkage following gelation\(^{258}\), the emulsion templating technique has also been applied to produce macroporous titania, silica and zirconia with pore sizes ranging from 50 nm to several \(\mu\)m\(^{259-261}\). In still another approach, organic polymeric frameworks such as polyurethane foams\(^{262}\) and urea-formaldehyde resins\(^{263}\) have been utilized to generate porous silica, zirconia and titania with hierarchical structures. Other colloidal objects, such as mixed surfactants\(^{264}\), poly(methyl methacrylate) (PMMA) spheres\(^{265-266}\), polystyrene (PS) spheres\(^{267}\), nanoparticles\(^{268-270}\) or biological templates\(^{271,272}\) are also widely employed as macropore templates. However, in all of the above approaches, macropore structures are derived from pre-existing particles or molds, and it is problematic to adjust the macropore size and to disperse the colloidal templates in the materials uniformly.
An alternative way to fabricate materials with hierarchical pore structure combines phase separation with supramolecular surfactant-based mesopore templating\cite{236,243,273-275}. The mechanism associated with this strategy has been described by Nakanishi and co-workers for the synthesis of monolithic silica with interconnected macropores and textural mesoporosity prepared using the sol-gel process in combination with a variety of water-soluble polymers, such as poly(ethylene oxide) (PEO)\cite{236,273-274}. This process is based on the reaction-induced phase separation of water-soluble polymers during hydrolysis and condensation of alkoxide precursors. Bi-continuous gels with macroporous morphology, consisting of one component rich in polycondensed silicate and the other rich in solvents, have been prepared by phase separation concurrent with sol-gel polycondensation. The phase separation is driven by the attractive interaction between PEO and silicate oligomers relative to polar solvent. Subsequent solvent exchange with a basic solution and thermal treatment yields a hierarchically porous structure. In this porous architecture, macropores arise from the solvent-rich phase, and mesopores are retained in the silicate rich phase. In some of the first reports of this approach, surfactants were not used and instead, aggregates of particles gave rise to textural mesoporosity in the walls with pore sizes in the range of 10-20 nm\cite{236,273-274}. Following a similar route, mesoporous-macroporous alkoxide-derived alumina-silica\cite{276} and silica-zirconia\cite{277} have been obtained, and the technique has been extended to create disordered hierarchically porous titanium\cite{278-279} and zirconium\cite{243} oxides. However, it is difficult to achieve well ordered mesopores by this approach using only phase separation of water-soluble polymers. Ordered mesopores provide several advantages over nonuniform mesoporosity in hierarchical porous materials\cite{280}, including uniform pore size, high surface area, and greater stability of the pore structure. Such structures can be synthesized by combining the self assembly of surfactants into ordered mesophases with the generation of macropore template by phase separation of a polymer\cite{281}. For instance, Vogt's group demonstrates that photopatterned porous silica films with 3-4 nm mesopores and 40-100 nm macropores can be obtained by using surfactant (Brij-78) / homopolymer [poly(4-hydroxystyrene)] mixtures as templates\cite{282}. In a more recent report, Malfetti et al. described the synthesis of hierarchically porous titania thin films with mesopores 13-18 nm diameter and large pores 20-150 nm diameter by using
supramolecular templates F127 and poly(propylene glycol) (PPG) along with co-solvents butanol and tetrahydrofuran (THF). The synthetic process is presumably similar to the approach of Nakanishi and coworkers in which precursor polycondensation drives the phase separation of an F127/titanate complex from a PPG-rich solvent phase, but the complexity of the mixture employed makes the mechanism difficult to elucidate and control.

In the present study, we combine P123 (a block copolymer with average formula \( \text{HO(\text{CH}_2\text{CH}_2\text{O})}_{20}\text{(\text{CHCH}_2\text{CH}_2\text{O})}_{70}\text{(\text{CH}_2\text{CH}_2\text{O})}_{20}\text{H} \)) surfactant templating and PPG phase separation to generate hierarchically porous titania thin films. Our previous work indicated that PPG with \( M_n \sim 3500 \) (which will be used in this study) has a lower consolute temperature in water near -8 °C, and that phase separation between water and this PPG happens at 4 °C with as little as 4 wt% PPG. When titania films were prepared and aged at 4 °C, the hydrophobicity of the PPG caused it to partition preferentially into the core of P123 micelles, and therefore to act as swelling agent. However, at lower temperatures, solubility of PPG in water increases and it adopts a more hydrophilic character. Therefore, films prepared with P123 and PPG which are aged at -6 °C are expected to incorporate a significant amount of PPG into the polar part of the structure, (the titanate-rich phase) rather than into the cores of the P123 micelles. As the films are heated during the subsequent drying and calcination steps, the PPG is expected to become hydrophobic but, because of the way that it was incorporated into the titanate phase, to form separate PPG droplets from the P123 micelles. Therefore, the hypothesis is proposed that aging P123/PPG templated sol-gel titania films at -6 °C followed by a heating and calcination step will lead to a hierarchical phase structure in which macropores arise from thermally-induced phase separation of PPG (perhaps aided by titanate condensation) and mesopores arise from a P123/titanate mesostructure in the remaining phase. This hypothesis will be tested and explored here by synthesis and characterization of a sequence of films with varying PPG:P123 ratios.
4.3. Experimental section

4.3.1. Preparation of Thin Films

The procedure to prepare thin films is same as that reported by Koganti et al. except that a lower aging temperature was used for the as-synthesized films, and various amounts of PPG were introduced to the films. Briefly, the coatings were cast onto commercially available borosilicate glass slides (Gold seal micro slides, 3×1”) which were cleaned using Nochromix, and modified by dip coating with a P123 cross-linking solution. This solution was prepared by first adding 0.696 mmol/L P123 and a drop of glycerol (to act as a cross linker) to acetone. An equimolar amount of 1,6-diisocyanatohexane (DH) was then added dropwise to this mixture under constant stirring. The resulting solution was dip coated onto the glass slides and then the slides were aged at 120 °C overnight to drive the isocyanate-hydroxyl cross-linking reaction to completion.

The titania sols were prepared by adding 2.1 g of titanium(IV) ethoxide to 1.53 g of concentrated HCl (36 wt%). After stirring this mixture for 10 minutes, a solution was added containing a variable amount of PPG and 0.65 g of P123 dissolved in 6 g of ethanol. The mass ratio of PPG to P123 (M) varied from 0 to 1. Films were dip coated using this sol onto modified glass slides and then aged in a high relative humid environment (RH ≈ 93±5.5%) in a refrigerator at a temperature of T ≈ -6 °C for 2 hours. The high RH environment was provided by placing the coated slides in a sealed chamber with two beakers containing saturated KNO₃ aqueous solutions. RH was measured with a humidity pen (Fisher Scientific). As-synthesized titania films were then calcined by transferring them directly from the refrigerator to a muffle furnace and ramping the temperature in air at 25 °C/min to 400 °C and holding for 10 minutes before rapidly cooling back to room temperature. The calcination processes were carried out immediately after as-synthesized films were transferred to the muffle furnace to prevent condensation of moisture from occurring on the surface of the films.

4.3.2. Characterization

Low-angle x-ray diffraction (XRD) analysis was performed using a Bruker D8 Advance diffractometer with Cu Kα (λ=1.5406Å) radiation to determine the titania mesostructure. Films were scanned at 0.5 °/min in 20 increments of 0.02° from 1° to 4°.
To directly examine the pore morphology, films were scraped from the glass slides and placed onto copper TEM grids. Interestingly, it was observed that in the presence of PPG, samples were easier to scrape from the glass slides compared with samples prepared in the absence of PPG. This may be caused by macroporosity and cracking of the films (see below) or weaker adhesion of the substrate. Transmission electron microscopy (TEM) was performed at 200 kV with a JEOL JEM-2010F high resolution transmission electron microscope with field emission. For plan-view imaging of the pore accessibility, films were left intact and the conductivity was increased by coating the samples with a layer of Au/Pt alloy using a sputtering process for 1 minute. Scanning Electron Microscope (SEM) images were subsequently collected with a Hitachi S-4300 microscope at 3kV. UV-visible spectra of the films were collected with an Ocean Optics Jaz Spectrometer in transmission mode. Glass slides coated with thin films were vertically positioned so that the spectrophotometer beam passed through the glass slide and film in sequence. For comparison, the UV-vis spectrum of a blank glass slide without coating was also measured.

4.3.3. Materials

P123 (Mₙ = 5800 Da, BASF), PPG (Mₙ = 3500 Da, Aldrich), titanium (IV) ethoxide (tech grade, Aldrich), anhydrous ethanol (99.5+% , Acros), acetone (histological grade, Fisher), glycerol (99+% , Aldrich), DH (98%, Aldrich), and concentrated HCl (GR grade, EMD chemicals) were all used as received.

4.4. Results and Discussion

Irrespective of the mass ratio of PPG to P123 (M), all of the as-synthesized titania films were found to be transparent after aging at -6 °C for 2 hours. After calcination, the resulting porous films were observed to be transparent and crack-free under visual inspection with M ≤ 0.1. The optical characteristics of the films were quantified by UV-visible transmission spectroscopy (Fig. 4.1). Consistent with their macroscopic appearance, films with M ≤ 0.1 have high visible light transparency, with transmittance above 75%. The broad, weak oscillations in the spectra are interference patterns that arise from wavelength-dependent constructive and destructive interference of partially reflected light in the thin films. The sharp transmittance decay that begins at about 380
nm is due to the UV light absorption caused by the excitation of electrons from the valence band to the conduction band of TiO$_2$. This corresponds to a band gap of ~3.4 eV, which is consistent with the reported band gap of mesoporous TiO$_2$ films$^{194-196}$. Not all films were observed to be transparent, however; for $M$ values of 0.3 and above, the calcined titania thin films were found to be cloudy, bordering on opaque. Consistent with this, in the UV-visible light spectra, the sharp decay caused by the band gap of the titania is replaced by a gradually decreasing slope from a maximum transmittance (all of which are below 40%) at the upper end of the wavelength range measured (800 nm) to zero at a wavelength above 400 nm. Since all films are comprised only of titanium dioxide with different pore structures, it is highly possible that the gradually increasing transmittance in the visible region of the spectrum can be attributed to light scattering rather than absorption. This result also differs from the results observed for P123/PPG template titania films aged at 4 ºC, which were observed to be crack free with high visible light transparency (transmittance >70%) even with $M$ as large as 0.5$^{197}$. The cloudiness of the films prepared with high $M$ suggests that the uniformity of the films is destroyed. The loss of uniformity could have two causes: the emergence of porosity due to phase separation with a length scale large enough to scatter light, or the formation of cracks arising from the formation of interconnected voids in the films that promote defect formation and propagation.

Additional evidence that a high mass ratio of PPG to P123 ($M$) causes a reduction in uniformity in the mesostructure of the titania thin films can be found in the XRD results. Low angle XRD (Fig. 4.2) shows one reflection for each calcined film regardless of the mass ratio of PPG to P123 ($M$), which is characteristic of an ordered mesostructure. In the film without PPG, no reflections (either from other high-order reflections or anatase crystallinity) were found at higher angles, in keeping with prior observations of mesoporous titania films prepared by this approach$^{89}$. Because the thermal treatment was the same for all films, it is unlikely that there was a substantial difference in crystallinity among samples. As for other P123-templated films, this is likely to be a high-order reflection. In the absence of PPG, a sharp, narrow peak is observed in the XRD pattern (Fig. 4.2a), which indicates that the film has a highly ordered pore structure. Assuming that the film has a mesostructure with hexagonal symmetry, and this reflection
corresponds to a (200) lattice plane with d-spacing of \( \sim 4 \) nm. We assume that all films prepared here have the same hexagonal symmetry. In the presence of a small amount of PPG \((M = 0.1)\), a strong narrow reflection is still observed in the XRD pattern which shifts to a lower angle (d-spacing \( \sim 5.5 \) nm). This suggests that a mesostructure with good long range order is retained within the calcined thin film when a small amount of PPG is added into the initial solution. Adding more PPG causes a limited amount of additional swelling of the mesostructure. The d-spacing value increases up to \( \sim 7 \) nm with an \( M \) value of 0.5 (Fig. 4.2d), while doubling the amount of PPG to \( M = 1 \)causes only a small increase to \( \sim 7.5 \) nm (Fig. 4.2e). Furthermore, the only observed reflection is broad and weak with \( M = 0.3 \), and its intensity decreases as \( M \) increases further, which suggests that the uniformity of the mesostructure is diminished upon the PPG addition. Previous work on PPG swelling showed that the addition of PPG into P123-templated titania thin films increases the mesopore size without affecting the wall thickness. Therefore, the increase in d-spacing upon PPG addition is attributed to swelling of the mesopores in the films, which is consistent with TEM observations (see below).

The reduction in XRD intensity noted above could be caused by two effects. One is a loss of long-range mesopore order (similar to what was found with PPG swelling at higher aging temperature\(^{197}\)). The other is that the size of the ordered mesoporous domains becomes smaller due to PPG phase separation. When \( M \) is small, no disruption of the long-range order of the films is found by TEM (Fig. 4.3), consistent with the sharp reflection found by XRD. In the absence of PPG (Fig. 4.3a, b), projections can be found for both pores arranged with hexagonal symmetry and columnar close-packed geometry in the calcined films. This is characteristic of films with 2D hexagonal columnar pores that may be mixed with a 3D hexagonal structure based on templating by globular micelles. The distance between adjacent pores is \( \sim 9 \) nm, which is close to the value estimated by XRD. In the presence of PPG with \( M = 0.1 \), highly organized mesopores with hexagonal symmetry are still observed, but the stripe-like projections from columnar pores are no longer observed (Fig. 4.3c), which indicates that the mesophase of films obtained with PPG changes from 2D hexagonal (or mixed) to 3D hexagonal symmetry (or that the fraction of 2D hexagonal material has decreased substantially). In pieces of film examined by TEM, large uniform regions of mesostructured titania without cracks.
are observable and the distance between adjacent pores is ~12 nm, which is consistent
with what was observed by XRD. Combined the results observed from XRD and TEM,
the conclusion is that introducing a small amount of PPG into P123-templated TiO₂ films
increases the pore size of mesopores without disrupting the long order of the
mesostructure throughout the film.

When a larger amount of PPG is added into the initial coating sol, the effects of
phase separation become evident in the TEM micrographs (Figs. 4.4 and 4.5). For
calcined titania thin films with high mass ratio of PPG to P123 ($M \geq 0.3$), uniform
mesopores with a high degree of long-range order and hexagonal symmetry are still
obtained (Fig. 4.4). However, the size of the domains becomes smaller, which explains
why the XRD intensity decreases as $M$ increases in these samples. Low-magnification
TEM images (Fig. 4.5) not only show that smaller fragments of ordered mesoporous
material are obtained as $M$ increases, but also indicate clearly defined circular edges of
spherical voids in the samples for $M = 0.5$ and $M = 1$. The low-magnification image of
the sample with $M = 1$ (Fig. 4.5d) clearly shows a foam-like structure due to a large
number of spherical voids in the sample. The distance between adjacent mesopores is ~
14 nm for $M = 0.3$ (Fig. 4.5a) and increases with increasing $M$ to ~17 nm for $M = 1$ (Fig.
4.5c). This is consistent with the evidence for mesopore expansion obtained from XRD
assuming that all films have hexagonal mesostructure. Furthermore, the TEM images
show that $M$ has little effect on the wall thickness, which remains at a constant value of ~
5 nm for films with various $M$ values, while the mesopore size increased gradually from
~4 nm to ~12 nm as $M$ increases from 0 to 1 (based on Fig. 4.3 and Fig. 4.4). Therefore,
the TEM results show that the introduction of PPG causes not only swelling of the
mesopores, but also the introduction of spherical macropore voids whose density
increases as $M$ increases.

Additional direct evidence that macropores are introduced into the films as PPG is
added to the coating sol is found by SEM (Figs. 4.6 and 4.7). In the absence of PPG, the
final calcined film has a smooth surface without cracks (Fig. 4.6a). However, in the
presence of PPG, open macropores/voids accessible to the surface can be observed (Fig.
4.6b and Fig. 4.7). Close inspection of the cross sections of the films visible in cracked
regions of the films show that macroporous voids are distributed throughout the thickness of the films for \( M \geq 0.3 \) (Fig. 4.8). For \( M = 0.1 \), isolated macropores are observed to be randomly distributed on the surface of the film with size ranging from \( \sim 50 \) nm to \( \sim 130 \) nm, and cracks with length less than \( 2 \) μm are observed in only a few regions (Fig. 4.6b). The size of the macropores increases as \( M \) increases, which is most clearly visible in the high-magnification images of single cracks (Fig. 4.8). The largest voids seem (for \( M=1 \)) appear to be in a range from \( \sim 250 \) nm to \( \sim 300 \) nm (Fig. 4.8c). However, it is clear that along with an increase in the number and size of voids, the number of cracks increases with increasing \( M \), and the cracks lengthen and connect together, finally leading to films composing of isolated islands of hierarchical mesoporous material. Because the titania films remain adhered to the substrate (although as noted in the Experimental section, not as firmly as in the absence of cracks), this is not necessarily a disadvantage, as the cracks provide large openings for solutes to diffuse into the pore space. From the SEM and TEM images, we conclude that the introduction of PPG into P123-templated titania films aged at -6 °C leads to hierarchical structures with 3 main effects. First, PPG swells the P123 micelles to some extent, although the capacity of the micelles is limited. The P123 still is able to form ordered mesoporous materials at the 10-20 nm length scale in the walls of the material. Second, macroporous spherical voids are introduced into the films whose size and number increase with PPG content. Finally, the large number of voids introduced with the largest PPG contents makes the films more fragile and susceptible to crack formation. As \( M \) increases, the crack pattern progresses from short, isolated cracks (\( M=0.1 \)) to a regular array of isolated cracks (\( M=0.3 \)) to a network of cracks (\( M=0.5 \)) to a "mud crack" appearance (\( M=1 \)). While the cracks have a negative effect on transparency, they should provide improved accessibility of the interior of the film to reactants.

Our previous work and TEM observations (see above) indicate that, in absence of PPG and after aging at \( \sim -6 \) °C, well organized lyotropic liquid crystals derived from self assembly of P123 micelles form and ultimately create highly ordered mesopores in titania thin films. A similar well-ordered structure is found in films prepared with the same composition and aged at 4 °C. However, at 4 °C, the effect of PPG addition is primarily to swell the pores. A fraction of the PPG at this temperature remains in the inorganic phase and gives rise to small mesopores in the titania matrix. The rest of it has been
observed to contribute to pore swelling, leading to a broad distribution of large pores\textsuperscript{197}. Here, a similar set of experiments with aging at -6 °C leads to only limited pore swelling and the formation of macroscopic voids. The phase diagram of PPG ($M_n \sim 3500$) in water explains why this is observed. At 4 °C, the system is well within the 2-phase envelope where PPG acts as a hydrophobic compound which partitions preferentially into the cores of P123 micelles, thus favoring extensive micelle swelling. A small amount of PPG remains in the polar (titania) phase, leading to small mesopores. In contrast, at the temperature used here (-6 °C), PPG acts as a hydrophilic compound because the temperature is close to the lower consolute temperature of the system. Thus, while some PPG enters into the P123 micelles to swell them, a large amount stays in the polar titania-rich phase of the film during the 2-hour aging period. The films are uniform and transparent at this point, suggesting homogeneous incorporation of the PPG in the titania phase. As soon as the films begin to be heated during drying and calcination, this PPG is expected to become much more hydrophobic in nature, providing a significant driving force for leaving the polar phase. The heating rate is apparently fast enough that the PPG phase separates into submicron droplets within the films, leading to the hierarchical structure observed. The net result is a separation into a PPG-rich phase and a well-organized P123/titania phase which leads to the ultimate hierarchical film structure. Consistent with this interpretation, adding PPG leads to more and larger voids, but PPG is excluded from the titania phase itself (thus causing no increase in mesostructure wall thickness) and partitions to only a limited extent into the P123 micelles.

A complex process illustrated in Scheme 4.1, where initial incorporation of PPG into the titanate-rich phase and subsequent phase separation seem to be responsible for the observed hierarchical pore structure. A key element of this mechanism is the propensity of PPG to switch from being hydrophilic at low temperature (during the film aging period) to hydrophobic at higher temperature (during drying and calcination). As illustrated in Scheme 4.1, a mesostructured framework analogous to a lyotropic liquid crystal is formed during the initial coating process and forms the basis for the observed first-order porosity (on the 10-20 nm length scale). P123 micelles are presumed at this point to assemble into an ordered mesophase in which hydrophobic PPO units segregate into a hydrophobic microphase while the PEO units remain in contact with the polar...
phase consisting of titanate oligomers and whatever water and alcohol remain in the film. During the initial low-temperature aging period, the high molecular weight PPG behaves as a hydrophilic compound and is incorporated into the polar titanate-rich phase (Scheme 4.1a). However, during drying and calcination at high temperature, the PPG switches to a hydrophobic compound due to a change in the effective Flory-Huggins \( \Theta \) parameter, thus driving phase separation. Based on the morphology of the final films, the phase separation appears to occur by nucleation and growth of PPG droplets. Distinguishing between this phase separation mechanism and spinodal decomposition could be done using in-situ or time-sequenced characterization techniques, but this is beyond the scope of the current investigation. The phase separation of PPG from the hydrophilic titanate-rich microphase can take place either due to a change in entropic driving force (driven by the polymerization of the titanate species) or the enthalpic driving force associated with PPG interactions with other species (Scheme 4.1b)\(^{236}\). Based on the measured phase diagram of PPG in water, it is likely that the latter is the primary factor leading to second order porosity on a length scale of 200-500 nm.

### 4.5. Conclusions

Hierarchically porous titania thin films were prepared by introducing PPG of moderately high molecular weight \( (M_n = 3500) \) into a P123-templated titania film synthesis process with initial aging of the films at low temperature. The hypothesis was proven that introducing PPG at low temperature where it has hydrophilic character and subsequently heating the films so that the PPG becomes hydrophobic leads to phase separation of the PPG into large droplets. The result is a film with dual hierarchical porosity in which mesopores are derived from the co-assembly of P123 with titania precursors, and macropores result from the droplets formed during PPG phase separation from the polar (titania) phase. The walls of the material are composed of titania with highly ordered mesopores with hexagonal symmetry. Adding PPG swells these pores, although the degree of swelling is limited. The larger 200-500 nm pores in the films are randomly distributed throughout the film due to phase separation of PPG which is not incorporated into the P123 micelles. The large number of macropores allow the films to undergo extensive cracking during drying and calcination, making the internal
The principle here of employing a surfactant-templated sol-gel process combined with temperature-induced polymer phase separation has great potential significance as a strategy to produce materials with hierarchical porosity. The strategy of using phase separation to introduce macropores has been explored in depth by Nakanishi and coworkers, but the unique feature here is the use of a polymer with a temperature responsive “switch” that allows it to remain in the polar phase during aging and to phase separate by raising the temperature to generate macropores. This synthetic approach is general and can be extended to prepare other porous materials with multiple length scales. It also may be possible to use other temperature-responsive polymer systems to tune the phase separation to give a desired structure, or to avoid cracking in applications where optical transparency is required. The final products generated here are hierarchical porous titania thin films with highly ordered tunable mesopores that provide a high surface area along with randomly distributed macropores above 200 nm in diameter that provide high mass transport efficiency. These films can be directly utilized in (photo)catalysis, sensing and separation process.
Figure 4.1. UV/visible transmission spectra of calcined TiO$_2$ thin films on glass slides prepared with various mass ratios of PPG to P123 ($M$).
Figure 4.2. Low angle XRD patterns of the calcined TiO$_2$ thin films prepared with $M = (a)$ 0, (b) 0.1, (c) 0.3, (d) 0.5, or (e) 1.
Figure 4.3. Representative TEM images of calcined TiO$_2$ thin films prepared with PPG:P123 mass ratios of $M = (a,b)$ 0 or (c) 0.1. All images have 100 nm scale bars.
Figure 4.3 (Continued). Representative TEM images of calcined TiO₂ thin films prepared with PPG:P123 mass ratios of $M = (a,b) \ 0 \ or \ (c) \ 0.1$. All images have 100 nm scale bars.
Figure 4.4. Representative high-magnification TEM images of calcined TiO$_2$ thin films prepared with mass ratios of PPG to P123 ($M$) = (a) 0.3, (b) 0.5, or (c) 1. All images have 50 nm scale bars.
Figure 4.4 (Continued). Representative high-magnification TEM images of calcined TiO$_2$ thin films prepared with mass ratios of PPG to P123 ($M$) = (a) 0.3, (b) 0.5, or (c) 1. All images have 50 nm scale bars.
Figure 4.5. Representative low-magnification TEM images of calcined TiO$_2$ thin films prepared with mass ratio of PPG to P123 ($M$) = (a) 0.3, (b) 0.5, or (c, d) 1. The scale bar of images is 100 nm (a, b, c) or 1 μm (d).
Figure 4.6. Representative SEM images of calcined TiO₂ thin films prepared with mass ratio of PPG to P123 (M) = (a) 0 or (b) 0.1. The brightness and contrast of figure (a) was digitally increased to enhance the visibility of the pores. The scale bar of images is 500 nm (a) or 2 μm (b).
Figure 4.7. Representative low-magnification SEM images of calcined TiO$_2$ thin films with mass ratios of PPG to P123 ($M$) = (a, b) 0.3, (c, d) 0.5, or (e, f) 1. The scale bar of images is 10 μm (a, c, e) or 2 μm (b, d, f).
Figure 4.8. Representative high-magnification SEM images of calcined TiO$_2$ thin films prepared with mass ratios of PPG to P123 (M) = (a) 0.3, (b) 0.5, or (c) 1. All images have 1 μm scale bars.
Scheme 4.1. Proposed formation mechanism of thin films with hierarchical porous architecture via an evaporation-induced self-assembly process combined with thermally-induced phase separation. (a) the proposed structure of the film after aging at -6 ºC, with PPG uniformly distributed throughout the polar titania matrix, (b) after raising the temperature during drying and initial heating of the film, and (c) after calcination.
Chapter 5. Tuning the Mesopore Structure of 3D Hexagonal Thin Films using Butanol as a Co-Solvent

5.1. Summary

Distorted 3D hexagonal (space group R-3m) mesoporous titania thin films with high visible-light transparency are produced by introducing a small amount of 1-butanol into sol-gel coating sols containing P123 as the primary pore template. The mesostructure of the titania thin films identified by grazing incidence small angle x-ray scattering (GISAXS), TEM and SEM has rhombohedral symmetry (space group R-3m) with the [111] direction normal to the substrate. In the absence of butanol at the ratio of P123:titania used, poorly ordered films which may contain 2D or 3D hexagonal domains form, but introducing as little as a 1:10 ratio (by mass) of 1-butanol to P123 (with ethanol as coating solvent) leads to a well-defined 3D hexagonal structure in the resulting films. Simulated GISAXS patterns obtained using the NANODIFT program confirm the assignment of the experimental patterns to this structure. The characterization results indicate that over a 1-butanol:P123 mass ratio of 0.1 to 2, the films are composed of ordered arrays of cage-like cavities, and that in contrast to the hypothesized role of butanol as a swelling agent, the pore size decreases with an increase in the ratio of 1-butanol to P123.

5.2. Introduction

Developments in the field of nanoporous materials over the last few decades have opened potential avenues for promising new applications in a wide variety of fields, such as catalysis\textsuperscript{283-285}, chemical and biological separations\textsuperscript{286-288}, drug delivery\textsuperscript{289-291} and electronic materials\textsuperscript{292-294}. These applications derive from the high surface area, multiplicity of pore structure and pore size, diversity of compositions and high accessibility of surface functional groups in these materials\textsuperscript{295}. Our understanding of the process of micellar aggregate formation and organization with metal precursors, which yields periodic pore structures in inorganic networks, has evolved significantly since the surfactant templating approach was first reported by Kresge, Beck and coworkers\textsuperscript{56-57}. A milestone in the development of thin films was the development of the Evaporation
Induced Self Assembly (EISA) process to synthesize nanoporous silicon-based films\textsuperscript{168} which was later extended to non-silicon based materials\textsuperscript{58}. This process takes advantage of initially dilute solutions, in which the hydrolysis and condensation reactions are slow. Drying of the solution drives the assembly of surfactant micelles and inorganic components whose gradual polycondensation leads to an ordered organic-inorganic hybrid material\textsuperscript{64}. The porous structures of the final inorganic framework derived from this approach can be controlled by employing different templates, varying the ratio of inorganic and organic components, and tuning the process parameters including time, humidity, temperature, etc.\textsuperscript{82}

To help guide the design and synthesis of materials by the surfactant-templating approach, Alberius and co-workers proposed that the volume fraction of water in an aqueous lyotropic liquid crystal should be replaced with the equivalent volume of hydrolyzed metal precursor to predict the mesophase of the final material\textsuperscript{69}. This concept narrows down the range of the synthesis parameters that need to be explored to obtain a desired mesophase. However, it is imperfect in that it has been shown, in many cases, that, although the final mesotstructure is sensitive to the interfacial curvature at the surfactant/inorganic species boundary, this curvature is dependent not only on the initial composition of the reactants, but also on the processing conditions used during self-assembly\textsuperscript{82,183-184}. Thus, the predominant majority of investigations on mesoporous materials still address the control of pore architecture, which profoundly affects the intrinsic properties of mesoporous materials including mechanical stability, optical clarity and electrical characteristics; and accessibility to guest molecules via diffusion and adsorption.

Films that have a highly accessible pore surface are important for potential applications including chemical sensors, highly selective separations, ultra-high-density recording media, etc.\textsuperscript{83}. Such applications require a high rate of diffusion of guest molecules within the pore network, and thus films with 2D hexagonal channels or bicontinuous cubic phases (space group Ia3d) are outstanding candidates in that they have continuous pores in at least one direction\textsuperscript{184}. Ia3d mesostructure films have the advantage that their cubic bicontinuous structure easily provides an accessible pore space regardless
of the orientation of the structure within a film. However, films with Ia3d symmetry are
difficult to fabricate since they can usually only be obtained in a narrow range of
composition and temperature, and typically coexist with a lamellar phase. A wide
composition over which the 2D hexagonal mesophases is observed for many surfactants
makes it more convenient to fabricate mesoporous thin films with this symmetry.
However, these films typically have their pore channels oriented parallel to the coated
substrate due to preferential interactions between the substrate and surfactants, which
makes the pores mostly inaccessible to guest molecules. By confining as-synthesized
films between two chemically modified substrates, our group has succeeded in
fabricating mesoporous thin films with 2D hexagonal symmetry and mesochannels
perpendicular to the substrate.

An alternative promising approach to fabricate films with good pore accessibility
is to form cage-like structures that are interconnected by windows or microporosity. In
general, spherical or elliptical voids can be created in the final inorganic materials after
the removal of organic templates if the initial organic-inorganic composite is based on the
assembly of cubic or 3D hexagonally close packed globular micelles. It has been shown
that for powders, the voids within these types of inorganic frameworks are connected
through mesoporous or microporous openings to form continuous pore
architectures, and the size of these openings can be controlled by hydrothermal
treatment. For films, Hillhouse and co-workers showed that in films synthesized
utilizing triblock copolymers as template, the cavities within the inorganic framework,
which have rhomboheral symmetry (space group R-3m) and [111] direction
perpendicular to the substrate, are at least interconnected by micropores in the walls
between pores (but often have mesoporous windows between pore voids). Thus, owing
to the photochemical and semiconducting properties of titana, it would be attractive for
many applications to generate titania thin films with this type of 3D interconnected cage-
like pore structure to provide an accessible, high-surface area porous network.

However, mesoporous titania thin films with 3D hexagonal cage-like structure
(space group P63/mmc) and the related rhombohedral structure (space group R-3m) are
unusual. More often, a body-centered cubic (Im3m symmetry) structure has been
reported in titania films with cage-like pores, for instance as reported by Alberius and co-workers. To achieve final R-3m symmetry, one route that has been shown is to prepare an as-synthesized film with face-centered cubic (Fm3m) symmetry, which transforms to trigonal symmetry due to unidirectional contraction normal to the coated substrate during the drying and calcination steps. Compared with Im3m symmetry, the maximum volume fraction possible for Fm3m symmetry is higher, and a higher micellar surface curvature is required in the mesophase assembly. It is easier to achieve cubic mesostructure (geometry Fm3m) using Pluronic F127(PEO106-PPO70-PEO106) as a template, which provides a high PEO/PPO ratio and thus a high curvature at the PEO-PPO interface to favor spherical micelles. On the other hand, Pluronic P123 (PEO20-PPO70-PEO20), which has relatively lower PEO/PPO ratio, may form a mixed lyotropic phase of P6_3/mmc and Fm3m symmetry in water over a narrow range of conditions, but reported lyotropic phase symmetry and composition range vary. While F127 forms a cage-like pore mesostructure readily, connectivity between the cages in titania films fabricated using F127 has been shown to be low because the distance from cage to cage is long. This distance may be reduced to generate larger windows between cages by using a template with shorter PEO blocks, such as P123. Recently, Ozin’s group reported that mesoporous titania thin films with 3D hexagonal symmetry can be obtained by utilizing P123 as template and 1-butanol as solvent in the coating solution. It has been proposed that the polar end of butanol is located at the hydrophilic/hydrophobic interface between the poly(ethylene oxide) and poly(propylene oxide) blocks in pluronic surfactants, thereby helping to stabilize mesophases with high surface curvature such as 3D hexagonal and globular cubic phases. This characteristic of butanol permits P123 to self assemble into a mesophases with Fm3m symmetry during the aging process of the as-synthesized films, and furthermore the addition of butanol may swell P123 micelles to tune the pore size within final inorganic framework. In mesoporous silica powders, the swelling of P123 micelles by butanol and preservation of 2D hexagonal pore structure was reported by Feng et al. However, in titania films the butanol:P123 ratio has not been systematically changed independent of other process variables, and in silica films F127 was used to generate Im3m symmetry mesostructures.
In triblock copolymer aqueous systems, alcohols with short alkyl chains such as methanol and ethanol have been ascribed roles as water-structure-breakers, resulting in increased polymer solubility and critical micelle concentration (CMC), while long-chain alcohols such as butanol act as water-structure-promoters, reducing CMC values\(^{301-302}\). However, while the goal of introducing a hydrophobic solvent such as butanol is usually to increase micelle (and therefore pore) size, butanol addition to aqueous solutions of sodium dodecyl sulfate (SDS) has been shown to decrease the radii of the hydrophobic cores of micelles as the CMC value decreased\(^{139,304-305}\). Therefore, the net effect of butanol in surfactant templating is not entirely known. With the above considerations in mind, the hypothesis behind the current work is that the introduction of a small amount of 1-butanol into the sol-gel process using P123 as the template can generate a titania mesostructure with oriented Fm3m symmetry within the as-synthesized films leading to a final mesoporous titania thin films with rhombohedral (R-3m) symmetry, and that the pore size can be tuned by adjusting the amount of butanol added. We anticipate that a low-temperature aging period can also accelerate the formation of a well-organized mesostructure in the films, as previously utilized to create oriented 2D hexagonal films\(^{191}\).

The most convenient nondestructive method to characterize and identify the mesopore structures in thin films is the well established reflection-mode x-ray diffraction (XRD)\(^{139-140,142}\). However, nanoporous thin films usually have soft mesostructured crystallites which can pack and align themselves preferentially in or out of the plane of substrate. With such ordering of pores, only the lattice planes parallel to the surface (in plane) can be detected by XRD patterns in \(\theta-2\theta\) scan mode\(^{131}\). In order to acquire the full information about pore structures in the film, the grazing incidence small angle X-ray scattering (GISAXS) technique has been employed. The scattering pattern generated by GISAXS can be understood by modeling based on the distorted wave Born approximation (DWBA) theory\(^{137-142}\). Here, a method using discrete Fourier transforms (DFTs) within the DWBA formalism, called NANODIFT\(^{141-142}\), is used to analyze the collected GISAXS patterns. In addition, direct characterization of the films by SEM and TEM is employed to confirm the accessible porous structure of the thin films.
5.3. Experimental section

5.3.1. Sample Preparation

The titania sols were prepared by adding 2.1 g of titanium(IV) ethoxide to 1.53 g of conc. aqueous HCl (~36 wt%). After stirring this mixture for 10 minutes, a solution containing various amounts of 1-butanol and 0.65 g of P123 dissolved in 6 g of ethanol was added. The mass ratio of 1-butanol to P123 ($M$) varied from 0 to 2. Films were dip coated from this sol onto commercially available glass slides (Gold seal micro slides, 3×1”, cleaned in Nochromix dissolved in concentrated H$_2$SO$_4$ before coating), and then were aged in a highly humid environment (RH≈93%) in a refrigerator (T = 4 °C) for 2 hours. The humidity was adjusted by placing the films in a closed container which also contained a beaker of deionized water. As-synthesized titania films were then calcined by increasing the temperature in a muffle furnace in air at 25 °C/min to 400 °C and holding for 10 minutes before cooling back to room temperature rapidly.

5.3.2. Sample Characterization

To measure information about mesostructures of the thin films, GISAXS measurements were performed at the 8-ID-E beamline at the Advanced Photon Source (APS) at Argonne National Laboratory. Scheme 5.1 shows the setup of the measurement. The samples were placed on a stage that can be tilted to precisely control the angle of incidence, and were impinged by a X-ray beam with a wavelength of 1.68 Å. The scattered photons were detected using a 2 dimensional charge-coupled device (2D CCD), positioned 1.3 m from the sample. In general, the incident angle impinged on films was set to the critical angle plus 0.03° to guarantee that information regarding features beneath the surface of thin films was collected. The pore spacing and orientation were determined by measuring the spacing between specific horizontal and vertical spots in the resulting patterns as described below. The NANODIFT program was obtained from the Hillhouse group and calculations were performed using experimental values of incident angle, camera length and x-ray wavelength, with symmetry and unit cell parameters adjusted to match the experimental GISAXS pattern. For inspection of pore morphology, films were scraped off of glass slides using a razor blade and placed onto copper TEM grids. A high-resolution JEM-2010F (JEOL) high resolution-transmission electron
microscope (HRTEM) with field emission at 200kV was used. For plan-view imaging of the pore accessibility, films were left intact and the conductivity was increased by coating the samples with a layer of mixed Au and Pt with thickness ~5 nm. Scanning Electron Microscope (SEM) images were collected with a Hitachi S-900 microscope at 3kV. UV-visible spectra were collected with an Ocean Optics Jaz Spectrometer in transmission mode. Glass slides coated with thin films were vertically positioned so that the spectrophotometer beam passed through the glass slide and film in sequence. For comparison, the UV-vis spectrum of a blank glass slide without coating was also measured.

5.3.3. Materials

P123 (MW ~ 5800, BASF), 1-butanol (HPLC grade from Sigma-Aldrich), titanium(IV) ethoxide (tech grade from Sigma-Aldrich), anhydrous ethanol (99.5+%, Acros), and concentrated HCl (GR grade from EMD chemicals) were all used as received.

5.4. Results and Discussion

After aging at low temperature (~4 °C) for 2 hours, as-synthesized films with various mass ratios of butanol to P123 (M) were calcined, and all of the resulting porous films were observed to be transparent and crack-free under visual inspection. To quantify the optical characteristics of the films, Figure 5.1 presents the UV-visible light spectra of the titania thin films on glass slides as a function of M. All films have high visible light transparence with transmittance above 75%, consistent with defect-free transparent films regardless of the butanol content. The broad, weak oscillations in the spectra are interference patterns that arise from the thickness of films. The sharp decay that begins with an offset at about 380 nm is due to the UV light absorption caused by the excitation of electrons from the valence band to the conduction band of TiO₂. This corresponds to a band gap of ~3.4 eV, which is consistent with the reported band gap of mesoporous TiO₂ films 194-196.

In the absence of butanol, the conditions used for preparation of the films led to a mesoporous film with a poorly ordered and somewhat ambiguous mesostructure under GISAXS analysis. Figure 5.2 shows the pattern, which has features consistent with either 2D hexagonal or R-3m symmetry (see below for more details). It is possible that the film
contains a mix of phases. This contradicts our earlier observation of a horizontally aligned 2D hexagonal structure in titania films prepared under comparable conditions without surface modification, but may reflect the high degree of sensitivity of the observed structure to conditions of curing and aging in the films. This contrasts the behavior of P123-templated silica films, which have 2D hexagonal structure under comparable processing conditions191.

To elucidate the effect of butanol on the pore architecture of within films, the sample with the smallest amount of butanol (0.065 g butanol, $M = 0.1$) was characterized in detail. Figure 5.3 shows a representative plan view SEM image of the calcined film. It is clear from the image that open pores can be accessed at the surface of the film. A highly ordered pattern of pores is observed with nearly perfect six-fold symmetry. This implies that possible space groups of the pore structure should only be those that have six-fold or three-fold axes perpendicular to the substrate. These include all cubic and rhombohedral space groups with [111] direction normal to the substrate and hexagonal space groups with [001] direction normal to the substrate.

The SEM results only provide local information obtained from a relatively small area of surface with micrometer scale, but it indicates that an oriented, accessible pore structure has been obtained. To supplement the microscopic studies, GISAXS was performed on the calcined films for a more statistically significant indication of mesostructure over a large area in both the lateral and thickness directions. In the scattering geometry used (Scheme 5.1), $q_y$ is the scattering vector normal to the plane of incidence and parallel to the films surface, which has the quantitative relationship $d=2\pi/q_y^{\text{max}}$ with d-spacing values. $q_z$ is the scattering vector normal to the sample surface and has the definition $q_z=4\pi/\lambda\sin2\theta$, where $\lambda$ is the wavelength of x-ray and $2\theta$ is the scattering angle out of the plane. The 2D GISAXS pattern (Fig. 5.4a) indicates a large number of well resolved diffraction peaks with strong intensity due to the large contrast of electron density between highly ordered empty pores and the titania matrix. The GISAXS pattern also indicates that the pores within the film are highly oriented (relative to the plane of the substrate) all the way through the thickness of the film. Otherwise
Debye-Scherrer rings would be observed, which are characteristic of pores randomly oriented throughout the depth of a film.

To characterize the pore structure in the direction normal to the surface of the film, the in-plane profile extracted from the GISAXS patterns, along the $q_y$ direction at constant $q_z = 0.03$ nm$^{-1}$, is shown in Figure 5.4b. A series of peaks with strong intensity are observed in the extracted profile, which reflects a high degree of long-range order in the direction parallel to the substrate. The ratio among $1/d$-spacing values of these peaks is very close to $1:\sqrt{3}:2: \sqrt{7}:3$, which is the characteristic of a structure with hexagonal symmetry. Accordingly, the peaks are indexed to (100), (110), (200), (210) and (300) lattice planes, as indicated in Figure 5.4b. The same process in the direction normal to the substrate along the $q_z$ direction at constant $q_y = 0$ nm$^{-1}$ was performed on the GISAXS pattern, and the out of plane profile has a very strong and a relative weak reflection with $d$-spacings of 4.5 nm and 2.5 nm, which can be indexed as (222) and (444) reflections of an oriented R-3m structure, respectively (confirmation of this assignment will be discussed below). The GISAXS pattern rules out the possibility that the pore structure is 2D hexagonal with the [001] normal to the substrate (because of the diffraction spots out of the plane of the film), and a more likely possibility is that the pores have rhombohedral symmetry (R-3m space group) with the [111] direction oriented normal to the films surface. If the pores were spherically symmetric, this structure would be identical to a face centered cubic with the [111] direction perpendicular to the substrate. However, unidirectional contraction normal to the film during the aging and sintering process leads to final porous titania thin films with R-3m symmetry.

Figure 5.5a illustrates the R-3m symmetry of the pore architecture, and shows how each pore connects to three pores in the layer above it and three pores in the layer below it in this structure. Based on the indexing of the peaks discussed above, the lattice parameter from the GISAXS patterns are 18 nm for the in plane unit cell dimension ($a=b$), corresponding to a $d$-spacing of 15.5 nm, and 9.0 nm for the out of plane dimension ($c$). Note that these parameters are obtained with hexagonal axes normal to the substrate, and this equivalent to a structure with rhombohedral axis normal to the substrate having lattice parameter as $a'=b'=c'$, and $\alpha=\beta=\gamma\neq90^\circ$. Parameters for the latter structure were
input into the NANODIFT simulation program and after careful manual adjustment of the parameters, the pattern generated with R-3m space group and parameters \(a' = 13.7\) nm and \(\alpha = 82^\circ\) matches the experimental data nearly perfectly. The overlay of simulated spot pattern with the experimental data shown in Figure 5.5b indicates that the proposed R-3m symmetry is the correct symmetry of the pore architecture within the porous titania film.

Another strong and direct piece of evidence that films with 3D hexagonal pore structure can be achieved with only a small amount of added butanol in the sol-gel process comes from TEM observations (Fig. 5.6). In the [111] direction of this pore structure, it is clear from Figure 5.5a that a projection of highly ordered pores with hexagonal symmetry should be observed, consistent with the low magnification image (Fig. 5.6a). With pores larger than the walls of the structure, the geometry of pore packing leads to projections in which an open pore has one trigonal pattern of walls below it (an “O” over a “Y”) and a second trigonal pattern of walls in the second layer down (pointing into the interstices between the walls in the previous layer). This pattern is evident everywhere in the observed region and is shown most clearly in the high-resolution TEM image (Fig. 5.6c). The distance between two adjacent pores is estimated from these images to be approximately 18 nm, which is consistent with the dimensions obtained from GISAXS. The diameter of the window between two cages is estimated from the TEM images to be approximately 5 nm. This further confirms the previously supposed pore architecture. The high resolution TEM image (Fig. 5.6c) also demonstrates that fringes of a crystalline lattice in the walls are observable, which indicates that the nanocrystalline titania forms during calcination. No wide-angle XRD peaks from crystalline titania could be observed in any of the samples. Based on the SEM, GISAXS and TEM analysis, it can be confidently concluded that the sample with \(M = 0.1\) is a 3D hexagonal mesostructured titania thin film. Unlike the previous report of a similar structure from Ozin’s group, this structure forms with a small amount of butanol additive and a solvent (ethanol) that readily evaporates from the film at a low temperature to allow for rapid further processing.

The effect of butanol on the pore structures is further investigated as a function of mass ratio of butanol to P123 by GISAXS measurements of the calcined films (Fig. 5.7).
It is clear from the 2D patterns that, even with a mass ratio as large as $M = 2$, the same series of discrete reflections with strong intensity as those observed with $M = 0.1$ is still observed. This implies that the R-3m pore architecture is still obtained within the films as butanol content increases. However, the position of reflection spots shift to higher $q$ values, especially for the (444) diffraction spot; only part of this spot can be observed on the edge of the measured area when the mass ratio is 0.3 (Fig. 5.7a), and, as the amount of butanol increases further, the position of this spot moves out of detector range and disappeared from the patterns (Fig. 5.7b/c). The extracted profile along $q_y$ at constant $q_z=0.003$ nm$^{-1}$ (Fig. 5.8A) shows that in plane, $q_y$ values increase as $M$ increases, which implies that increasing the amount of butanol added to the precursor sol leads to a reduction in d-spacing values. A similar trend is also observed on the extracted profile (Fig. 5.8B) along $q_z$ at constant $q_y=0$ nm$^{-1}$. Figure 5.9 shows how the rhombohedral unit cell of the R-3m structure decreases with $M$. Upon going from $M = 0.1$ to $M = 2$, the value falls by 14%, which clearly shows that in contrast to the observed role of butanol as a swelling agent in silica-based P123-templated materials$^{201}$, here butanol induces contraction of the pores in the final films.

The outcomes of TEM observations (Fig. 5.10) corroborate the observations in GISAXS. Figure 5.10 clearly shows that, as the mass ratio increases, the [111] projection of the 3D hexagonal mesostructured pores is preserved within the inorganic framework. From the images, the value of window diameter remains almost constant at a value of 5 nm even as the mass ratio is increased to 2. The high resolution TEM images clearly show lattice fringes for films obtained with high mass ratio, demonstrating that increasing the amount of butanol has no appreciable effect on the crystallization of titania. However, the distance between adjacent pores estimated by TEM decreases to about 15 nm for $M = 2$, which agrees with the change in d-spacing obtained from in plane GISAXS profile. This means that the pores size decreases from about 13 nm, at a mass ratio of 0.1, to about 10 nm at a mass ratio of 2. Although they are surprising from the standpoint of micelle swelling, the observations here are consistent with the effects of butanol in aqueous systems reported by other researchers$^{301-302}$. As a water-structure-promoter, the introduction of butanol into polymer aqueous system favors the formation of polymer micelles and decreases the CMC values. The aggregation number of micelles also
decreases with the increase of butanol concentration and, in turn, the size of micelles decreases\textsuperscript{304-305}. Thus, the pore size of the final sintered films can be controlled by butanol content, although in the opposite direction from what might have been supposed if butanol were simply a hydrophobic swelling agent. Another possible explanation consistent with the observed trends is that as butanol enters into P123 micelles, its hydrophobicity may allow it to substitute for some P123 molecules, which would also lead to shrinkage of the micelles.

The R-3m symmetry observed for the titania/P123 system in the presence of butanol is surprising. If we were to make an analogy between the lyotropic phase behavior of P123/water/butanol systems, we would expect that butanol should go to the hydrophilic/hydrophobic interface of the system and contribute to decreasing interfacial curvature, thus favoring hexagonal or even lamellar mesophases rather than those composed of globular micelles\textsuperscript{74}. As little as $M = 0.17$ would be expected to lead only to lamellar mesophases and micellar solutions (or even inverted micelle phases) according to the ternary diagram of the P123/water/butanol system\textsuperscript{74}. Of course, some of the butanol present in the initial solution may evaporate if it is not incorporated into the P123 micelles, so this can be partially explained by butanol partitioning. A more important factor is that, unlike silica, titanium precursors can enter into complexation with the PEO units of the block copolymer template. Soler-Illia and Sanchez have proposed that this is likely to occur readily in a low-water environment\textsuperscript{67}, and as alcohols and water leave the film it may be promoted under the present conditions. In this case, hydrolyzed titanium precursors would remain in intimate contact with the PEO blocks of P123, thus favoring a high interface curvature which allows the R-3m phase to form. As more butanol is added, the decrease in P123 aggregation numbers lead to a shrinkage of globular micelles analogous to the decrease in cylinder and lamellae dimensions in the aqueous system\textsuperscript{74}, but not to a change of mesophases symmetry. This contrasts the swelling observed in the silica/P123/butanol system\textsuperscript{306} because silica does not interact strongly with P123 headgroups, and thus may not “solvate” the headgroups to favor globular aggregates.
5.5. Conclusions

Mesoporous titania thin films with 3D hexagonal symmetry were prepared by adding a small amount of butanol (as little as 0.1 g butanol / g P123) to an ethanol-based P123-templated sol. The space group of the pore architecture was characterized by GISAXS and TEM and confirmed using simulated results obtained from the NANODIFT program. This confirms the hypothesis that the pore architectures within the inorganic framework can be tuned by the introduction of a small amount of butanol. The experimental observations also show that the pore size decreases from about 13 nm to 10 nm as the mass ratio of butanol to P123 increases from 0.1 to 2. This is proposed to be caused by a combination of reduction in the aggregation number of the P123 micelles as butanol is added, and the reduced molar volume of butanol that is substituted into the micelles. Thus, butanol introduced into the initial sol-gel solution has dual effects on the pore architecture within the final titania films. One is to favor the mesophase assembly of triblock copolymer P123 into a phase with high micelle surface curvature, owing to the location of butanol at the PEO/PPO interface of the micelles. The other is to tune the pore size by influencing the aggregation numbers of block copolymer micelles.

The approach utilized here to fabricate 3D hexagonal mestructured titania thin films with tunable pore size is general and, in principle, can be extended to deposit films on any substrates with various coating techniques. The illustration that the mesophase structure can be tuned with only a small amount of butanol is of importance in the scale up and realistic fabrication of titania films with accessible mesopores, and can be employed to fabricate other metal oxide films with nanoporous structures. The 3D hexagonal mestructured titania thin films produced with butanol addition have promising applications in separation processes, gas sensors and solar cells, for which the accessibility to pore network and substrate is essential for guest molecules.
**Scheme 5.1.** Geometry of Grazing Incidence Small Angle X-ray Scattering (GISAXS) experiment. Upper: An incident X-ray beam impinges on the surface of a thin film and scattered photons are collected on a two dimensional charge-coupled detector (2D CCD): $\alpha_i$, incidence angle; $\alpha_f$, exit angle with respect to the film surface; $2\theta_f$, exit angle with respect to the plane of incidence. Lower: A schematic structural diagram of a nanoporous thin film deposited on a glass substrate: medium 1, air; medium 2, porous titania thin film; medium 3, glass substrate; d, thickness of titania thin film.
Figure 5.1. UV/visible transmittance spectra of TiO$_2$ thin films obtained with various mass ratios of 1-butanol to P123 ($M$) after calcination at 400 °C.
Figure 5.2. GISAXS patterns of titania thin film obtained without butanol.
Figure 5.3. Top view SEM image of the titania thin film obtained with mass ratio of butanol:P123 $M = 0.1$. 
Figure 5.4. GISAXS pattern ($M=0.1$) indexed with representative lattice planes with R-3m symmetry (a), and in plane GISAXS profile (b) extracted along the $q_y$ direction at constant $q_z=0.003\text{nm}^{-1}$ from a. Reflections are indexed to a 3D hexagonal(R-3m) mesostructure.
Figure 5.5. Illustration of the R-3m pore architecture (a) (every filled sphere represents a pore within the titania thin film), and overlay of experimental data ($M=0.1$) with simulated spot pattern from NANODIFT (b). Circles and squares represent transmitted and reflected Bragg peaks respectively.
Figure 5.6. Representative TEM images of sintered TiO$_2$ thin films obtained with mass ratio 0.1. The inset is a fast Fourier transform (FFT) of the image. (a) Low magnification image, (b) high magnification image and (c) high resolution image.
Figure 5.6 (Continued). Representative TEM images of sintered TiO$_2$ thin films obtained with mass ratio 0.1. The inset is a fast Fourier transform (FFT) of the image. (a) Low magnification image, (b) high magnification image and (c) high resolution image.
Figure 5.7. GISAXS patterns of titania thin films obtained with various mass ratio, $M = (a) 0.3$, (b) 1, and (c) 2.
Figure 5.8. In plane GISAXS profiles (A) extracted along the $q_y$ direction at constant $q_z=0.003$ nm$^{-1}$, and out of plane GISAXS profiles (B) extracted along $q_z$ at constant $q_y=0$ nm$^{-1}$ from the 2D GISAXS patterns with various mass ratios. Mass ratio, $M =$ (a) 0.1, (b) 0.3, (c) 1, or (d) 2.
Figure 5.9. Variation of unit cell parameters (R-3m) of titania thin films with the mass ratio of butanol to P123 (M).
Figure 5.10. Representative TEM images of calcined TiO$_2$ thin films obtained with various mass ratios of butanol to P123. Insets represent fast Fourier transforms (FFTs) of the images. $M = (a, b, c)$ 1 or (d, e, f) 2.
Figure 5.10 (Continued). Representative TEM images of calcined TiO$_2$ thin films obtained with various mass ratios of butanol to P123. Insets represent fast Fourier transforms (FFTs) of the images. $M = (a, b, c)$ 1 or $(d, e, f)$ 2.
Figure 5.10 (Continued). Representative TEM images of calcined TiO$_2$ thin films obtained with various mass ratios of butanol to P123. Insets represent fast Fourier transforms (FFTs) of the images. $M = (a, b, c)$ 1 or (d, e, f) 2.
Chapter 6. Aligned nanoporous titania thin films as high capacity, durable lithium ion battery anodes

6.1. Summary

Vertically aligned amorphous titania nanotubes are produced by anodizing Ti foils at various applied potentials in a neutral electrolyte solution containing fluoride ions. The pore size and wall thickness can be controlled in the range from 30-70 nm and 17-35 nm, respectively, by adjusting the applied potential, in addition to tuning the tube length from 355 nm to 550 nm. Utilizing all of these films as anode materials in lithium ion batteries delivers stable capacities of 130–230 mAh g⁻¹ up to 200 cycles. Microstructural analysis shows that there is no structural change or mechanical degradation in the active material, and the amorphous active material maintains good contact with the substrate/current collector. A diffusion induced stress (DIS) model is developed to interpret the effect of tubular geometry on the stress developed during lithium insertion/deinsertion in TiO₂ nanotubes. Modeling results indicate that stable reversible capacity retention occurs in tubes with a high ratio of inner to outer diameter, in other words, tubes with thinner walls more easily accommodate expansion or contraction during the lithiation/delithiation process. This DIS model is extended to calculate the concentration and stress profiles of well-ordered mesoporous thin films with different pore symmetries. The simulation results obtained in 2 dimensional space indicate that the mesoporous electrode with hexagonal symmetry has higher charge/discharge rate than an electrode with square symmetry. The analysis of stress and strain energy done performed by Rutooj Deshpande based on the calculated concentration profiles indicates that electrodes with both of these symmetries experience only compressive stress during lithiation, and that the films with hexagonal symmetry have lower strain energy than those with square symmetry. Simulations in 3 dimensional space indicate that the porous structure has no effect on the charge/discharge rate when the thickness of the films is below a specific value with respect to the unit cell size of the pore structure, but above that size, the time required for battery charge/discharge cycles decreases as pore size increases. The simulation results imply that materials with hexagonal symmetry are better candidates to use as electrodes of lithium ion batteries.
6.2. Introduction

Lithium ion batteries (LIBs) are among the most promising technologies for stationary energy storage where safety, stable cycle life, and low cost are major concerns and the gravimetric or volumetric energy densities of electrodes are less important. Many advanced LIB anode materials including Si, Ge, and Sn, have the advantage of higher capacity than graphite, which is currently used in commercial production of these batteries. However, the use of these materials is currently limited because at low operating voltage (below 1 V vs. Li/Li+), the lithium salt-based liquid electrolyte decomposes, leading to the release of gases and potential buildup of pressure in the cells, and because of the formation of an unstable solid electrolyte interface (SEI) on the electrode surface. Furthermore, drastic and fast capacity loss accompanies the application of these high capacity materials, such as Si, due to large volumetric changes upon cycling. Thus, anode materials with high discharge potentials in which the electrolyte solution is stable are of interest for stationary energy applications. Titania is one of the most promising candidates for this application due to its high discharge voltage plateau of about 1.7 V, good cycling ability, and small volume expansion (~4%) during lithiation/delithiation.

However, one significant disadvantage of TiO2 is that it has poor lithium ionic and electronic conductivities, which limit the charge/discharge rate in bulk titania. It has been well established that the lithium intercalation activity and cycling stability depend on the morphology of electrode materials, and these properties of titania-based electrodes have improved dramatically as materials with nanoscale features have been developed. Therefore, numerous studies have been reported aimed at reducing lithium diffusion length by fabrication of nanostructured TiO2 materials, such as nanosized anatase titania, TiO2-B nanowires, and mesoporous rutile.

Of all available nanostructured titania materials, well-oriented nanotube arrays are perhaps one of these promising forms for LIB anodes because of several advantages of this structure. The first is that the porous structure offers a short Li+ diffusion length in the solid phase and high accessibility for the transport of electrolyte ions into the material framework, thus potentially decreasing the polarization and enhancing the rate of
charging and discharging. The second advantage is that the large surface area provided by this porous structure increases the electrode/electrolyte contact area and decreases the current density. The third potential advantage is that the tubular structure can effectively accommodate the expansion/contraction occurring during the lithium ion insertion/removal process. In fact, the latter advantage of titania nanotube arrays as anodes for lithium ion batteries has been utilized already by several researchers. For instance, Fang et al. reported that amorphous TiO$_2$ nanotube arrays with an average pores size of 54 nm and wall thickness of 10 nm exhibited a high capacity and excellent capacity retention, with less than a 5% loss of capacity after 100 cycles$^{316}$. Ortiz et al. demonstrated improved capacity retention of up to 90% over 50 cycles by utilizing amorphous and anatase TiO$_2$ nanotube arrays as LIB electrodes which had an average diameter of 80 nm and wall thickness of 20 nm$^{29}$. More recently, Wei et al. demonstrated that excellent durability of 96.4% capacity retention over 140 cycles could be achieved in anatase TiO$_2$ nanotubes arrays with an average pore diameter of 50 nm and wall thickness of 25 nm$^{317}$. However, the capacity retention dropped quickly to 53% as the pore diameter and wall thickness increased to 100 and 40 nm, respectively; further decay of capacity was observed as the pore diameter and wall thickness continued to increase$^{317}$. A unifying feature of these reports is that excellent capacity retention (over 90%) can be observed over many cycles when the wall thickness of titania nanotubes is below 40 nm; above this thickness, drastic capacity fading can be observed, irrespective to the pore diameter. However, the effects of wall thickness, or the ratio of inner to the outer diameter of the tubes, on the durability of titania nanotube arrays electrodes has not been directly elucidated in the above reports. In addition to pore structure, the effect of the crystal structure of titania on the performance of LIBs has also been reported. For instance, Fang et al.$^{316}$ and Furukawa et al.$^{318}$ separately reported that, compared with anatase TiO$_2$, amorphous TiO$_2$ has higher capacity for lithium ions because of the large density of defects in the disordered structure. With all of the above discussion in mind, the hypothesis is tested here that the use of titania nanotube arrays with wall thickness less than 40 nm as anode materials in lithium ion batteries effectively increases capacity retention regardless of the pore diameter, and that the amorphous form of titania results in a high capacity of the batteries.
Among various approaches explored to fabricate titania nanotubes\cite{92-95}, anodic oxidation is the most widely used since it was first applied to fabricate self-ordered TiO$_2$ nanotube arrays by Grimes and co-workers in 2001\cite{97}. Utilizing this approach provides the possibility of controlling pore size, length of nanotubes, and uniformity over large areas at low cost. In the initial reports of fabricating titania nanotube arrays through this approach, the electrolyte used for anodization was aqueous hydrofluoric acid, but it was found to be difficult or impossible to achieve nanotube arrays with length greater than 500 nm with this electrolyte solution although the wall thickness could be controlled by varying the applied potential\cite{99}. Later, utilizing aqueous fluoride-containing solutions with high pH values or nonaqueous solution consisting of organic solvents allowed the fabrication of titania nanotube arrays with lengths up to hundreds of micrometers\cite{100,103-106}. However, the average pore diameters of nanotubes derived from these electrolyte solutions are almost all above 50 nm and wall thicknesses are above 15 nm. Schmuki and co-workers reported that using neutral fluoride solutions comprised of (NH$_4$)$_2$SO$_4$(1M) and NH$_4$F (0.5 wt\%) as the electrolyte solution can lead to titania nanotube arrays with lengths up to micrometers\cite{101}. This strategy successfully takes advantage of a relatively mild environment to reduce the dissolution rate of titanium oxides in the electrolyte solution containing fluoride ions during anodization\cite{102}. Here, we utilize the same electrolyte solution to fabricate aligned TiO$_2$ nanotubes and adjust the pore size and wall thickness by controlling the applied potential during the anodization of pure Ti foils. Electrochemical performance of TiO$_2$ nanotubes as LIB electrodes is examined by means of galvanostatic cycling, and excellent capacity retention is observed for TiO$_2$ tubes of selected dimensions.

Titania with well-ordered mesoporous structure is another promising candidate for use as an anode material in lithium ion batteries. Compared with nanotube arrays, mesoporous structures afford titania thin films with higher surface area, thinner walls and a highly ordered interconnected network of solid phase. Higher capacity retention would be expected for electrodes fabricated from these mesoporous titania films. In fact, the advantages of mesoporous structures have been demonstrated on the porous electrodes of LIBs. For instance, the investigation on the electrochemical performance of low temperature LiCoO$_2$ as a cathode done by Jiao and co-workers shows that mesostructured
LiCoO₂ has higher initial discharge capacity than that of nanowires, although both forms exhibited superior capacity retention on cycling compared with normal low temperature LiCoO₂. Kim and co-workers demonstrated that the capacity retention of SnO₂ nanowires was 31% at a 10 C discharge rate (which is equal to 4000 mA h g⁻¹), however, that of mesoporous SnO₂ was improved up to 98%. Porous structures in these electrode materials can not only provide channels for the transport of electrolytes, but also act as a buffer zone during the volume contraction and expansion of Sn leading to better retention of capacity. Furthermore, several groups have reported the advantages of using mesoporous titania as electrode materials in lithium ion batteries. The work done by Guo and co-works indicates that mesoporous titania spheres have the capability to reversibly accommodate Li up to Li₀.₆₃TiO₂ (210 mA h g⁻¹) at 1-3V vs Li⁺/Li, thus leading to higher capacity and better cycling performance compared with commercial TiO₂. Wang and co-workers recently reported that mesoporous crystalline rutile obtained via a low temperature solution growth route on TiO₂ nanoparticles within an anionic surfactant matrix, shows excellent capacity retention with less than 10% capacity loss after more than 100 cycles. The high durability of this material is considered to be the result of maintaining a stable mesostructure within the electrode material over Li⁺ ion insertion cycles. A similar effect of increased capacity retention could be expected by using mesoporous titania thin films as electrode materials in lithium ion batteries. Therefore, it can be imagined that the utilization of thin films with well ordered porous structure in a large area as an electrode should have a significant effect on the reduction of strain energy and will open new opportunities for the development of electrode materials with outstanding electrochemical performance.

Mechanical fracture has been considered one of the key factors responsible for capacity fading and has historically hindered growth in the application of lithium ion batteries. One important cause responsible for fracture generation is the diffusion-induced stresses (DIS), which arises from the dimensional changes due to variations in composition. Analogous to thermal stress, a great deal of theoretical models of diffusion induce stresses (DIS) have been developed to understand the mechanical degradation of lithium alloy electrodes and optimize the design of electrodes with excellent electrochemical performances. However, most of these
models limit the electrode materials to be a framework in which the porosity of electrodes is the result of random packing of nonporous solid particles and its contribution is limited to the improvement of electrolytes diffusion into electrodes\textsuperscript{123,330}. In fact, the presence of pores in a single particle will affect not only the transport of electrolyte, but also the stress distribution in the solid phase. For instance, Lee and co-workers proposed using a DIS model that the distribution of concentration and stresses in hollow cylinders electrodes are drastically different from those in solid cylinder electrodes\textsuperscript{126-128}. Furthermore, Harris and co-workers reported that the presence of a mesopore in an electrode can reduce the dimensionless strain energy to a little more than half of that for a homogeneous solid electrode assuming that the mesopore is cylindrical in nature\textsuperscript{130}. Even a single mesopore present in an electrode has a significant effect on the lithium ion diffusion and fracture strength of the particle leading to complex changes in the stress intensity factor. Therefore, it can be anticipated that the emergence of well-ordered mesospores with a large area will remarkably change the mechanical properties of electrodes fabricated from those porous materials and open tremendous opportunities to the development of electrodes with outstanding electrochemical performances.

Here mechanical properties of electrodes with well-ordered mesoporous architecture are investigated through the Diffusion Induced Stress (DIS) model analogous to thermal stress by using COMSOL 4.1 software. Thin films possessing highly ordered columnar mesopores with square and hexagonal symmetry are investigated and, to obtain the optimal pore structure for battery cell design, the effect of pore size and wall thickness on the stress and strain distribution are also simulated.

6.3. Experimental section

6.3.1. Preparation of TiO\textsubscript{2} Nanotube Arrays

Pure Ti foils (99.6%, Strem Chemicals) with a thickness of 0.025 mm were used to prepare TiO\textsubscript{2} nanotube electrodes. Electrochemical anodization was carried out at room temperature in a homemade cell with a two electrode configuration. A DC power supply (Model 3603D, SpenceTek) was used to provide a constant potential during the anodization process. Ti foils with an exposed area of 3.14 cm\textsuperscript{2} acted as the anodes, and a Pt foil with an area of 2.25 cm\textsuperscript{2} was used as the cathode. The distance between the anode
and the cathode was maintained at 7 cm. The electrolyte was a solution of 0.5 wt% NH₄F dissolved in 1 M (NH₄)₂SO₃. The potential was increased from 0 V to the final potential at a ramp rate of 200 mV s⁻¹ and then was held at the designated potential of 5, 10, 20, or 30 V for 2 hours. After anodization, samples were washed with deionized water and then dried in vacuum oven at 110 °C before electrochemical measurements.

### 6.3.2. Materials Characterization

The electrochemical performance of TiO₂ nanotubes was tested in CR2025 coin cells (Hohsen) using the anodized TiO₂ foils as the working electrodes (WE), and pure Li metal foils (99.9%, Sigma Aldrich) as the counter electrodes (CE). The cells were fabricated in an Ar-filled glove box (MBraun) where the oxygen and moisture levels were below 0.1 ppm. The electrolyte was 1 M LiPF₆ salt dissolved in equal volume of ethylene carbonate and dimethyl carbonate (Novolyte). Coin cells were galvanostatically cycled between 1.0 and 2.7 V at a rate of C/3 controlled by a multi-channel potentiostat (VMP3, Bio-Logic).

X-ray diffraction (XRD) analysis using Cu Kα (λ=1.5406Å) radiation was employed to determine the titania film structure. Measurements were conducted directly on the thin films in Bragg-Brentano geometry using a Bruker D8 Advance diffractometer. For plan-view imaging of the pore accessibility, films were left intact and the conductivity was increased by coating the samples with a layer of Au/Pt alloy using a sputtering process for 1 minute. Scanning Electron Microscope (SEM) images were subsequently collected with a Hitachi S-4300 microscope at 3 kV. To observe the cross section of films, samples were mechanically bent before mounting onto the stage. For samples after cycling, cells were taken apart and anodized titania (working electrodes) were washed with dimethyl carbonate (99.9%, Alfa Aesar) in a glove box under argon. These “clean” samples were dried in a vacuum oven and then mounted onto aluminum stubs for SEM observation.
6.4. Computational Methodology

6.4.1. Construction of Mesoporous Thin Films

Mesoporous films with open pores accessible to the surface and meso-channels vertical to the surface are of particular interest for application as electrodes in lithium ion batteries. Our lab has successfully fabricated hexagonally close-packed columnar mesoporous titania thin films with meso-channels oriented perpendicular to the coating substrate.\textsuperscript{191} Other geometries including cubic, 3D hexagonal and lamellar symmetry have also been reported in other researcher groups\textsuperscript{82,212}. In some of these porous titania thin films which may be of interest for battery applications, the pores are of cylindrical shape and almost vertically aligned and parallel to each other (Sch.6.1). In the strictest sense, mesoporous thin films are not atomically crystalline. However, due to the presence of domains of well-ordered pores, mesoporous materials are usually considered as quasi-crystals possessing a structure unit with geometry corresponding to the arrangement of pores within ordered domains\textsuperscript{131,331}. In crystallography, an ideal crystal is constructed by the infinite repetition of identical structural units in space with a certain unit cell shape and symmetry. This concept is also used in the simulation of diffusion of lithium into porous titania by simulating only one unit cell and using boundary conditions to replicate the symmetry of the system. Here, to keep the intrinsic symmetry of the structure without losing an intuitive representation of the material, the structure unit is chosen to have an integral pore at the center of a domain with the same symmetry as the lattice. For instance, the unit for mesopores aligned with hexagonal symmetry is defined as a hexagon with a pore at the center (Sch. 6.2a). Similarly for pores alignment with square symmetry, the unit is chosen as a square with a pore at the center (Sch. 6.2b). When used as an electrode material in lithium ion batteries, an electrolyte fills the pores and thus solute diffuse from the top surface of films and inner surface of the pores into the solid electrode material.

6.4.2. Modeling equations

A number of papers have been published that describe the analogy between thermal stresses and diffusion induced stresses (DISs)\textsuperscript{332-333}. In the model used here, the relationship between stresses and concentration can be written as following\textsuperscript{324},

\[ \text{Stress} = \text{function of concentration} \]
\[
\varepsilon_{xx} - \bar{V} C/3 = \frac{1}{E} (\sigma_{xx} - \nu (\sigma_{yy} + \sigma_{zz})) \tag{6.1}
\]
\[
\varepsilon_{yy} - \bar{V} C/3 = \frac{1}{E} (\sigma_{yy} - \nu (\sigma_{xx} + \sigma_{zz})) \tag{6.2}
\]
\[
\varepsilon_{zz} - \bar{V} C/3 = \frac{1}{E} (\sigma_{zz} - \nu (\sigma_{xx} + \sigma_{yy})) \tag{6.3}
\]
\[
\varepsilon_{xy} = \frac{1 + \nu}{E} \sigma_{xy}, \varepsilon_{yx} = \frac{1 + \nu}{E} \sigma_{yx}, \varepsilon_{xz} = \frac{1 + \nu}{E} \sigma_{xz} \tag{6.4}
\]

Here, \(E\) is Young’s modulus, \(C\) is the molar concentration of solute (in this case \(\text{Li}^+\)), \(\bar{V}\) is partial volume, \(\sigma\) is stress, \(\varepsilon\) is strain, and \(\nu\) is Poisson’s ratio. Therefore, to obtain the stress distribution in the electrode, it is first necessary to calculate the concentration distribution of lithium ions in the electrode.

The diffusion process of lithium ions in solid phase of electrodes is assumed to follow Fick’s law and the governing diffusion equation is:

\[
\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \tag{6.5}
\]

Where \(D\) is the diffusion coefficient of lithium ions in titania, and is assumed to be a constant. In reality, the top surface of films contacts the bulk electrolyte solution and the diffusion process will happen along the thickness direction and from the inner pore walls. The diffusion within the bulk electrolyte solution is assumed to be very fast so that the concentration is constant at the top surface of the films and the inner walls of the pores (b2) in contact the electrolyte solution. Thus for example, at the boundary 'b2' of a structure unit with square symmetry (Sch. 6.2b), the lithium ion concentration is assumed to be a constant \(C_{r0}\) (reflecting facile electrochemical kinetics and a porous-electrode system dominated by solute-diffusion resistance\(^{121,326,334}\)) and the initial lithium concentration inside the electrode is set to be a uniform value of \(C_0\). At the boundary b1 (Sch. 6.2b), the concentration profile is assumed to be symmetric. The bottom surfaces are assumed to be impenetrable boundaries to lithium ions. Therefore, initial and boundary conditions for porous electrodes in 3 dimensional space are:

\[C(r, t) = C_r, \quad \text{for } x^2 + y^2 = r_0^2 \text{ or } z = 0\]
\[ C(r, 0) = C_0, \quad \text{for } x^2 + y^2 > r_0^2 \text{ and } L > z > 0 \]

\[
\left. \frac{dC}{dr} \right|_{b_1} = 0, \quad \text{for } t \geq 0
\] (6.6)

Where \( L \) is the thickness of the films, \( r \) represents a 2D vector with coordinates \( x, y \) and \( z \) and \( r_0 \) is the radius of the pore. For the nonporous electrode, the initial and boundary conditions are:

\[ C(r, t) = C_r, \quad \text{at } z = 0 \]

\[ C(r, 0) = C_0, \quad \text{at } z > 0 \]

\[
\left. \frac{dC}{dr} \right|_{b_1, \text{ or } z=L} = 0, \quad \text{for } t \geq 0
\] (6.7)

Equation (6.5) can be made dimensionless by defining the following dimensionless variables:

\[ X = \frac{x}{a}, \quad Y = \frac{y}{a}, \quad Z = \frac{z}{a}, \quad T_t = \frac{Dt}{a^2}, \quad Q = \frac{C-C_0}{C_r-C_0} \]

(6.8)

Where \( a \) is defined as the length scale of the structural unit (Sch. 6.2a and 6.2b). In terms of these variables, equation (6.5) can be written as:

\[
\frac{\partial Q}{\partial T_t} = \frac{\partial^2 Q}{\partial X^2} + \frac{\partial^2 Q}{\partial Y^2} + \frac{\partial^2 Q}{\partial Z^2}
\] (6.9)

Since the diffusion coefficient of lithium in electrolyte is about six orders of magnitude higher than in the solid electrode material\(^{318,335}\), here the solute diffusion in the pores is assumed to be much faster than the solute diffusion inside the solid electrode material. From the simulated results on the 3D films (see below), we found that, when the thickness is above a certain value, the lithium ion insertion time for porous structure units remains constant with increasing thickness of the film. This indicates the contribution of diffusion along the thickness direction can be ignored when the thickness of films is large enough. Thus, the diffusion problem is reduced to a 2D diffusion
problem in which the z-direction can be ignored (Sch. 6.1a and 6.1c). Similar to 3D films, the initial and boundary conditions for 2D films are,

\[ C(r, t) = C_{r_0}, \quad \text{at} \quad x^2 + y^2 = r_0^2 \]

\[ C(r, 0) = C_0, \quad \text{at} \quad x^2 + y^2 > r_0^2 \]

\[ \left. \frac{dC}{dr} \right|_{b_1} = 0, \quad \text{for} \quad t \geq 0 \quad (6.10) \]

For convenience, the square unit is rotated so that four points at corners are right on the X and Y axis. The initial and boundary conditions can be written in dimensionless forms as follows:

\[ Q(\text{Runit}, T_t) = 1, \quad \text{at} \quad X^2 + Y^2 = \frac{r_0^2}{a^2} \]

\[ Q(\text{Runit}, 0) = 0, \quad \text{at} \quad X^2 + Y^2 > \frac{r_0^2}{a^2} \]

\[ \left. \frac{dQ}{dT_t} \right|_{\text{Runit}} = 0, \quad \text{for} \quad T_t \geq 0, \quad \text{at} \quad X \quad \text{or} \quad Y = \pm 0.5 \quad (6.11) \]

Where \( \text{Runit} \) represents the 2D dimensionless vector with coordinates X and Y. The same types of boundary and initial conditions are used for simulation of films with hexagonal symmetry to calculate the distribution of lithium ion concentration.

Due to the insertion of lithium ions, the volume of electrodes will go through expansion during insertion and contraction during de-insertion. Analogues to the thermal expansion, the coefficient of volume expansion derived from the insertion of lithium ions can be defined as:

\[ \alpha = \frac{1}{V} \frac{\partial V}{\partial C} \quad (6.12) \]

Where \( \alpha \) is the volume expansion coefficient (here assumed to 0.03) and \( V \) is the volume of structure units. Before the calculation, structure units are meshed and then equation (6.9) and (6.12) are coupled to calculate the concentration distribution with time step setting as 0.0001. The volume expansion is only considered for calculations on 2D films.
6.5. Results and Discussion

6.5.1. TiO₂ Nanotubes Arrays Prepared by Anodization

After anodization, refraction of visible light to give regions of different color, including green and red, is observed in anodized regions on Ti foils under visual inspection. To get further information about the crystallinity of the titania films, XRD measurements were performed on the Ti foil before and after anodization. Representatively results with anodization potentials of 5 V and 20 V respectively, are shown in Figure 6.1. It is clear from the patterns that all observed diffraction peaks can be assigned to Ti metal and no characteristic diffraction peaks ascribed to crystalline titania (including anatase, rutile or brookite) are observed. This implies that the resulting products after anodizing Ti foil are amorphous titania regardless of the applied potential, which is consistent with reports by other researchers that only amorphous titania can be formed via anodization without high temperature annealing²⁹,³¹⁶,³³⁶.

Although it has no influence on the crystallinity, anodization potential strongly affects the morphology of TiO₂, which is illustrated in plan-view SEM images in Figure 6.2. When the anodization potential is above 10V under the conditions employed, uniform and vertically aligned TiO₂ nanotubes are observed with pores accessible to the surface (Figs. 6.2b to 6.2d). In contrast to the appearance of the surface at high anodization voltages, when the anodization potential is 5 V, only a porous layer of oxidized material without tubular feature is observed in the anodized region (Fig. 6.2a). At intermediate voltatges (10 V and 20 V), the surface is uniform and smooth looking but the surface of the anodized region obtained at 30 V is rougher and less uniform. Convex features are observed at the top surface of the titania nanotube walls, which suggests that the top surfaces of nanotubes are partially eroded at the high applied potential. Cross sectional views of the films obtained by fracturing them (Fig. 6.3) indicate that all nanotube arrays consist mainly of straight cylindrical tubes aligned vertical to the substrate foil. In contrast to the top surface, a domelike structure is observed at the bottom surface of the tube arrays. This is a thin oxidized layer separating the porous layer from the metal substrate, which is the so-called barrier layer commonly reported by other researchers⁹⁷. The length of the tubes is measured from these cross section images.
and the diameters and wall thicknesses are estimated by averaging 70~100 tubes from the images in Figure 6.2. The diameters and wall thicknesses of titania nanotubes obtained as a function of anodization potential are shown in Figure 6.4. The average pore diameters of the tubes increases from about 30 nm to about 70 nm as the anodization potential is increased from 10 V to 20 V. However, the pore diameter does not change significantly when the anodization potential is further increased to 30 V. The higher anodization potential does significantly increase the thickness of the walls of the nanotubes, which increases from about 17 nm at 10 V to 19 nm at 20 V, and to 35 nm at 30 V. The effect of the applied potential on the length of tubes is not monotonic, and probably reflects a tradeoff between the rate of formation of tubes and the rate of etching away material. The tubes are 350 nm long at 10 V, and the length increases to 550 nm at 20 V, while the length decreases again to 350 nm as the anodization voltage increases to 30V, which is an indication of erosion.

The influence of applied potential on the porous architecture of anodized titania nanotubes can be interpreted by the well accepted field-enhance dissolution mechanism

\[ \text{Ti} \rightarrow \text{Ti}^{4+} + 4e^- \quad (6.13) \]

\[ \text{Ti}^{4+} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ \quad (6.14) \]

However, the oxidized layer that is initially formed begins to dissolve in water in the presence of fluoride ions and the electric field by the following reaction:

\[ \text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow \text{TiF}_6^{2-} + 2\text{H}_2\text{O} \quad (6.15) \]

The dissolution of titanium oxide occurs preferentially at defects to generate pinholes on the surface of the oxide layer, and unanodized metallic portions exist between these pinholes\(^9\). With a sufficiently high potential, \(\text{Ti}^{4+}\) ions migrate out of these unanodized regions due to the nonuniformity of the electric field at the surface. The migration of these ions leaves voids in the interpore areas and separates the initial

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pinholes from each other, eventually leading to the formation of discrete tube-like structures\textsuperscript{103,337}. The observation of porous structure without tubular features is the result of the titanium ions not migrating from metallic areas when an insufficient potential is applied (in the 5V case, as indicated in Fig. 6.2a).

The growth of pores is a result of the different current intensities between the top surface of the metal and at the bottom of pores. Compared with the top surface of the oxide layer, the higher current intensity at the bottom of pore drives titanium oxide dissolution at a higher rate, leading to the continuous growth of pores into the metal. The growth of tubes stops when a balance of etching rate between the top and bottom of tubes is reached\textsuperscript{90,99}. Therefore with a higher anodization potential, tubes with longer length could be obtained (Figs. 6.3a and 6.3b). The enhancement of pore size with higher potential can also be understood by this formation mechanism as being a result of an increase in the spacing of heterogeneities in the lateral distribution of the electric field as the voltage increases (Fig. 6.4). Furthermore, more current distributed in the pore rather than in the wall at higher potential hinders the development of pinholes between tubes, finally leading to the enhancement of wall thickness with higher potentials (Fig. 6.4). However, pores with much larger diameter will connect with each other, eventually leading to the collapse of the nanotubes and a drop of tube length (comparing Fig. 6.2d and 6.2e).

The electrochemical performances of these titania nanotubes arrays as lithium ion battery anodes has been examined by researchers in the group of Y.T. Cheng at the University of Kentucky. All samples prepared with anodization voltages above 10 V exhibit excellent capacity retentions upon charge / discharge cycling after an initial capacity drop. For determination of the specific capacities of the films, the geometric parameters (tube length, diameter, and wall thickness) from the above analysis were used and the titania density was assumed to be 3.84 g/cm\textsuperscript{3}. After 200 cycles, the discharge capacity remains as high as 130 mAh g\textsuperscript{-1} for the sample prepared at 30V, and increases to 150 and 210 mAh g\textsuperscript{-1} when the applied anodization voltage decreases to 20 and 10 V, respectively. The total capacity fade is less than 6% during the period from the 10\textsuperscript{th} to 200\textsuperscript{th} cycle for samples anodized 20 and 30 V, and is 12.5% for the sample anodized at
10 V. Even for the sample fabricated at 10 V, the capacity fade is as low as 4.5% during 100\textsuperscript{th} to 200\textsuperscript{th} cycle while it is 9% during 10\textsuperscript{th} to 100\textsuperscript{th} cycle. The capacity retention in these films rivals the capacity retention reported previously for titania nanotubes arrays in lithium ion applications, and the capacity is as high as 63% of the theoretical capacity.

Figure 6.5 shows plan-view images of the morphologies of the titania nanotubes arrays after 200 electrochemical cycles. No crack or other long-range defects are observed on the surface of the films after cycling, and tubular structures are well preserved after 200 cycles and remain in contact with the Ti metal substrates. A surface layer deposited on top of titania nanotubes appears compared with those before cycling shown in Figure 6.2, which could be the remaining electrolyte salt after sample rinsing, or may reflect titania grown upon lithium insertion/removal cycling. Two aspects of this titania nanotubes structure may be responsible for the stable reversible capacity and stability of these materials upon cycling. One is the intrinsic low volume expansion of titania during lithium ion insertion and extraction\textsuperscript{27}, and the other is the hollow structure of titania nanotubes which accommodates volume expansion to allow the morphology to be retained after many discharge/charge cycles. To better understand the effect of the hollow structure of titania nanotubes on their electrochemical performance, the diffusion induced stress (DIS) model developed in Cheng’s group has been used to predict fracture tendency in this structure. The simulated results indicate that in nanotubes arrays such as these, which have relatively thin walls compared to their diameter, the current density must be at least 2 magnitude orders higher than that used in these experiments to induce DIS-based failure. In other words, titania nanotubes produced in this work would be expected to show stable cycle life with even higher discharging/charging current densities and higher cycling rates than those used here. From the simulated results, it is found that both stresses and fracture tendency increase with an increase in the wall thickness of the tubes. Therefore, it is possible that 40 nm is a critical value for wall thickness of titania nanotube arrays, above which the cracks may occur leading to the capacity degradation. However, from the experimental observations and simulation results, it is safe to draw the conclusion that titania nanotube arrays with thin walls have excellent electrochemical performances without mechanical degradations after long time cycling, while it is
difficult to tell an exact critical value of wall thickness, above which the mechanical degradation can be observed.

6.5.2. Calculations of Concentration Distribution in Mesoporous Thin Films

As discussed above, mesoporous titania thin films have smaller pores, thinner walls and well-ordered interconnected solid frameworks than nanotubes arrays, which may be anticipated to better accommodate the expansion and contraction that occur during the lithiation/delithiation process. Therefore, the DIS model has been extended to predict the stress evolution and strain energy distribution in electrodes with mesoporous structure. Here, we present only calculations of the concentration distribution of lithium in mesoporous titania electrodes having pores aligned with square or hexagonal symmetry, based on which the mechanical analysis will be performed by Cheng’s group in a future contribution.

To predict the behavior of titania thin films under practical experimental conditions, the above analysis is first performed on thin films with three dimensional pore geometry and nonporous thin films. The concentration distribution in nonporous films is shown in Figure 6.6. In the absence of mesopores, it is obvious that the regions close to the top surface have higher concentration, while those close to bottom surface have the lowest concentration (Fig. 6.6). At a small value of dimensionless time \( T = 0.05 \), the concentration along the thickness direction in nonporous films gradually decreases from 1 at the top surface to 0 at the bottom surface (Fig. 6.8). However, in the presence of mesopores, regions close to the top surface and close to the surface of the pores have higher concentration, while the points at corners on the bottom surface have the lowest concentration (Fig. 6.7). At the same early dimensionless time \( T = 0.05 \), the concentration along the thickness direction in mesoporous thin films sharply decreases to a value above 0 at \( Z \approx -0.6 \), and then decreases so slowly deeper in the films that the concentration can be considered to be constant from that point on (Fig. 6.8). The value of this constant increases as the ratio of pore diameter \( D \) to structure unit parameter \( a \) increases, the effect of which is more obvious for films with hexagonally close packed pores (Fig. 6.8).
We define the maximum time for lithium insertion as the time where the entire films has a uniform concentration, which is the point at which a point at the corner of the unit cell and the bottom surface of the film reaches a dimensionless concentration of $C = 0.999$. The insertion time vs. film thickness and pore diameter results are summarized in Figure 6.9. In the absence of mesopores, the maximum time increases sharply and continuously with increasing film thickness. However, the insertion time can be effectively reduced in the presence of mesopores with hexagonal symmetry and remains constant after the thickness of the films reaches a particular value determined by the value of $D/a$. There exists a threshold value for the film thickness, below which the insertion time for both nonporous and mesoporous films is the same, and this threshold value increases with decreasing $D/a$. At this threshold value, the diffusion of lithium from the pores begins to compete with diffusion from the top surface and so the time for insertion of lithium ions is dictated not by the thickness of the film but by the diffusion from the pore surface, which under the assumption of constant lithium concentration in the electrolyte always takes the same amount of time. A similar effect is also observed for mesopores with vertically aligned pores with square symmetry. Thus, the porous structure has no advantage in reducing the insertion time when the films are very thin, although this porous structure may have some benefit in the reduction of stress and strain energy. However, in all cases this occurs at a thickness of less than one unit cell parameter, which in the case of most surfactant templated structures is on the order of 5-20 nm, so the films would have to be so thin as to be of questionable value as energy storage devices. To further elucidate the advantages of porous structure in films and the difference between aligned mesopores with hexagonal and square symmetry, mechanical analysis needs to be performed on these 3 dimensional films in the future. Also of interest will be to compare films with 3D symmetry such as gyroid cubic films and films prepared with close-packed globular structures (cubic or 3D hexagonal).

As discussed above, the thicknesses of mesoporous thin films derived from the surfactant templated sol-gel process are generally tens of nanometers. For films with such thickness, the length scale for diffusion from the pore into the corner of the unit cell is much smaller than the length scale for diffusion from the top of the film. Therefore, 3D thin films can be simplified into 2D thin films and the calculation can be performed
on the 2D film geometry in which diffusion from the top surface of the electrode is neglected, which substantially saves the calculation time. Since electrodes are assumed to be composed of elastic materials, the compressed state derived from insertion is relaxed and the materials get back to the initially free state during de-insertion. Therefore, it is reasonable to only consider the behavior of the materials during insertion. After the insertion of lithium ions into the bulk material from the pores, the solid phase swells and deformation of the center of the pore is observed, the deformed shape of which depends on the symmetry of structure unit (Fig. 6.10). It is clear from these images that, consistent with the diffusion of lithium into the material from the surface of the pore, along a line from the pore surface to the corner/edge of the structure unit, the concentration decreases gradually, and the lowest concentration can be observed at the corner of the structure unit (Fig. 6.10). The shape of the contour lines matches the symmetry of the structure, with the contour lines rotating 90° (for square structure unit) or 60° (for hexagonal structure unit). The concentration of the whole unit will therefore be uniform when the concentration at the corner reaches the initial concentration at the edge of the pore. Form the concentration profiles, it is observed that the value of concentration distributes symmetrically along the diagonal lines and decreases gradually from 1 at inner pore wall to a minimum value at the corner of structure units (Fig. 6.11). However, the value of lowest concentration can be effectively improved with increasing D/a. Compared with films with cubic aligned pores (Fig. 6.11a), films with hexagonally close-packed pores (Fig. 6.11b) have higher concentration at the corners of structure unit with the same D/a. As defined for 3D films, the maximum time for 2D films decreases as the D/a increases and, to get uniform concentration in the whole structure unit, unit with hexagonal symmetry requires a shorter time than that with square symmetry (Fig. 6.12). It is understandable that, with the same structure unit parameter, the distance between the center and the corner is shorter in a hexagon than that in a square. This implies that aligned pores with 2D hexagonal symmetry is preferable for battery applications, especially for materials with poor lithium ion diffusion within solid phase. However, the enhancement of charge/discharge rate comes at the expense of power density, because structure units with hexagonal symmetry have higher porosity than those with square symmetry, especially when the ratio of pore diameter to structure unit parameter is high.
The advantage of hexagonal geometry as electrodes is further elaborated by the results of mechanical analysis during insertion, which is shown in work done by Rutooj Deshpande at the University of Kentucky. Only compressive stresses are found through films regardless of the pores symmetry. Compared with square structure unit, hexagonal structure unit has less maximum stresses and lower strain energy due to the higher symmetry in hexagonal pore packing which can more effectively accommodate the volume expansion during insertion. Simulated results also demonstrate that the maximum stresses and strain energy can be reduced by decreasing the wall thickness. In summary, films having aligned pores with hexagonal symmetry appear for many reasons to be better candidates than those with square symmetrical pores for electrodes of lithium ion batteries, in which high charge/discharge rate is required and low strain energy and stresses are expected.

6.6. Conclusions

Vertically aligned amorphous titania nanotubes with tunable inner pore diameter and wall thickness were fabricated by anodization of Ti foils at various voltages. The pore diameter and wall thickness of the titania nanotubes were varied from 30 nm to 70 nm and 17 nm to 35 nm respectively, although the process of anodization does not allow for independent control of both dimensions. The fabricated titania nanotubes were employed as anode materials for lithium ion batteries and present good cycling behavior, with capacities between 150-230 mAh g\(^{-1}\) and little drop in capacity for up to 200 cycles. From the SEM observation, no cracks are found on the surface of titania nanotubes after 200 cycles. Therefore, the hypothesis that titania nanotube arrays with thin wall have excellent electrochemical performance with high stability during the lithiation/delithiation process has been proven. This hypothesis is further confirmed with predictions from the DIS model that cracks should only occur in nanotubes arrays at a current density at least two order of magnitude higher than those used in this experiment.

The calculation results indicate that the use of mesoporous materials as electrodes may provide the advantage of high charge/discharge rates due to reducing reduction in diffusion time of electrolytes into the material compared with nonporous electrodes. Furthermore, materials having aligned pores with hexagonal symmetry have slight
advantages over those with square symmetry. The first one is that hexagonal arrays can effectively reduce the time for lithium ions to reach an uniform concentration throughout the materials compared with square arrays. The second one is that hexagonal symmetry can more effectively accommodate the expansion and contraction during lithiation/delithiation process and reduce the stresses and strain energy due to its higher symmetry relative to square alignment.

Although further investigations on more complicated arrangements of pores in two or three dimensional spaces are needed, the results obtained here are general and can be extended to other materials with similar pore structure. Results obtained here should be significant for the design of lithium ion batteries using materials with nanoporous architecture.
Figure 6.1. XRD patterns of pristine Ti metal foil and after anodization at 5 and 20 V for 2 hours, respectively. All peaks indicated belong to Ti metal.
Figure 6.2. Plain view SEM images of TiO$_2$ nanotubes after anodization for 2 hours. The applied anodization voltages are (a) 5V, (b) 10V, (c) 20V, and (d) 30V. The scale bars are 250 nm in all figures.
Figure 6.3. Cross section SEM images of TiO$_2$ nanotubes after anodization for 2 hours. The applied anodization voltages are (a) 10 V, (b) 20 V, and (c) 30 V. The scales bars are 250 nm in (a) and (c), and 1000 nm in (b).
Figure 6.4. Dependence of pore diameter and wall thickness of TiO$_2$ nanotubes on anodization potential.
Figure 6.5. Plain view SEM images of TiO$_2$ nanotubes after 200 electrochemical cycles. The applied anodization voltages are (a) 10V, (b) 20V, and (c) 30V. The scales bars are 500 nm in all images.
Figure 6.6. The concentration variation in nonporous structures unit with nonporous. All lengths and concentration have dimensionless units and the ratio of thickness (L) to structure unit parameter (a) is 1. Dimensionless time to extract data $t = 0.01$. The definition of $D$, $a$ and $L$ is shown in scheme 6.1 and 6.2.
Figure 6.7. The concentration variation in porous structures unit with cubic symmetry (a), or hexagonal symmetry (b). The ratio of pore diameter (D) and thickness (L) to structure unit parameter (a) is 0.5 and 1 respectively. All lengths and concentrations have dimensionless units. Dimensionless time to extract data $t = 0.01$. The definition of D, a and L is shown in scheme 6.1 and 6.2.
Figure 6.8. Concentration profiles of structure units. Nonporous represents structure unit without pores. All data are extracted along the dashed lines in Fig.6 and Fig.7 at time $T=0.05$. C and H represent square and hexagonal structure units respectively, and the numbers followed indicate the ratio of pore diameter ($D$) to the structure unit parameter ($a$). Both concentration and $Z$ have dimensionless units.
Figure 6.9. Dependence of maximum time where structure unit has uniform concentration on the thicknesses of film with various ratios of pore diameter (D) to structure unit parameter (a). The structure unit has hexagonal symmetry and the pore diameter (D) and structure unit parameter (a) are defined in scheme 6.2. The thickness of film and time has dimensionless units. The definition of D, a and L is shown in scheme 6.1 and 6.2. Time and thickness of films have dimensionless units.
Figure 6.10. Concentration variation in structure units with cubic (a) and hexagonal (b) symmetry. The black lines indicate the initial edge of pore before deformation and color lines represent contour lines of concentrations. Both length and concentration have dimensionless unit. The ratio of pore diameter (D) to structure unit parameter (a) is 0.5. Dimensionless time to extract data $T = 0.01$. The definition of D and a is shown in scheme 6.2.
Figure 6.11. Concentration profiles of structure unit with cubic (a) or hexagonal (b) symmetry at various ratios of pore diameter (D) to the structure unit parameter (a). Data are extracted along the lines with Y = 0. Both length and concentration have dimensionless units. The dimensionless time to extract data is 0.01.
Figure 6.12. The dependence of lithium ion insertion time on the ratio of pore diameter (D) to the structure unit parameter (a). Time has the dimensionless unit.
Scheme 6.1. Illustration of mesoporous architectures possessing pore arrangement with hexagonal (a, top view; b, cross section) and cubic (c, top view) symmetry. Mesopores with quasi crystal structure are divided into separated structure unit with its unique symmetry along dash lines. L represents the thickness of films.
Scheme 6.2. Representative structure units of mesoporous architectures with hexagonal (a) and cubic (b) symmetry. D and a represents pore diameter and the parameter of structure unit respectively. b1 and b2 represents the boundary of structure unit and pore respectively.
Chapter 7 Conclusions and Future Works

7.1. Conclusions

In this dissertation, triblock copolymer P123 having average structure (PEO)_{20}(PPO)_{70}(PEO)_{20} (where PEO = poly(ethylene oxide) and PPO = poly(propylene oxide)) is used as the pore template to fabricate mesoporous titania thin films by the sol-gel route. As discussed in Chapter 1, well ordered mesopores are generated by the removal of highly ordered self-assembled P123 micelles which assemble into structures analogous to the lyotropic liquid crystals formed in the P123/water system. The cores of these micelles are comprised of a cluster of hydrophobic PPO segments, while the hydrophilic PEO head groups of the surfactants point outwards and interact with polar inorganic components through hydrogen bonding. The whole environment of as-synthesized films can be conceptually divided into two parts. One is the hydrophobic part which includes PPO blocks (and any compatible swelling agents or solvents), and the other is the hydrophilic part including PEO blocks and polar inorganic components outside of the micelles. Therefore, the main part of this dissertation involves understanding how the formation mechanism of micelle-templated films can be directed to generate materials with well-defined nanoporous structures, and utilizing porous titania films for applications in alternative energy.

Titania thin films with tunable pores have been synthesized by controlling the characteristics of the hydrophobic part of as-synthesized films. In fact, the pore size of the final products is determined by the micelle size of P123, which is determined by the length of the hydrophobic cores (perhaps with a swelling agent). Therefore, hydrophobic organics compatible with P123 which are added into the initial sol-gel solution are more likely to be incorporated within the hydrophobic PPO blocks, thus increasing the pore size. This has been corroborated in Chapter 3, which demonstrated that the introduction of an amphibious polymer, PPG (which with molecular weight $M_n \sim 3500$ behaves hydrophilic at low temperature and hydrophobic at high temperature) into the sol-gel process, resulted in titania thin films with swollen pores. With the introduction of PPG, the final calcined films were observed to have well defined mesoporous structures,
although the degree of long-range order diminished with the addition of more PPG. The mesopore size of the films increased with increasing amounts of PPG, but PPG also introduced smaller mesopores into the films under our synthesis conditions to generate a bimodal pore size distribution due to the partitioning of PPG between the PPO cores of micelles and the titania matrix.

Similar effects of hydrophobic organics on swelling pores were also observed when 1-butanol was added into the initial sol-gel solution, as described in Chapter 5. In the presence of a small amount of 1-butanol, titania thin films with swollen pores were obtained. In contrast to the swelling effect observed in silica / P123 / 1-butanol system, the pore size decreased with increasing amounts of 1-butanol in the titania thin films. The reason for this is probably that the presence of more 1-butanol reduces the P123 aggregation number leading to shrinkage of globular micelles, or that part of P123 molecules in the micelles are replaced by short chain 1-butanol molecules. However, the most remarkable observation in Chapter 5 is that introducing a small amount of 1-butanol resulted in titania thin films possessing 3D hexagonal mesoporous structure (space group R-3m) via the P123 templated sol-gel process. The most likely explanation for this phenomenon is that 1-butanol locates preferentially at the hydrophilic/hydrophobic interface between the PEO and PPO blocks of Pluronic surfactants, thereby helping to stabilize mesophases with high micelle surface curvature such as 3D hexagonal and globular cubic phases. There are two advantages for the technique used here to prepare 3D hexagonal mesoporous titania thin films over others previously reported. One is that the use of P123 as pore structure directing agent generates shorter distance between neighboring pores in the resulting films compared with those derived from F127 (another Pluronic surfactant shown to give 3D hexagonal titania films). This is expected to improve the connectivity between pores, in addition to providing open pores accessible to the surface of the films. The other advantage is that using a small amount of 1-butanol to produce films with 3D hexagonal porous structure results in a low-cost fabrication process compared with processes using 100% butanol as solvent or butoxytitanate precursors. The 3D hexagonal structure is found over a wide range of butanol contents, thereby suggesting that a robust process with only a small amount of butanol required could be developed for the fabrication of 3D hexagonal mesoporous titania thin films.
Returning to polymeric additives, one of the contributions of this dissertation is a quantitative link between the effects of PPG on mesostructured titania and the behavior of the same PPG in aqueous solution. The behavior of PPG polymer in aqueous solution was modeled with Flory-Huggins theory to estimate the full two-phase envelope (Chapter 3). The phase diagram reveals that the commercially available PPG of $M_n = 3500$ (from Sigma-Aldrich) and water have a lower consolute temperature of about $-9 \, ^\circ C$, and that at a film aging temperature of $4 \, ^\circ C$, the composition of PPG for preparing titania thin films is well within the two-phase region. This is consistent with the observation of swelling in films prepared at this relatively high aging temperature in Chapter 3. The repulsion between PPG molecules and polar inorganic components at this temperature drives PPG into the hyphobic cores of P123 micelles leading to final products with larger pore sizes. However, when the film aging temperature is reduced to about $-6 \, ^\circ C$, the composition used for preparing titania thin films is well within the one-phase region. This changes the qualitative effect of PPG by promoting its inclusion in the polar (titania-rich) phase during the aging process and allowing phase separation of a separate PPG-rich phase to occur upon heating the film. This is the first study we know of that quantifies the low-temperature phase behavior of moderately high molecular weight PPG, and correlates this phase behavior with materials synthesis.

Based on our understanding of the assembly of Pluronic surfactants into lyotropic mesophases, the interaction between hydrophilic blocks of polymers and polar inorganic components was fully utilized to synthesize titania thin films possessing tunable wall thickness or pore sizes with multiple scales. It is widely accepted that aging titania / Pluronic thin films at low temperature favors the formation of well-ordered lyotropic liquid crystals by slowing the hydrolysis and condensation reactions of inorganic precursors. This allows a higher concentration of inorganic precursors to be used without accelerating the curing reactions excessively, thus allowing lower surfactant contents to be used to generate thicker walls in the final products. Therefore, well ordered lyotropic liquid crystals are likely to be formed by aging films at low temperature. This has been verified in Chapter 2, where it was shown that titania thin films with well-ordered mesopores were obtained even with a molar ratio of P123:Ti as low as 0.006. Aging the as-synthesized films at temperature down to $-6 \, ^\circ C$ still led to titania thin films with 2D
hexagonal mesopores. The wall thickness increases as the molar ratio of P123 to titanium \((R)\) decreases, although the mesophase transforms from 2D hexagonal to 3D hexagonal for \(R\) below 0.008. In addition, this chapter represents the first report to show that ordered mesophases can be formed over a large composition range under low temperature aging, which could not have been predicted from the existing phase diagrams or theories. The outcomes of chapter 2 facilitate the design of well-ordered Pluronic-templated transition metal-based thin films with tunable wall thickness by low temperature aging.

The understanding of the effects of temperature on PPG polymer behavior developed in Chapter 3 was also utilized to push the film synthesis in new directions. By decreasing the aging temperature below that used to swell pores with PPG, hierarchical pore structures were formed. Hierarchically porous titania thin films containing large voids (>100 nm in diameter) and well-ordered mesoporous walls were prepared by low-temperature aging in Chapter 4. The pore size and amount of voids could be controlled by adjusting the amount of PPG added into the P123 templated sol-gel process. Based on the phase diagram from Chapter 3, the observed structure was interpreted as coming from two different types of aggregation. The well-ordered mesopores within the walls of the materials were generated from the self-assembled P123 micelles. On the other hand, the large voids came from the phase separation of PPG from the titania matrix. This phase separation is the result of the amphibious temperature-dependent properties of PPG. At -6 °C, PPG of \(M_n = 3500\) is hydrophilic and, thus, able to disperse in the titania-rich phase of the as-synthesized composites during aging. However, when the films were removed from the low-temperature aging stage, the PPG rapidly reached a temperature where it becomes hydrophobic, and thus it separated into separate PPG-rich droplets which became the large voids in the film. This chapter represents the first report of using temperature to switch the properties of a polymer additive, and thus to obtain a hierarchically porous architecture. The principle demonstrated here is of general use to fabricate porous structure with multiple length scales, and could be tuned by selection of the structure of the amphibious polymer additive.

Finally, in addition to the surfactant templating sol-gel approach, anodization was also employed in this dissertation to prepare well aligned vertical titania nanotubes arrays
attached to a conductive (titanium) substrate. The application of these arrays showed outstanding cycling stability as an anode electrode in lithium ion batteries. This excellent electrochemical performance is ascribed to excellent accommodation of expansion/contraction occurring during the lithiation/delithiation process by the tubular structures with thin walls. To better understand the importance of this structure, a diffusion induced stresses (DIS) model was used to show that tubular structures should be able to handle much higher current densities than used experimentally without risk of fracture. This DIS model was further developed to model porous electrodes with well-ordered mesopores. Simulated results illustrated that materials with hexagonally aligned mesopores have advantages over those with square aligned pore arrays. These advantages include higher charge/discharge rates in hexagonally porous structure and lower maximum stresses and strain energy due to the higher symmetry in hexagonal than square unit cells. The model developed here and outcomes obtained in this modeling work are expected to have great impacts on the future design of electrodes with high levels of electrochemical performance by using surfactant-templated nanoporous materials.

7.2. Future Works

In the context of materials synthesis, the methods described here are general and they can be extended to prepare other transitional metal–based mesoporous thin films. For instance, indium tin oxide (ITO) thin films are widely used in solar cell applications because their outstanding electrical conductivity compared with other oxides, coupled with optical transparency. Several procedures have been reported to prepare mesoporous ITO thin films by surfactant templating. However, efforts to reproduce these procedures were not fruitful for reasons that could not be determined by either adjusting synthetic protocols or attempting to contact the authors of those reports. Therefore, the methods used for titania thin film preparation were explored for mesoporous ITO thin film fabrication. Unfortunately, films with well-ordered, stable mesopores were not consistently obtained, and further work will be needed to control crystallization, curing and self-assembly based on the results obtained successfully here for titania thin films. Mesoporous ITO would be of great interest as a transparent conductive support for photoactive metal oxides. For instance, certain phases of iron oxide are predicted to have appropriate band gaps for photocatalytic water splitting, but their insulating properties
make them untenable in forms that require them to also serve as electrical conduits (such as nanoparticle or nanowire arrays). If good electrical contacts made, supported iron oxide nanoparticles on a mesoporous ITO support may be able to combine high photoactivity with good electrical conductivity to make an efficient water-splitting photosystem.

A second new direction that was explored but not concluded during the course of this dissertation was the preparation of titania / carbon nanotube (CNT) composites. The electrical conductivity is poor in titania, so it is necessary to support titania on a conductive substrate (usually ITO or fluorinated tin oxide). However, CNTs have extraordinary electrical conductivity and there is great interest in the use of CNT/titania composites as photoelectrocatalytic platforms\textsuperscript{338-339}. It is anticipated that the combination of titania and CNTs can effectively improve the electrical conductivity while still having a band gap and photoconversion efficiency consistent with the active titania layer, and thus benefit the energy conversion of solar energy. The CNTs are expected to rapidly carry photogenerated electrons away from the titania, thus reducing recombination and enhancing photon utilization. Titania / CNT composite synthesis and application were performed during the course of this dissertation in collaboration with Xin Su in the Hinds group at the University of Kentucky. The composites were explored for photocatalytic degradation of methylene blue and for water splitting photocatalysis, and showed to have moderate activity which is described in separate publications. In the future, it may be possible to create titania thin films supported on CNT bucky paper supports as a way of taking advantage of the ability to control mesopore structure as described in this dissertation. However, with the current synthesis techniques, titania particle / CNT composites have been found to have photocatalytic properties equivalent or better than the sol-gel coated titania/CNT materials and the reasons for this observation need further investigation.

One other direction for exploring the application of the titania films developed in this dissertation is in inorganic/organic photovoltaic thin films. As described by McGehee’s group, incorporating a hole conducting polymer such as poly-3-hexylthiophene (P3HT) into the pores of titania thin films is expected to form a high-
surface area heterojunction composite. The hole conductivity in P3HT incorporated into cylindrical mesopores has been shown to be much higher than in bulk P3HT (most likely due to preferential alignment along the pore axis), thus making it likely that higher efficiencies can be obtained than were observed in cubic titania / P3HT composite films. Our group previously attempted to incorporate P3HT into oriented mesoporous titania films with 4-5 nm pores and met with limited success due to the small pore size of the materials. The products described in this dissertation have larger pores and thicker walls, which should provide higher conductivity in the titania films, greater stability during calcination, and improved capacity for incorporation of P3HT. Therefore, it will be worthwhile to revisit the incorporation of P3HT into the mesopores of these materials and to test the photoconversion efficiency of the resulting inorganic/organic heterojunction photovoltaic films. If they show reasonably high efficiency, they would be low-cost, scalable photovoltaic materials that could be cast onto a wide variety of substrates, including transparent or porous substrates.

Another natural direction to move in order to improve photocatalytic performance is altering the titania matrix. The band gap of titania is 3.0-3.2eV, and it is somewhat higher (~3.4 eV) for mesoporous titania thin films and titania nanotube arrays. This is in the ultraviolet (UV) wavelength range. However, UV radiation accounts for only a small fraction (8%) of the solar spectrum compared to visible light (45%). Therefore, any shift in the optical response of titania from the UV towards the visible range will improve the utilization of solar energy and bring more opportunities for application of mesoporous titania in the photocatalytic and photoelectrochemical fields. One method to improve photocatalytic performance in the visible wavelength range is to dope titania with elements including F and N, which are the most effective dopants due to their similar electronegativity and size to oxygen. We have successfully prepared titania nanotubes arrays by anodizing titanium foil in electrolyte solutions containing NH₄F and (NH₄)₂SO₄. In this strategy, titanium is exposed to the fluoride containing solution, and it is highly possible for fluoride and nitrogen compounds to diffuse into the framework of the final titania during anodization. Therefore, the doping level of F and N element can be controlled by adjusting the composition of the electrolyte solution or the applied potential. At this point, only preliminary experiments regarding the preparation
of doped titania nanotubes arrays by varying the composition of the electrolyte solution have been done, and further work including characterizations of these arrays, optimizing fabrication conditions, and applications of these materials need to be carried out in future. There would also be room to change the chemistry used in the sol-gel technique to introduce nitrogen and to change the valence of the titanium precursors to tune the properties of the final materials, but this is beyond the scope of this dissertation.

Finally, in addition to potential application in energy conversion, titania also has great potential for use in energy storage, especially used as an anode electrode material for lithium ion batteries. However, only titania nanotube arrays have been applied as electrode materials in the work completed as part of this dissertation. This was in part due to challenges fabricating and creating a good electrical contact with a conductive substrate compatible with standard battery testing procedures. Well-ordered mesoporous titania thin films have a higher degree of organization of pores, smaller pores and thinner wall thickness compared with nanotube arrays. There may be tradeoffs between mechanical strength and transport properties, but there are many reasons (based on the modeling work completed in Chapter 6) to anticipate that ordered mesoporous films should have improved electrochemical performance over anodized titania films as electrodes in lithium ion batteries. Therefore, it will be worthwhile to develop methods of fabricating stable oriented 2D hexagonal mesoporous titania films on conductive substrates for battery testing. Also, because of the variety of structures available, it would be beneficial to expand the diffusion induce stresses (DIS) model for the mesoporous structures with 3D geometries including 3D hexagonal, globular cubic phases, and an interconnected cubic (gyroid) phase. This will allow the promising synthetic techniques developed here to find their way into commercial application as alternative energy materials in a timely fashion.
Appendix Nomenclature

\( a \): the length scale of the structural unit

\( A^* \): the constant that does not depend on \( h v_f \)

\( c \): constant related to the heat of adsorption of nitrogen gas

\( C \): the molar concentration of lithium ion

\( C_0 \): the initial lithium ion concentration inside the electrode

\( C_{wp} \): the lithium ion concentration at the wall of pores

\( d \): the spacing between planes of objects

\( D \): the diffusion coefficient of lithium ions in titania

\( E \): Young’s modulus

\( E_g \): band gap

\( \Delta G_{mix} \): the Gibbs free energy change of mixing

\( h \): Planck’s constant

\( k \): Boltzmann’s constant

\( L \): the thickness of the films

\( m_{Ti(OH)_4} \): the mass of \( Ti(OH)_4\)

\( m_{HCl} \): the mass of HCl

\( n \): integer

\( N_1 \): the number of molecules of the solvent

\( N_2 \): the number of molecules polymer

\( q_y \): the scattering vector normal to the plane of incidence and parallel to the films surface,
q₂: the scattering vector normal to the sample surface

Q: the dimensionless concentration

r: 2D vector with coordinates x, y and z

r₀: the radius of the pore

r₁: the number of lattice sites occupied by the solvent

r₂: the number of lattice sites occupied by polymer

R: the universal gas constant

R_{unit}: the 2D dimensionless vector with coordinates X and Y

t: time

tₙ: the film thickness of nitrogen gas absorbed on the surface of titania

T: the absolute temperature

Tᵢ: the transmission (%) of light

Tᵢ: the dimensionless time

vₙ: the volume of nitrogen absorbed onto the material at any relative pressure x (= p/p₀)

V: the volume of structure units

V_{inorg}: the volume of the nonvolatile components in the solutions

Vₖₐₜ: the molar volume of the liquid nitrogen

V_{pol}: the volume of the block copolymer

Ṽ: partial volume

X: the dimensionless x coordinate

Y: the dimensionless y coordinate
Z: the dimensionless y coordinate

\( \alpha \): the coefficient of volume expansion derived from the insertion of lithium ions

\( \alpha_{ab} \): the absorption coefficient of light

\( \gamma \): the surface tension of liquid nitrogen

\( \sigma \): the stress

\( \varepsilon \): the strain

\( \theta \): the angle between the incident beam and the detector

\( \nu \): Poisson’s ratio

\( \nu_f \): the frequency of light

\( \nu_m \): the volume of gas adsorbed when the entire adsorbent surface is covered with a complete unimolecular layer

\( \lambda \): the wavelength of the x-rays

\( \rho_{\text{Ti(OH}4)} \): the density of Ti(OH)\(_4\)

\( \rho_{\text{HCl}} \): the density of HCl

\( \chi \): temperature-dependent interaction parameter

\( \phi \): the volume fraction of a species in the lattice model

\( \Phi \): the volume fraction of block copolymer

\( \Delta \mu_i \): the chemical potential changes of mixing for each species \((i)\)
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