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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**POROUS STRUCTURED TITANIA BY CHEMICAL
METHODS**

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Supervisors: Prof. Ma Jan; Dr. Gregory. K. L. Goh

A THESIS SUBMITTED TO NANYANG TECHNOLOGICAL UNIVERSITY IN
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ABSTRACT

This thesis describes the synthesis and characterization of various porous titania structures, with specific emphasis on surface area and crystallinity. Materials having pore diameters ranging from ~2 nm to ~250 nm were prepared from hard anodic aluminium oxide templates (AAO) and soft block copolymer templates. The photocatalytic performance of these titanias was also evaluated.

It is demonstrated that aperiodic with mesopores ~2 nm to 4 nm diameter could spontaneously form in anatase films and powders without templates by Liquid Phase Deposition (LPD), and progressively infill as the reaction proceeds. During film growth two kinetic mechanisms are operative: phase-boundary-controlled continuous nucleation and diffusion-controlled grain growth, the preponderance of each regulated by the supersaturation of the precursor solution to yield different grain morphologies. Increasing the reaction temperature from 50°C to 200°C during LPD improved film crystallinity from 75 to 90%, the balance being X-ray amorphous. Ordered macroporous titania was synthesized from porous AAO templates and a starting material by LPD. In the process, titania displaced alumina in the AAO templates but the parent structure was retained through in-situ growth of H_3AlF_6 . The resultant titania membranes were constructed from well-ordered macropores and aperiodic mesopores within the tube walls. The titania membranes were shown to have excellent photocatalytic activity due to the large surface area ($>100 \text{ m}^2/\text{g}$). For these titania materials deposited by LPD, photocatalytic activity correlated directly with surface area.

For soft templating, a block co-polymer was employed to create an ordered mesoporous titania film. Mesopores in F127 templated titania films were 12~13 nm in

diameter with primitive cubic symmetry. By adjusting respectively the proton concentration and the F127 template content in the titania precursor, the crystallinity and surface area were improved. The thermal stability of the mesoporous structure is limited by titania crystallization at $\sim 400^{\circ}\text{C}$, but by using the block copolymer PS(polystyrene)-*b*-PEO, it was increased to $\sim 600^{\circ}\text{C}$. Well-ordered homogeneous mesopores in PS-*b*-PEO templated titania films were ~ 30 nm in diameter. Self-aligned titania islands on the substrate surface could be synthesized by increasing the volume fraction of the PS block in PS-*b*-PEO. Moreover, the titania islands could be tuned from a few nanometers to hundreds of nanometers in diameter through the adjustment of the content of the titania source. For the mesoporous titania synthesized via sol-gel techniques, photocatalytic activity is controlled primarily by crystal perfection rather than the surface area.

CHAPTER 1

INTRODUCTION

The provision of drinking water to an expanding global population has become a major technological challenge in the 21st century. In addition to this, advanced technology-induced hazards such as the major chemical contaminants such as benzene rings found in modern dyes, are difficult to biodegrade or oxidize through ozonation. Therefore, advanced oxidation processes need to be enhanced to manage such water borne toxic chemicals. One promising class of photocatalyst materials are titania-based polymorphs which are the focus of the present work.

1.1 Background and Motivation

In the last decade, titania has drawn much attention because of its many useful functions. First, titania is a biomaterial capable of sterilizing and inhibiting viral infections by destroying membranes within the virus cell, solidifying virus proteins and restraining virus activities, such as aerobic bacteria (up to 99.7%). Second, titania is an effective photocatalyst that can destroy recalcitrant environmental pollutants that contain aromatic rings. The hydroxyl free radicals produced during catalysis can destroy organic molecules and reduce them to benign gas molecules. The oxidation strength of titania has proven greater than that of ozone, in addition, was stronger adsorption ability than activated carbon. According to authoritative laboratory tests in Europe and America, the deodorization ability of titania is nearly 150 times stronger than high-efficiency carbon fiber, and equivalent to a 500-rated active carbon refrigerator deodorant. Third, the hydrophilic and antipollution abilities of titania decompose the grease, hence making attachment of dust particles

difficult. Last, titania can effectively defend against the harmful effects of sunlight due to its ability to absorb ultraviolet radiation. These advantages and potentials have made high purity titania, an efficient, safe and stable material for technology development.

Titania, as a raw industrial material, has been named “the alumina of the 21st century” due to its excellent mechanical properties such as low density, corrosion resistance and biocompatibility [1]. Traditionally, titania is widely used as a pigment for paints and in varnishes, paper and plastics. With the emergence of biomaterials, the bioactivity of titania has also facilitated applications in orthopedic and dental implants [2, 3]. Moreover, it is an attractive photocatalyst in solar cells [4-11], anti-bacteria, and self-cleaning coatings [12], optical devices [13-15], gas sensing [16-19] and water treatment [20].

Figure 1-1 Titania crystallographic geometries with TiO_6 octahedra

Titania exists in three crystallographic geometries (Fig. 1-1): rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). With respect to the physical properties of each phase (Table 1-1), rutile is the thermodynamically stable form, while anatase and brookite transform to rutile when heated to $\sim 700^\circ\text{C}$. Rutile is applied in white pigments and various optical devices due to its chemical stability, high UV absorbance and refractive index. Brookite has similar mechanical properties to rutile, but it is the least common of the three phases and is rarely used commercially. Anatase is a highly oxidizing form and widely

applied as an effective photocatalyst for the decomposition of aldehyde gas [21] and water borne pollutants [22], as well as in water splitting for hydrogen generation [23-25].

This photocatalytic activity arises mainly from a combination of two properties in titania - surface area and crystallinity [26]. Consequently, nanostructured anatase with an optimized combination of these parameters has become the most extensively studied crystallographic form in recent years. Titania as a photocatalyst is most often suspended in batch solutions, which requires expensive recovery and re-suspension steps when implemented at the industrial scale. In an effort to improve the performance of titania and avoid these costly procedures titania films and membranes are also investigated widely.

Table 1-1 Physical properties of titania [26]

	Rutile TiO ₂	Anatase TiO ₂	Brookite TiO ₂
Form.Wt.	79.890	79.890	79.890
Z	2	4	8
CrystalSystem	Tet	Tet	Orth
PointGroup	4/mmm	4/mmm	mmm
SpaceGroup	P4 ₂ /mm	I4 ₁ /amd	Pbca
UnitCell			
a(Å)	4.5845	3.7842	9.184
b(Å)			5.447
c(Å)	2.9533	9.5146	5.145
Vol	62.07	136.25	257.38
MolarVol	18.7	20.2	19.4
Density	4.27	3.90	4.12
Bandgap Energy (eV)	3.0	3.2	3.78
Thermal Expansion(Volumetric)			
a ₀	0.2890		
alpha	28.9		

With the strong interest in titania films, many traditional physical deposition techniques, such as sputtering [27-32], chemical vapor deposition (CVD) [33-39], molecular beam epitaxy (MBE) [40-42] and pulsed laser ablation (PLA) [43], have been

extensively used to deposit titania thin films on various substrates. However, for most of these methods, the deposition temperatures are high which could result in thermal damage to the substrate and induce reactions between the substrate and film during deposition. Moreover, the expensive apparatus used in these techniques increases the cost of fabrication. Most importantly, although high crystallinity titania films have been deposited by these techniques, the photocatalytic activity is limited by the dense morphologies with low surface area. Compared to physical methods, chemical methods offer an attractive alternate route that does not require high vacuum, high temperature or expensive apparatus. Moreover, chemical methods can form various titania architectures with high surface area and crystallinity. Among the chemical methods, the *sol-gel technique* is a traditional approach, which provides flexibility in film nanostructure and composition. *Liquid phase deposition* (LPD), on the other hand, is relatively new and refers to the deposition of thin films directly from an aqueous solution. These two chemical methods are currently considered to be the most effective ways to control the nanostructure and crystallinity of titania.

In practice, porous titania films and membranes are the most favorable morphologies due to their robustness and high surface area. According to the IUPAC definition, porous materials are divided into three categories: microporous with pore diameter < 2 nm, mesoporous with pore diameter in the range of 2~50 nm, and macroporous with pore diameter > 50 nm [44]. In LPD, titania films composed of aperiodic and unstable mesopores can be directly deposited from aqueous solutions without a template. Nevertheless, the ability to control the porous structure in titania, requires skill in using both soft and hard templates during fabrication. In soft templates, evaporation induced self-assembling (EISA) in the sol-gel through block polymer micelle-assisted templating has become a novel approach to tailor the inner structural arrangement of transition metal oxides since the first description of this method for M41S periodic mesoporous silica in the early 1990s [45].

The EISA terminology was first coined by Brinker et al. [46] to encompass all synthesis methods, that lead to ordered hybrid mesophases from dilute solutions upon solvent evaporation. Various three-dimensional ordered mesoporous structures of silica with cubic, hexagonal and lamellar arrangements were successfully synthesized, and this method subsequently applied to tailor porous structures of titania and other materials. Anodized aluminium oxide (AAO) is a hard template for molding titania nanotubes, nanofibers and membranes [47-48]. The diameter of nanofibers and nanotubes can be controlled by the pore diameter in AAO. Interestingly, alumina in AAO can directly react in LPD, to form titania macroporous membranes by the merging of individual tubes. AAO templates can also tailor pore diameter of titania in the macro-range by LPD.

1.2 Objectives

The objectives of this research are to develop, understand and evaluate porous titania in the forms of films and membranes as advanced photocatalysts. Liquid phase deposition (LPD) and sol-gel techniques were employed to fabricate aperiodic and periodic porous titania at low temperature with pore diameter ranging from ~2 nm to ~250 nm. AAO (hard template) and block polymer (soft template) were used to control the porous structure of titania films and membranes. Advanced characterization techniques, such as small angle X-ray diffraction (SAXS), transmission electron microscopy (TEM), and physical adsorption and desorption (ASAP), are used to investigate the pore structure and surface area. Methods to control the chemical processes for fabricating porous titania films and membranes were developed to systematically study the microstructure and crystallinity of porous films. The mechanisms involved in film growth in LPD and hybrid mesophase formation were explored using the Hancock and Sharp model and evaporation induced self-assembling (EISA) respectively.

In this work, the photocatalytic activities of the synthesized films and membranes were evaluated by degradation of methylene orange and methylene blue in aqueous solution.

The optimized combination of crystallinity and surface area in the porous films and membranes for higher photocatalytic activity was established.

1.3 Organization of the Thesis

Following this introductory **Chapter 1**, **Chapter 2** focuses on the deposition and characterization of mesoporous film by LPD without templates. The film morphology, nucleation mechanism and growth kinetics are studied as a function of reaction temperature and reaction time. Finally, the photocatalytic performance is evaluated by considering the crystallinity and surface area. **Chapter 3** discusses the LPD method by using an AAO template as a starting material to synthesize well-ordered macroporous titania membranes with an aperiodic mesoporous anatase matrix, which exhibits photocatalytic properties and filtration function. The reaction mechanism and structure evolution in the membrane are also discussed. **Chapter 4** presents block copolymer template-directed ordered mesoporous titania film formation through an EISA process in a sol-gel. An F127 templated titania film is developed. Firstly, the effects of proton concentration, template content and water availability on crystallinity and mesoporous structure of the titania film are systematically studied after calcination at 400°C. Secondly, to increase the thermal stability of mesoporous structure and crystallinity of the titania film, PS-*b*-PEO block copolymer directed mesoporous film was developed at 600°C, and various nanostructured titania films are also developed by adjusting the composition of the PS-*b*-PEO templated sol-gel system. Thirdly, the photocatalytic activity of the films was also evaluated as a function of crystallinity. Conclusions and recommendations for future work are given in **Chapter 5**.

1.4 References

- [1] T. Lyman (1961). *Metals Handbook, Properties and Applications of Titanium*. Ohio: American Society for Metals (pp. 1147).
- [2] S. Kaneko, K. Tsuru, S. Hayakawa, S. Takemoto, C. Ohtsuki, T. Ozaki, H. Inoue, A. Osaka. (2001). In vivo evaluation of bone-bonding of titanium metal chemically

- treated with a hydrogen peroxide solution containing tantalum chloride, *Biomaterials*, 22, 875.
- [3] C. Ohtsuki, H. Iida, S. Hayakawa, A. Osaka, (1997). Bioactivity of titanium treated with hydrogen peroxide solutions containing metal chlorides, *J. Biomed Mater. Res.*, 35, 39.
 - [4] Y. Ohsaki, N. Masaki, T. Kitamura, Y. Wada, T. Okamoto, T. Sekino, K. Niihara, S. Yanagida, (2005). Dye-sensitized TiO₂ nanotube solar cells: fabrication and electronic characterization, *Chem. Phys.*, 7, 4157.
 - [5] C.G. Granqvist, (2003). Solar energy materials, *Adv. Mater.*, 15, 1789.
 - [6] E. W. McFarland, J. Tang, (2003). A photovoltaic device structure based on internal electron emission, *Nature*, 421, 616.
 - [7] S.Y. Huang, G. Schlichthörl, A. J. Nozik, M. Grätzel, A. J. Frank, (1997). Charge recombination in dye-sensitized nanocrystalline TiO₂ solar cell, *J. Phys. Chem. B*, 101, 2576.
 - [8] T. Nakahira, Y. Inoue, K. Iwasaki, H. Tanigawa, Y. Kouda, S. Iwabuchi, K. Kojima, (1988). Visible light sensitization of platonized TiO₂ photocatalyst by surface-coated polymers derivatized with ruthenium, *Makromol. Chem., Rapid Commun.*, 9, 13.
 - [9] A. Zaban, S. Ferrere, J. Sprague, B.A. Gregg, (1997). pH-dependent redox potential induced in a sensitizing dye by adsorption onto TiO₂, *J. Phys. Chem. B*, 101, 55.
 - [10] C.L. Huisman, A. Goossens, J. Schoonman, (2003). Aerosol synthesis of anatase titanium dioxide nanoparticles for hybrid solar cells, *Chem. Mater.*, 15, 4617.
 - [11] J. Wienke, J.M. Kroon, P.M. Sommeling, R. Kinderman, M. Späth, J. A. M. van Roosmalen, W.C. Sinke, (1997). Effect of TiO₂-electrode properties on the efficiency of nanocrystalline dye-sensitized solar cells, In: *Proceeding of 14th European Photovoltaic Solar Energy Conference*.
 - [12] K. Takagi, T. Makimoto, H. Hiraiwa, T. Negishi, (2004). Photocatalytic, antifogging mirror, *J. Vac. Sci. Technol. A*, 19, 2931.
 - [13] G. Gülsen, M.N. Inci, (2002). Thermal optical properties of TiO₂ films, *Optical Materials*, 18, 373.
 - [14] A.H. Yuwono, B. Liu, J. Xue, J. Wang, H.I. Elim, W. Ji, T.J. White, (2004). Controlling the crystallinity and nonlinear optical properties of transparent TiO₂-PMMA nanohybrids, *J. Mater. Chem.*, 14, 2978.
 - [15] M. Cardona, G. Harbeke, (1965). Optical properties and band structure of wurtzite-type crystals and rutile, *Phys. Rev.*, 137(5A), 1467.
 - [16] S.K. Hazra, S. Basu, (2006). High sensitivity and fast response hydrogen sensor based on electrochemically etched porous titania thin film, *Sens. Actuators, B*, 115, 403.
 - [17] E. György, E. Axente, I.N. Mihailescu, C. Ducu, H. Du, (2006). Doped thin metal oxide films for catalytic gas sensors, *Appl. Surf. Sci.*, 252, 4578.
 - [18] K. D. Benkstein, S. Semancik, (2006). Mesoporous nanoparticle TiO₂ thin films for conductometric gas sensing on microhotplate platforms, *Sens. Actuators, B*, 113, 445.
 - [19] D. Caiteanu, E. György, S. Grigorescu, I.N. Mihailescu, G. Prodan, V. Ciupina, (2006). Growth of oxide thin film for optical gas sensor applications, *Appl. Surf. Sci.*, 252, 4582.
 - [20] W. Lawrence, M.I. Tejedor-Tejedor, M.A. Anderson, (1999). Titanium dioxide-coated silica waveguides for the photocatalytic oxidation of formic acid in water, *Environ. Sci. Technol.*, 33, 2070.
 - [21] M.S. Hamdy, O. Berg, J.C. Jansen, T. Maschmeyer, J.A. Moulijn, G. Mul, (2006). TiO₂ nanoparticles in mesoporous TUD-1: synthesis, characterization and photocatalytic performance in propane oxidation, *Chem. Eur. J.*, 12, 620.

- [22] M. Grätzel, J. Moser, (1983). Multielelectron storage and hydrogen generation with colloidal semiconductors, *Proc. Natl. Acad. Sci. USA*, 80, 3129.
- [23] G. Balasubramanian, D.D. Dionysiou, M.T. Suidan, I. Baudin, J.M. Laine, (2004). Evaluation the activities of immobilized TiO₂ powder films for the photocatalytic degradation of organic contaminants in water, *Appl. Catal., B*, 47, 73.
- [24] H. Kato, A. Kudo, (1998). New tantalate photocatalysts for water decomposition into H₂ and O₂, *Chem. Phys. Lett.*, 295, 487.
- [25] Mineral Data Base Index, University of Colorado, *GEOL 3010 Syllabus*. Available: <http://ruby.colorado.edu/~smyth/min/tio2.html>.
- [26] A. Nakayama, E. Suzuki, T. Ohmori, (2002). Development of high throughput evaluation for photocatalyst thin-film, *Appl. Surf. Sci.*, 189, 260.
- [27] O. Treichel, V. Kirchhoff, (2000). The influence of pulsed magnetron sputtering on topography and crystallinity of TiO₂ films on glass, *Surf. Coat. Technol.*, 123, 268.
- [28] S.H. Kim, Y.L. Choi, Y.S. Song, D.Y. Lee, S.J. Lee, (2002). Influence of sputtering parameters on microstructure and morphology of TiO₂ thin films, *Mater. Lett.*, 57, 343.
- [29] M. Yamagishi, S. Kuriki, P. K. Song, Y. Shigesato, (2003). Thin film TiO₂ photocatalyst deposited by reactive magnetron sputtering, *Thin Solid Films*, 422, 227.
- [30] W. Zhang, T. Li, S. Zhu, F. Wang, (2004). Influence of argon flow rate on TiO₂ photocatalyst film deposited by reactive magnetron sputtering, *Surf. Coat. Technol.*, 182, 192.
- [31] V. Vancoppenolle, P.Y. Jouan, M. Wautelet, J.P. Dauchot, M. Hecq, (1999). D. C. magnetron sputtering deposition of TiO₂ films in argon: oxygen gas mixtures-theory and experiments, *Surf. Coat. Technol.*, 116-119, 933.
- [32] K. Takamura, Y. Abe, K. Sasaki, (2004). Influence of oxygen flow ratio on the oxidation of Ti target and the formation process of TiO₂ films by reactive sputtering, *Vacuum*, 74, 397.
- [33] N. Kaliwoh, J.Y. Zhang, I.W. Boyd, (2002). Characterisation of TiO₂ deposited by photo-induced chemical vapor deposition, *Appl. Surf. Sci.*, 186, 241.
- [34] D. Byun, Y. Jin, B. Kim, J.K. Lee, D. Park, (2000). Photocatalytic TiO₂ deposition by chemical vapor deposition, *J. Hazard. Mater.*, B73, 199.
- [35] T.N. Murakami, Y. Kijitori, N. Kawashima, T. Miyasaka, (2004). Low temperature preparation of mesoporous TiO₂ films for efficient dye-sensitized photoelectrode by chemical vapor deposition combined with UV light irradiation, *J. Photochem. Photobiol., A*, 164, 187.
- [36] M. Kang, J.H. Lee, S.H. Lee, C.H. Chung, K.J. Yoon, K. Ogino, S. Miyata, S.J. Choung, (2003). Preparation of TiO₂ film by the MOCVD method and analysis for decomposition of trichloroethylene using in situ FT-IR spectroscopy, *J. Mol. Catal. A: Chem.*, 193, 273.
- [37] H.Y. Ha, S.W. Nam, T.H. Lim, I.H. Oh, S.A. Hong, (1996). Properties of the TiO₂ membranes prepared by CVD of titanium tetraisopropoxide, *J. Membr. Sci.*, 111, 81.
- [38] V.G. Bessergenev, I.V. Khmelinskii, R.J.F. Pereira, V.V. Krisuk, A.E. Turgambaeva, I.K. Igumenov, (2002). Preparation of TiO₂ films by CVD method and its electrical, structural and optical properties, *Vacuum*, 64, 275.
- [39] T. Oota, I. Yamai, (1984). Vapor phase growth of titania whiskers by hydrolysis of titanium fluoride, *J. Cryst. Growth.*, 66, 262-268.
- [40] G.S. Herman, Y. Gao, (2001). Growth of epitaxial anatase (001) and (101) films, *Thin Solid Films*, 397, 157.
- [41] Y. Gao, S.A. Chambers, (1996). MBE growth and characterization of epitaxial TiO₂ and Nb-doped TiO₂ films, *Mater. Lett.*, 26, 217.

- [42] C.K. Ong, S.J. Wang, (2001). In situ RHEED monitor of the growth of epitaxial anatase TiO₂ thin films, *Appl. Surf. Sci.*, 185, 47.
- [43] D.G. Syarif, A. Miyashita, T. Yamaki, T. Sumita, Y. Choi, H. Itoh, (2002). Preparation of anatase and rutile thin films by controlling oxygen partial pressure”, *Appl. Surf. Sci.*, 193, 287.
- [44] IUPAC Manual of Symbols and Terminology (1972). Appendix 2, Part I, Colloid and Surface Chemistry, *Pure Appl. Chem.* 31, 578.
- [45] J.Y. Ying, C.P. Mehnert, M.S. Wong, (1999). Synthesis and application of supramolecular-templated mesoporous materials, *Angew. Chem. Int. Ed.*, 38, 56.
- [46] G.J. de A.A. Soler-Illia, E.L. Crepaldi, D. Grossso, C. Sanchez, (2003). Block copolymer-templated mesoporous oxide, *Curr. Opin. Colloid. Interface. Sci.*, 8, 109-126.
- [47] A.M. Michailowski, D. AIMawlawi, G.S. Cheng, M. Moskovits, (2001). Highly regular anatase nanotubule arrays fabricated in porous anodic templates, *Chemical Physics Letters*, 349, 1.
- [48] M.S. Sander, M.J. Côté, W. Gu, B.M. Kile, C.P. Tripp, (2004). Template-assisted fabrication of dense, aligned arrays of titania nanotubes with eell-controlled dimension on substrate, *Adv. Mater.*, 16(22), 2052.

CHAPTER 2

LIQUID PHASE DEPOSITED TITANIA FILMS

In this chapter, the deposition of titania films by a chemical method, liquid phase deposition (LPD), are studied. First of all, a fundamental review on the current state of the liquid phase deposited titania film and powder at low temperature was performed. After that, the mechanisms of titania film nucleation on glass and film growth kinetics were studied at 50°C. In order to increase film crystallinity, the reaction temperature was increased from 50°C to 100°C and 200°C by a hydrothermal process. Meanwhile, film growth kinetics and microstructure evaluation indicating film surface area, morphology and grain orientation, and crystallinity were studied at higher temperatures. It was observed that when film crystallinities between 60 and 90%, the photocatalytic activity is significantly affected by the surface area.

2.1 State of the Art

2.1.1 Hydrothermal and Liquid Phase Deposition

Traditionally, chemical methods refer to the synthesis of oxide thin films hydrolyzed from aqueous solutions of metal salts. However, the term “liquid phase deposition (LPD)” refers to the formation of oxide films from an aqueous solution of a metal-fluoro complex $[MF_n]^{m-n}$ (M stands for metal atom) which is slowly hydrolyzed by the addition of water, boric acid or alumina metal [1]. The addition of water induces precipitation of the oxide, while boric acid, aluminium or alumina acts as a fluoride scavenger, which destabilizes the fluoro-complex and forces the oxide precipitation. Oxides cannot continuously precipitate if

such a catalyst is absent from the reaction. The mechanisms of the LPD are based on the overall equilibrium equation,

LPD is a relatively new method since it was first reported as a new process for producing silica coatings in 1988. It was used to deposit titania films for the first time in 1995 [2]. Since then, it has been used extensively to grow amorphous or crystalline titania on a variety of substrates at temperatures of 60°C or below [3-6]. The low deposition temperature is of great advantage as it allows the use of temperature sensitive substrates such as polymers. Titania can therefore bond to specific functionalities on the substrate surface by a heterogeneous nucleation process. Another important advantage is that irregular and porous bodies can be coated evenly as deposition by LPD is not a line-of-sight process.

However, as a photocatalyst, the crystallinity of liquid phase deposited titania film is found to be low which limits its photocatalytic performance. Compared with post heat treatment, a hydrothermal route is more attractive since it increases crystallinity of the titania film at a relatively low temperature and does not damage the substrate. The advantages of hydrothermal route synthesized titania include: simple experimental setup, strong adherence between substrates and films, versatile morphologies of titania particles [7-11], and also formation of various polymorphs of titania at low temperatures [12, 13]. For example, rutile is usually crystallized from anatase by annealing above 700°C, but it can also be directly deposited from TiO_4^{2-} solutions hydrothermally at 140°C [14]. Up to now, anatase, rutile and brookite phases of titania have been successfully deposited under different hydrothermal condition from TiO_4^{2-} , TiCl_4 and TiF_6^{2-} aqueous solutions [15-18].

Film crystallinity in LPD titania can be improved by increasing the hydrothermal reaction temperature.

2.1.2 Titania Formation Mechanism in LPD

Homogeneous nucleation. In LPD, ammonium hexafluoridтитania (AHFT) and boric acid are used as the titania precursor and F^- scavenger, respectively. The formation mechanism of the titanium dioxide in LPD can be simplified as:

According to equation (2.2), AHFT first hydrolyses in water. After equilibration, boric acid decreases the F^- concentration in the solution by the formation of BF_4^- and forces equation (2.2) to the right side through equation (2.3) [19].

Subsequently, titania precipitates from the hydrolysis of the Ti-centered $TiF_{6-n}(OH)_n^{2-}$ octahedral complexes. It is well accepted that both anatase and rutile phases are generated from edge-sharing of $TiF_{6-n}(OH)_n^{2-}$ octahedra. During the formation of original nuclei, liner chains can only form through sharing equatorial edges, which can result in the rutile phase through TiO_6 chains linked to each other via corner connection. However, the edges of $TiF_{6-n}(OH)_n^{2-}$ are not actually identical due to the relatively stable Ti-F bond. As a result, zigzag chains, create anatase-type nuclei, with octahedra linked by edge-sharing [20-22]. In summary, the Ti-F bonds indirectly control anatase phase formation in LPD.

Heterogeneous nucleation. Titania films can grow on various substrates through heterogeneous nucleation. The stepwise hydrolysis of the precursor produces six-coordinated complexes of the type $TiF_{6-n}(OH)_n^{2-}$ that are not analogous to TiF_4 and $TiCl_4$ (they are reacted to four co-ordinates). Many factors, such as the functionalities on the substrate surface and pH value of solution, control the initial bonding between the titania and substrate in heterogeneous nucleation. In previous studies, film nucleation behavior was

Figure 2-1 (A) Heterogeneous nucleation on the surface of glass/modified polystyrene by titania colloidal assembling. (B) Heterogeneous nucleation on the surface of glass/silicon by chemical bonding [31, 37].

investigated on various functional groups such as amino, sulphonate, methyl and hydroxyl in the solutions with different pH values [23-37]. It was observed that heterogeneous nucleation of the titania film was mainly generated by assembly of titania colloids (Fig. 2-1 A) [31] and chemical bonding with the functional groups (Fig. 2-1 B) [37]. In the titania colloidal assembling mechanism, an electrical attractive force between the titania colloidal surfaces and functional groups was generated by adjusting the pH of the solution, which controls the charges on titania colloidal surfaces in the solution. This allows the positively/negatively charged titania colloids to attach to functional groups with opposite charge on the substrate surface. Micro-patterning of anatase thin films on substrates with different functional groups was successfully applied to control the colloidal assembly during heterogeneous nucleation [31-36].

However, heterogeneous nucleation through chemical bonding at the glass surface takes place at varying pH as shown by equations (2.4) and (2.5). When $\text{pH} > 2$, the heterogeneous nucleation is Ti-O-Si bonding through nucleophilic attachment between the

Ti-centered complex and $\equiv \text{Si}-\text{O}^-$ on the glass surface. When $\text{pH} < 2$, the nucleation is a condensation reaction between the two hydroxyl groups, $\equiv \text{Si}-\text{OH}$ and $\text{OH}-\text{Ti}$. Nevertheless, hydrolysis of AHFT in the solution results in enrichment of H^+ locally on the substrate surface, which produces the condensation reaction in equation (2.5) (Fig. 2-1 B), such as epitaxial growth of titania on Si (100) surfaces. Earlier studies suggested that these mechanisms would operate when there are hydroxyl groups on glass, silica or silicon substrate, rather than colloidal assembly as proposed by Masuda et al. [39].

After the initial attachment of Ti by Ti-O-Si bonding, the heterogeneous nucleations from nucleation sites start to form titania islands, which later coalesce into a titania layer on the glass substrate. A film grows on this titania layer through hydrolysis and condensation of the $\text{TiF}_{6-n}(\text{OH})_n^{2-}$ in the solution.

Titania precipitation by LPD. The *concentrations* of precursors were first studied for the precipitation of pure anatase by LPD in 1996 (Fig. 2-2) [2]. The phase diagram, as a function of precursor concentration, indicates that the concentrations of AHFT and boric

Figure 2-2 Titania precipitation diagram in LPD [2].

acid in the solution were important for pure anatase phase formation. First, as a catalyst ensures the precipitation, the concentration of boric acid should be above 0.1 M. Higher boric acid concentrations in this range was proved to accelerate titania precipitation. However, it was also noted to limit the film nucleation speed on the glass surface [9, 19]. Second, pure anatase phase only precipitates within the range of the molar ratio of $\text{Ti}^{4+}/\text{B}^{3-}$ 0.2 to 2.

The *supersaturation* of the solution is an important factor in precipitation. Excessively high supersaturation typically leads to heavy bulk precipitation and stops film nucleation and growth. However, the effect of supersaturation on film growth kinetics was not clear until now. As the degree of supersaturation decreases with titania formation, the film and powder growth mechanisms may also change due to lower supersaturation. This part will be discussed in detail in sections 2.3.2 and 2.3.3.

The *pH* value of the reaction solution plays an important role in determining the crystal phases, precipitation rate and degree of supersaturation. According to reaction (2.2), a lower pH inhibits ligand exchange between F^- and OH^- because fewer hydroxyl groups are available in the solution, inhibiting the initial hydrolysis of AHFT [39]. In other studies of titania deposited from aqueous solution, pH also controls the crystallographic forms of titania. For example, in hydrolysis of TiOSO_4 , the anatase phase was precipitated at a relatively high pH, while the rutile phase appeared only at a relatively low pH value [40-41]. Nevertheless, in LPD, no other titania phases have been reported through the adjustment of the pH of the reaction solution.

It is well accepted that *reaction temperature* influences chemical reaction rate, crystallization and the total yield of precipitation. So far, films have been deposited by LPD at room temperature or 60°C. A traditional method of synthesizing titania with high crystallinity and various morphologies is hydrothermally from aqueous solution [42-44], and recently, was applied with sol-gel processing to synthesize high crystallinity titania

nanocrystallines [45-48]. However, this work is the first to the increase reaction temperature to above 100°C in LPD by hydrothermal method, in which the film and powder morphology, microstructure, crystallinity and performance are systematically studied.

2.1.3 Microstructure of Titania Films by LPD

Film morphologies. The columnar morphology of an anatase film grown by LPD at low temperature consists of titania nanocrystallines (Fig. 2-3 A, B). However, it was reported that there were pores between these anatase nanocrystallines which resulted in film cracking due to capillary forces when the liquid came out of the pores during drying. Such as cracking was also observed in films deposited from TiCl_4 aqueous solution (Fig. 2-3 C, D). The surface of liquid phase deposited films was quite smooth, but the particles from the solution were observed to be embedded in the film surface.

Film orientation. The orientation of the films was studied by the Lotgering factor (L) calculated from the X-ray diffraction pattern. High c -axis orientation in the film was

Figure 2-3 Titania film morphologies and cracking (A) (B) deposited by LPD on glass (C) (D) deposited from TiCl_4 aqueous solution on glass surface (E) (F) deposited from TiOSO_4 aqueous solution on glass surface [39, 40, 48].

observed in the aqueous solution deposition with F^- , SO_4^{2-} and Cl^- . As we know, the crystal plane with the lowest Gibbs free energy will grow preferentially. This would be plausible if the (001) surface of an anatase crystal possesses the lowest Gibbs free energy compared to other crystallographic surfaces. However, it is noted that the (110) plane has the lowest Gibbs free energy: that is, the preferred orientation should be (110) providing there are no other significant influences on atomic diffusion. However, the preferred orientation is affected more by thermodynamic factors. Preferential adsorption of ionic or polymeric species from the solution onto certain crystallographic faces can induce anisotropic growth. The film will have an oriented fiber structure if crystals grow anisotropically, which was observed in the titania powder structure synthesized from aqueous solution [39, 48].

As (001) orientation was observed to exhibit a columnar structure (Fig. 2-3), the degree of orientation could also be affected by the nucleation density on the substrate. It was noted that a higher degree of orientation in the films was observed on surfaces with denser nucleation sites [3]. The initial non-oriented nucleation was identical on a substrate until

Figure 2-4 Degree of orientation model deposited from low, medium and high densities of nucleation sites [3]

two islands were in contact and terminated the horizontal growth, where further material deposition from the supersaturated solution could only advance vertically (Fig. 2-4).

2.1.4 Surface Area Characterisation

The pore size distribution, surface area and porosity can be analyzed by characterization of nitrogen adsorption and desorption on mesoporous materials. Most analysis of adsorption equilibrium begins with classification of the isotherms. This classification is important in theoretical modeling of adsorption phenomena. As an illustration, consider surface area measurements using the BET method. There are international standards and a number of commercial devices for using this method in different applications. However, according to the IUPAC, the first step is “to identify the isotherm type” and hence the nature of the adsorption process. The modern version of IUPAC classification scheme has six types of isotherms for gas-solid equilibria (Fig. 2-5), that are based on an earlier classification by Brunauer, which had five standard types of isotherms [49].

Figure 2-5 The IUPAC classification N_2 adsorption and desorption isotherms for gas-solid equilibria [49]

The type I isotherm ‘approaches a limiting value’ and usually is used to describe adsorption on microporous adsorbents. Types II and III describe adsorption on macroporous adsorbents with strong and weak adsorbate-adsorbent interactions respectively. Types IV and V represent monolayer and multilayer adsorption related to capillary condensation, which refer to mesoporous structure. Type VI, which was not included in the Brunauer classification, indicates those adsorption isotherms with one or more steps. The characteristic shape of a Type IV isotherm is the result of surface coverage of the mesopore walls followed by pore filling. The onset of capillary condensation (the pore filling process) is indicated by an upward departure of the isotherm from the multilayer Type II isotherm for the same gas-solid system. The plateau at higher P/P_0 is attained when the mesopore filling is complete.

To determine the size of mesopore, it is necessarily assumed that the meniscus curvature is simply related to the pore shape and size. To obtain the mesopore volume from the amount adsorbed at the plateau, the condensate is assumed to have the same density as the liquid adsorptive at the operational temperature. It is of great advantage to have independent information on the pore shape and connectivity, but the size and shape of the loop itself can also give a useful indication of the predominant pore filling-emptying mechanisms. Thus, a narrow Type I hysteresis loop, with almost vertical and parallel branches, is generally associated with delayed condensation and very little percolation hold-up; whereas a much broader Type II hysteresis loop with a very steep desorption branch has the typical features associated with network-percolation [50].

The scientists in *Mobil Composition of Mater.* synthesized ordered mesoporous silica by hydrothermal method using cationic surfactant in 1992 for the first time, and the materials were labeled as MCM-41. The pore structure of MCM-41 is in the form of 2-dimensional hexagonal cylinder of uniform tubular channels of controlled width. The absorption analysis is shown in Fig. 2-6. The traditional method for analyzing pore-size

distributions in the mesopore range is the Barrett–Joyner–Halenda (BJH) method which is based on the Kelvin equation. Capillary condensation-evaporation of nitrogen at 77 K occurs over the narrow range of P/P_0 of 0.41-0.46. By applying the Kelvin equation and correcting for multilayer thickness, pore diameters of 3.3-4.3 nm is obtained, which agrees well with a mean value of approximately 4 nm derived from the volume-surface ratio. Moreover, the theoretical basis for the BJH analysis becomes fairly weak if the step for N_2 at 77 K lies below $P/P_0=0.42$, because this is considered to be the stability limit of the meniscus [51-54].

Figure 2-6 Nitrogen adsorption-desorption isotherm plots of the large-pore MCM-41. The inset is the pore size distribution curve from adsorption [52].

2.1.5 Photocatalytic Activity Principles

In 1972, Fujishima and Honda [55] discovered the photocatalytic splitting of water on titania electrodes. This event has marked the beginning of a new era in heterogeneous photocatalysis. Since then, understanding the process and enhancing the photocatalytic

Figure 2-7 Schematic drawing of photocatalytic events [55]

efficiency of titania have been extensively studied by chemists, physicists and chemical engineers. Such properties of titania have also become the performance indicators of the material.

Mechanism. In a heterogeneous photocatalysis system, photon-induced molecular transformations or reactions take place at the surface of a catalyst, when there is a void energy region with no energy level available to promote recombination of an electron and a hole produced by photon activation in the solid. The void region which extends from the top of the filled valence band to the bottom of the vacant conduction band is called the band gap. Once excitation occurs across the band gap, the lifetime must be in the nanosecond regime to promote chemical reaction. The initial photocatalysis process in semiconductors is the generation of electron-hole pairs in the semiconductor particles. The excitation of an electron from the valence band to the conduction band is initiated by light absorption with energy equal to, or greater than, the band gap of the semiconductor (Fig. 2-7). The surface of the semiconductor can donate electrons to reduce an electron acceptor, such as oxygen in an aerated solution (Fig. 2-7 path c); in turn, a hole can migrate to the surface with an

electron from a donor species, such as hydrogen (Fig. 2-7 path d). In competition with charge transfer to adsorbed species is the electron and hole recombination. Recombination of the separated electron and hole can occur in the volume of the semiconductor particles or on the surface with the release of heat (Fig. 2-7 path a and b).

Hydrogen generation. The formation of $\text{HO}_2^\cdot$, $\cdot\text{O}^-$, $\cdot\text{O}_2^{3-}$ and $\cdot\text{OH}$ radicals were observed on titania surfaces under ultraviolet irradiation [56]. The hydrogen generation by photodecomposition of water in the water-titania system remains a controversial issue because H_2O cannot be photon decomposed on clean titania surfaces. Hence, a micro-photoelectrochemical cell is necessary to guide the photon-induced electrons and holes to the external circuit Pt or RuO_2 cathode and anode. Another way is to use sacrificial species to remove one of the decomposed products, so that the reaction equilibrium shifts to further decomposition. For example, with the addition of CH_3OH in aqueous titania, H_2 was observed to release while CH_3OH oxidizes to CO_2 .

Photo-oxidation at the liquid-solid interface. Titania photocatalysis is mainly used for treatment of polluted waters by photo-oxidation of organics. The primary event of photo-oxidation at the liquid-solid interface is a fundamental process in heterogeneous photocatalysis of titania, as shown in equation (2.6), where h_{vb}^+ and e_{cb}^- represent the holes and electrons, respectively. In many aqueous processes, the trapped holes react with surface hydroxyl groups ($\text{H}_2\text{O}_{\text{ads}}$) to produce hydroxyl radicals ($\cdot\text{OH}_{\text{ads}}$) which are strongly oxidizing as shown in equations (2.7) and (2.8). The chemical identification of hydroxylated oxidation intermediates and the ESR detection of hydroxyl radicals provide good evidence for the occurrence of this process.

2.1.6 Pseudo-First-order Kinetics of Dye Decomposition

Although the removal of vinyl chloride gas phase has been used to study the photocatalytic performance of titania, in most cases, the photocatalytic activity of titania was usually evaluated by the decomposition of organics in aqueous solution such as methylene blue (MB), methylene orange (MO), 4-chlorophenol, 4-nitrophenol, acetone, malonic and p-coumaric acid [57-67]. In this work, degradation of methylene orange dye by a liquid phase deposited titania film was studied.

The kinetics of photodegradation of organic dyes by titania is well suited to a pseudo-first-order model as shown in equation (2.9) when the organic dye concentration is low, and where C and C_0 are the concentrations of organic dye at time t and zero, respectively. k is the **apparent rate constant** that evaluates the photocatalytic efficiency in this model [68-73].

$$\ln(C/C_0) = kt \quad (2.9)$$

2.1.7 Influences of Titania Properties on its Photocatalytic Activity

Phase Content. Two different crystal structures of titania, rutile and anatase, are commonly used as photocatalysts, with anatase showing a higher photocatalytic activity. Differences in crystal structures cause different densities and electronic band gaps between the two forms of titania. It is generally accepted that anatase is more active than rutile in photocatalysis and photo electrochemical reactions, which is attributed to the Fermi level of anatase being higher than that of rutile by about 0.1eV. Additionally, differences in the extent of surface hydroxylation of the solid may also contribute to the differences in their activity [74].

However, titania containing anatase and rutile phase in a ratio of about 3:1 shows the best performance of photocatalytic activity, such as Degussa P-25, a standard material in the field of photocatalytic reaction. The higher photocatalytic activity is attributed to the interaction of rutile and anatase particles in photo-oxidation and the pores between the rutile and anatase crystalline [75-78].

Crystallinity and crystalline size. The photocatalytic activities of titania increase significantly with the decrease of amorphous content. On the other hand, the completely crystallized titania nanoparticles exhibit a size effect in photocatalytic reaction; because the shift of band gap is inversely proportional to the diameter of particle by $1/R^2$. It is also noted that the shift of the band gap of rutile is much higher than that of anatase [79, 80].

Surface area. Titania photocatalytic reactions take place at the crystallite surfaces. Hence, the surface area which the organic dye can access becomes very important for the photocatalytic performance. Generally, morphologies, crystallite size and nanostructure greatly influence the surface area of titania. Both high surface areas and high crystallinity are important for achieving good photocatalytic activity. Researchers commonly subject the films to post deposition heat treatments of 200°C and higher to improve crystallinity. However, these heat treatments inevitably decrease the surface area and limit the choice of substrates. In this work, various porous structured titania films were fabricated by chemical methods, with the photocatalytic activity of porous titania evaluated with consideration of the effects from surface area and crystallinity.

It is also noted that photocatalytic activity is related to photocatalysis experimental processes such as the type of dye used in experiment, the concentration or content of dye, the amount of photocatalyst, pH of the solution, oxygen supply and also UV light intensity [81-85]. So, in our comparison of the titania photocatalytic properties with other published work, these factors are normalized to identical conditions.

2.2 Experimental Procedure

2.2.1 Film Formation

Titania films were grown on glass microscope slides supported by an annular Teflon holder sealed in a Teflon-lined acid digestion bomb (Parr). The substrates were cleaned with Piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2=1:4$) at 100°C for 15 minutes followed by rinsing in deionised water. The precursor solution was prepared by dissolving ammonium hexafluorotitanate ($(\text{NH}_4)_2\text{TiF}_6$, AHFT) in 0.2 M boric acid (H_3BO_3) to a concentration of 0.1 M and a pH of 3.94. This solution (25 ml) was added to the bomb and heated at 50°C , 80°C , 100°C , 150°C and 200°C , for periods ranging from 15 minutes to 12 hours (Fig. 2-8). The temperature inside the bomb was measured by a thermometer. When the reaction was completed, the bomb was cooled by natural convection to room temperature and the films rinsed with deionised water before drying at 50°C for 24 hours in an oven or by vacuum. Baseline materials were prepared as powders, using the same reaction, with the product collected by centrifugation and oven dried.

Figure 2-8 Flowchart of experimental procedure

2.2.2 Characterization

Film morphology was examined by secondary electron imaging (SEI) using a field emission scanning electron microscope (SEM, JEOL JSM 6300F, Japan), together with reflection optical and atomic force microscopy (Multimode-Digital Instruments DI3000, Santa Barbara, CA). Texture was investigated by powder X-ray diffraction (XRD, Rigaku Dmax 2200) using CuK α radiation (40 kV, 40 mA) and a scan speed of 0.045°/min in θ -2 θ mode. The divergence, anti-scatter and receiving slits were fixed at 0.5°. Crystallographic characterization of the small quantities of film removed from the substrates was accomplished using a Bruker D8 GADDS diffractometer, with data collected in transmission mode from material loaded in a glass capillary. Transmission electron microscopy (TEM) was performed using a Jeol JEM 2010 electron microscope operating at 200 kV. Before TEM, the films were removed from the substrates, suspended in deionised water, and then deposited on holey carbon-coated copper grids. Nitrogen adsorption and desorption isotherms were collected at 77K using an Accelerated Surface Area and Porosimetry System (ASAP 2010 system) after the titania powders were vacuum dried at 100°C for 12 h to remove surface moisture. The pore size distribution was calculated from the nitrogen adsorption isotherm using the Barrett-Joyner-Halenda (BJH) method. The presence of protons in the powders was also determined by Fourier transformed infrared (FTIR) spectroscopy (Spectrum 2000, Perkin Elmer). Powders were diluted to about 1 wt% with KBr that had previously been heated at 100°C for at least 12 hours to remove excess surface water before analysis in dry nitrogen. Each spectrum collected (400-4000cm⁻¹) was the average of 32 measurements at 4 cm⁻¹ resolution. Thermogravimetric analysis (TGA7, Perkin Elmer) was carried out to quantify the total water content of the powders by heating at 20°C/min to 900°C in a dry nitrogen atmosphere. To identify the components evolved from the powder during the heating process in TGA, the Fourier transformed infrared

(FTIR) spectroscopy (Spectrum 2000, Perkin Elmer) was used to analyze the gas component.

The average crystallite size of the titania powder can be calculated from the XRD pattern of the film according to Scherrer equation (2.10) using (101) plane. The crystallite size of the film was calculated from (004) plane because the (101) plane was covered by the reflection of amorphous glass substrate. Where T_A is the average crystallite size (Å) for phase A, B is the full width at half maximum of the peak.

$$T_A = \frac{0.9\lambda}{B\cos\theta} \quad (2.10)$$

The crystallinity of the precipitated powder was determined by powder X-ray diffraction (XRD) patterns collected from $2\theta = 10$ to 80° in increments of 0.02° and a scan rate of $0.045^\circ/\text{min}$, with a Rigaku Dmax 2200 employing Cu $K\alpha$ radiation. Each sample was mixed with 20 wt% of powdered standard alumina with 100% crystallinity. Structure refinements were then performed using the Rietveld method [86]. By comparing the weight percentage of the alumina, X, determined from the Rietveld scale factors with the known proportion (20 wt%), the amorphous material, W_0 wt%, in the mixture can be determined as:

$$W_0 = 1 - \frac{20\%}{X} \quad (2.11)$$

And conversely, the percentage crystallinity of the TiO_2 material, W wt%, can be expressed as:

$$W = 1 - \frac{80\%}{W_0} \quad (2.12)$$

It is assumed that the crystallinity of the film is the same as that of the powder precipitated in the reaction solution. It is reasonable because the amorphous glass substrates should not influence the crystallization of the titania film. It is also evident that films (78%) deposited at 80°C for 5 hours and the powder precipitate (79%) have almost the same

crystallinity, with the crystallinity of the film was determined by scratching film from the glass substrate.

2.2.3 Photocatalytic Testing

The photocatalytic activities of the selected titania films were evaluated by monitoring the degradation of methylene orange as a function of time. Methylene orange (MO) has two desirable features for these studies. Firstly, it has a high visible wavelength extinction coefficient, which allows the use of low concentrations that are linearly related to the adsorption intensity at 463 nm ($C=0.2619 \times 10^{-5}$ I, Appendix I). The concentration of methylene orange remaining after each experiment was determined with a UV-Vis-NIR scanning spectrophotometer (Shimadzu UV-3101PC). Secondly, methylene orange has reasonable transparency to the band of UV light most often used for irradiation of titania photocatalytic tests.

Figure 2-9 Experimental setup in photocatalytic test

Large amount of titania particles precipitated in the solution are embedded in the upper side of substrate through gravity forces because the substrate was suspended in the solution. The film morphology on upper side of substrate is far from pure titania film, but most likely is the stack of powder. Hence, before photocatalysis, the film and powder on the upper side of the glass was removed by KOH solution (11 M). Four pieces of film with a geometrical surface area of 9.68 cm^2 were placed in a glass container (98% UV transparency) containing 15 ml $1 \times 10^{-5} \text{ M}$ methylene orange that was irradiated in a UV reaction chamber (RPR-100) where the light intensity of 365 nm at the center of the glass container was $213 \mu\text{W}/\text{cm}^2$ (Fig. 2-9).

2.3 Film Growth Kinetics

2.3.1 Film Nucleation

The stepwise hydrolysis of the $(\text{NH}_4)_2\text{TiF}_6$ precursor produced six-coordinated complexes of the type $[\text{TiF}_{6-x}(\text{OH})_x]^{2-}$ complex. This is followed by heterogeneous nucleation of titania on the glass surface that is initiated by the formation of Si-O-Ti linkages. In this study, the pH of 3.94 was above the isoelectric point of the glass substrate (pH=2) as reported by Yang and Zeng [37]. Hence, the linkages of titania with glass substrate in LPD form through the nucleophilic attachment of the Ti atom in the $[\text{TiF}_{6-x}(\text{OH})_x]^{2-}$ complex with $\equiv \text{Si-O-}$ on the glass surface as in equation (2.4).

After the initial nucleation on the substrate, hemispherical islands form, grow and coalesce to form a continuous film as previously observed for growth from TiF_4 -based precursors [41]. The diameter of the islands range from ~ 20 to $\sim 85 \text{ nm}$. The wide size distribution is indicative of an on-going nucleation process (Fig. 2-10). The number of nucleation sites (islands) initially increases and then decreases at the later coalescence stage. When the temperature of the solution was increased to $\geq 50^\circ\text{C}$, coalescence was completed. Thus, three stages of film coverage can be identified - nucleation, growth and

coalescence, during which removal of titania from the solution gradually reduces the supersaturation.

Table 2-1 Island number / μm^2 on the surface of glass

Reaction Temperature Reaction Time	Maximum Islands Number (number)	Powder weight (mg/25ml solution)
50°C 60 minutes	~36.3	~0.1
80 °C 30 minutes	~34.6	~0.1
100°C 25 minutes	~24.0	~0.1
150 °C 15 minutes	~18.3	~21.5
200 °C 12 minutes	~16.5	~54.5

It was expected that with hydrolysis and dehydration of the precursor occurring faster at higher temperatures, the island density would correspondingly be greater and the film should have coalesced at thinner thickness. Nevertheless, the film thickness at coalescence was not significantly different for all oven temperatures (216 nm at 50°C, 208 nm at 100°C and 194 nm at 200°C). It can be explained that, at the same time, the titania powder formed in the reaction solution. The supersaturated solution gives rise to two kinds of nucleation - heterogeneous and homogeneous. The reaction rate in solution is rapid at higher temperatures, while heterogeneous nucleation becomes slower, as homogeneous nucleation reduces the concentration of titania complexes available for chemical reactions on substrate surface. This interpretation was supported by the observation that no nucleation and growth occurred when the substrate was immersed in a solution pre-heated at 200°C (oven temperature) for 15 minutes. However, films did develop on substrates introduced to the solution at pre-heated at 200°C (oven temperature) for 10 minutes. This is due to the fact that homogeneous precipitation had caused the supersaturation to drop to a level that drove resolubilization of the deposits. Therefore, the maximum numbers of islands appeared after short immersion at 50°C rather than 200°C (Table 2-1). The increasing weight of the precipitated powder in suspension accompanies the decreasing density of the nucleation islands on the substrate in the nucleation stage. This indicates that the competition of the

Figure 2-10 Secondary electron micrographs of titania islands on the glass surface at each temperature.

(temperatures in the bracket indicate the solution temperature in bomb. The scale bar is 1 μm)
 heterogeneous and homogeneous nucleation is operative through the influences on supersaturation in the film nucleation stage [87, 88].

Figure 2-11 (A) Film thickness and powder weight by LPD at 50°C (B) Empirical fitting on film thickness

2.3.2 Film Growth Kinetics at 50°C

Hancock & Sharp model. In order to develop a deeper understanding of the film growth mechanisms in operation, a kinetic analysis employing the Hancock and Sharp method was performed. This isothermal transformation process was analyzed by the Johnson-Mehl-Avrami [88] equation modified by Hancock and Sharp [89], which was established by assuming the formation of the nucleation sites in a uniform mixture of

reagents from which crystal growth occurs. This method has been applied to model kinetic data from a variety of hydrothermal powder precipitation reactions, but to the our knowledge, this is the first application to the formation of titania films by solution deposition. The Hancock and Sharp treatment plots the extent of the reaction, f , for a given temperature, against the reaction time, t , according to equation (2.13).

$$\ln[-\ln(1-f)] = \ln r + m \ln t \quad (2.13)$$

In this description, f is the fraction crystallized isothermally and scaled from zero at the onset of the reaction to unity at its conclusion, with r a constant relating to nucleation frequency, and m is a system constant that can vary according to the geometry of the system, called the Avrami exponent. Generally, nucleation and growth kinetics give rise to approximately linear plots of $\ln[-\ln(1-f)]$ against $\ln t$ over the range of $0.15 < f < 0.50$. The slopes of such plots are diagnostic of the three reaction kinetic groups. When $m=0.54\sim 0.62$, growth is slow and diffusion-controlled kinetics becomes the rate limiting step, while for $m= 1.0\sim 1.24$, a faster phase-boundary-controlled reaction is indicated, and $m= 2\sim 3$ is indicative of a rapid continuous nucleation and growth which obey the Avrami-Erofe'ev equation [89-93].

Film growth kinetics at 50°C in LPD. As the temperature in the reaction bath takes about 90 to 120 minutes to reach the pre-set oven temperature, only film growth at the 50°C oven temperature had sufficient data points for the kinetic analysis. In addition, the 'induction time' was taken as 120 minutes (at which time the extent of the reaction, f , is taken zero) as the film coalesces around this time and any subsequent film thickness increase would be representative of an increase of the total film volume. The increase in film thickness from 120 minutes onwards was taken to represent the extent of the reaction, which would be zero at $t = 120$ minutes. As shown in Fig. 2-11, a simple empirical curve fit of the film growth curve at 50°C indicates that the film thickness saturates at 2300 nm, and this is taken as reaction extent = 1, because it could be observed that precipitation (film

growth and powder weight) is gradually saturated with reaction time (Fig. 2-11); f was calculated by taking into account the increasing thickness of the product layer [94].

Figure 2-12 Sharp-Hancock plots for the film growth at 50°C

The resultant Hancock and Sharp plot for film growth at 50°C is shown in Fig. 2-12. Interestingly, it shows a transition in the rate limiting step at 9~10 hours. This corresponds to the earlier observations in section 2.3.1 of decreased supersaturation no longer being able to sustain film nucleation on fresh glass substrates and also SEM of the film cross section (Fig. 2-13) showing a change to a more pronounced columnar structure. Before the transition, m has a value of 1.06 while after the transition, $m=0.55$. This indicates that film growth before the transition, m_1 , was controlled by a reaction at the phase boundary (i.e. between the growing titania film surface and the reaction bath). Presumably the dehydration of the $\text{Ti}(\text{OH})_4$ species to form titania is required for continuous nucleation and growth at this stage. Film growth after the transition, m_2 , is diffusion-controlled; that is, diffusion of

the precursor species to the advancing titania film surface is controlling the rate of columnar growth.

Figure 2-13 Cross-section of liquid phase deposited film and powder at 50°C (a) powder for 17 h (b) film deposited for 216 h.
(||||| diffusion-controlled grain growth; ▨ phase boundary controlled continuous nucleation)

In the phase-boundary-controlled kinetics, continuous nucleation on the titania layer was most likely to form the nuclei at the liquid-solid (titania-solution) interface [95-99]. This non-classical nucleation and growth mechanism for precipitation was also reported by Rossetti et al. [100]. In the early study of solid-state reaction, Gardner et. al. [101] obtained Avrami exponent $m=1.05\pm0.8$, which described the phase-boundary-controlled kinetics of silica reduction in hydrogen. Recently, this equation has been applied to investigate hydrothermal reaction kinetics corroborated by microstructural evidences. Walton et al. [102] successfully diagnosed phase-boundary-controlled kinetic ($m=1$) on hydrothermal crystallization of BaTiO_3 .

The Avrami exponent in the second stage belongs to the diffusion-controlled reaction where the growth unit is incorporated into the structure through diffusion [103-105]. Hence, grain growth by diffusion-controlled kinetics was supposed to operate after 9 h of reaction

(film thickness ~ 900 nm), which also can be evident by the elongated columnar grain structure in the powder and film (Fig. 2-13).

However, not all Avrami exponents calculated in liquid phase reactions can be identified to respective kinetics behind. The abnormal Avrami exponent m (8.83 and 5.11) in crystallization of perovskite lead titania in hydrothermal reaction was indicative of a competing process. Later, Moon et. al. [106] explained the abnormal Avrami exponent m ($m=0.7$) in the second region in the hydrothermal synthesis of BaTiO_3 as a dissolution and precipitation mechanism in accord with the solid state nature of the transformation.

2.3.3 Film Growth Kinetics at Higher Temperature

According to the previous analysis, titania growth kinetics may be identified by the morphologies observed at higher reaction temperatures, with both film and powder cross-sections produced at 50°C , 100°C , and 200°C showing distinct layer structures (Fig. 2-14). The bottommost film layer and inner shells of the powders consist of randomly packed acicular particles. This layer type is thickest at lower deposition temperatures (~ 920 nm at 50°C , ~ 350 nm at 100°C and ~ 200 nm at 200°C). Covering this layer in both film and powder is a distinct columnar structure. Decreasing supersaturation by raising the solution temperature will promote more rapid grain growth, and the formation of thicker columnar structures.

Supersaturation of the solution has been reported to have great influence on the kinetics and association to the precipitated particle morphology [107]. The precipitation rate of the film was relatively fast from highly saturated solution and the particles tended to grow into an isotropic shape. Consequently, the bottom layer of the film was governed by the continuous nucleation consisting of acicular particles formed by phase-boundary-controlled kinetics, but still faceted by (001) slowest growing plane, which later produced the texture in the film.

As the reaction proceeded, the degree of supersaturation decreased to a level below that sustaining continuous nucleation, and diffusion-controlled grain growth became dominant. In conclusion, heterogeneous and continuous nucleation will be dominant when the solution is highly supersaturated; at lower supersaturation, grain growth, rather than nucleation, will control the film structure.

Figure 2-14 Cross-section secondary electron micrographs of titania films and respective powders at setting temperatures A: 50°C/12h 1020 nm, 100°C/70 mins 803 nm and 200°C/40 mins 966 nm.

(▨ stands for the thickness by grain growth ■ stands for the thickness by continuous nucleation)

2.3.4 Film Growth Rate

The thicknesses of the films deposited at different temperatures with various reaction timings are shown in Fig. 2-15 A B (see appendix V). The effect of temperature on film growth rate and time to coalescence (the time when a continuous film covers the glass surface) is shown in Fig. 2-15 C D respectively. It was observed that after film coalescence, a continuous film (~200 nm) was already formed, with the film growth rate almost constant for each temperature. However, film growth rate increases with reaction temperature, while the time to coalescence decreases with the increase.

Figure 2-15 (A) (B) Relation between the film thickness and reaction time at different temperatures (data referring to appendix V). Effect of temperature on film growth rate (C) and time to coalescence(D)

2.4 Film Morphology and Microstructure

2.4.1 Film Morphology

Film Roughness. The roughness of film was calculated by root mean square (rms) method according to $10 \times 10 \mu\text{m}^2$ images by atomic force microscope in the tapping mode to minimize damage of surface structures. It was observed that the roughness of the film decreases with increasing thickness. For films of similar thickness, the roughness was greater at high reaction temperature (Fig. 2-16), and is attributed to the particles formed in the solution. In the initial film growth stage, the particles in the solution are small enough to be embedded in the film surface, which results in higher film roughness. This suggests that the force of attraction between titania surfaces in the aqueous environment was strong enough to counteract the gravitational force acting on the particles. However, when particles in solution were big enough to overcome the attraction forces, they hence did not embed in the film surface which decreased roughness. Greater numbers of particles

Figure 2-16 Film roughness deposited at 50°C and 200°C

precipitating at higher reaction temperatures contributed to the higher roughness of the film deposited at 200°C.

Particles in solution usually have charged surfaces. The anatase phase has been reported carrying a charge of -21 mV at pH=3.94 in the same reaction solution. This means that titania surfaces are negatively charged. Since two similarly charged surfaces repel each other, particles precipitated in the solution should not agglomerate and not be attracted to the film surface. But the powders synthesized at 200°C and 50°C did agglomerate. This can be explained by the high concentrations of counterions in the acidic solution used in this study shrinks the electrical double layer, so that it no longer shields neighboring particles from experiencing the attractive Van der Waals forces, and agglomeration ensues. Shrinkage of the electrical double layer resulting in agglomeration was previously alluded to by Klein et al. [45] who employed alkoxide precursors in their study. The very high concentration of counterions in the solution is caused by NH_4^+ , BF_2^+ and BF^{2+} ions.

Figure 2-17 Film surface morphology deposited at 200°C for 20 minutes

Film Morphology. Film surface morphology was observed by SEM and AFM. The structure of the film consists of clusters, which are made up of crystallites (comparing with the crystallite size of the respective film). The structure of the film can be observed in Fig.

2-17. The cluster size can be measured by AFM, but the crystallite size sometimes can not be confirmed as they are too small. The change of the film cluster size was determined by AFM images (Appendix II). The cluster sizes of the films deposited at 200 °C increases with the film thickness (Fig. 2-18). However, the size of cluster deposited at 50°C almost remains constant. As discussed above, two kinds of kinetics governed different film growth behavior at 50°C and 200°C. The growth of cluster size was dependent on the diffusion-controlled grain growth in the film deposited at higher reaction temperature. Film growth by continuous nucleation produced the same size titania clusters when the supersaturation of the solution is high at 50°C.

Figure 2-18 Film cluster size deposited at 50, 100, 150 and 200°C

2.4.2 Film Orientation and Crystallinity

Film orientation. It was observed that only anatase appeared in both the films and powder at 200°C (Appendix III). It should be pointed out that the actual reaction temperature is ~130°C after putting the reactor in the oven setting at 200°C for 40 min. Well developed texture of the anatase crystals was evident in XRD patterns as (004) and (105)

reflections were observed (Fig. 2-19). The weakest (105) reflection and the missing (101) reflection indicates that the (00 l) texture of the film was imperfect (Fig. 2-20). The same crystallite tuning mechanism had been discussed by Goh et al. [48] in rutile films deposited from TiCl₄ aqueous solution.

Figure 2-19 XRD patterns of the same thickness film

Lotgering factor. From the X-ray diagrams the sum of the intensities of the (00 l) reflections and the sum of the intensities of all (hkl) and (00 l) reflections (which occur in a certain range of θ values) were obtained, and the ratio of the two sums was calculated for an oriented sample (value P) and also for the non-oriented material (value P_0). For an increase in orientation P , the quantity $L = (P - P_0)/(1 - P_0)$ increases from 0 (non-oriented) to 1.0 (ideally oriented). The quantity L , which may be considered as a measure of the degree of orientation (although of course L does not describe the orientation distribution), was taken as a quality factor for the orientation [109].

Figure 2-20 Tuning of the columnar in the film causing the (105) peak showing up

The intensities of the peak for (101) were affected by the amorphous glass substrate (covered or enhanced), so the selected 2θ range was modified from 30° to 60° . The degree of crystal-axis orientation (L) was evaluated using the Lotgering method taking into account the following diffraction peaks in $2\theta=30^\circ\sim 60^\circ$: $2\theta_{(103)}=36.9^\circ$, $2\theta_{(004)}=37.8^\circ$, $2\theta_{(112)}=38.6^\circ$, $2\theta_{(200)}=48.05^\circ$, $2\theta_{(105)}=53.9^\circ$, $2\theta_{(211)}=55.06^\circ$. The Lotgering factor of films deposited at different temperatures at a fixed thickness of ~ 1100 nm has shown a slight increase of L at higher deposition temperatures (Table 2-2). Highly orientated titania film was observed at all reaction temperatures investigated in the present work because the nucleation density on

the glass surface was constant as discussed previously. This indicates that the reaction temperature has almost no effect on the degree of film orientation.

Table 2-2 Lotgering factor (L) of the films with same thickness (~1100nm)

Film thickness ~1100nm	Lotgering factor(L)
Commercial anatase powder	0
Film deposited at 50 °C for 12 hours	0.94
Film deposited at 80 °C for 150 minutes	0.89
Film deposited at 100 °C for 120 minutes	0.93
Film deposited at 150 °C for 60 minutes	0.97
Film deposited at 200 °C for 40 minutes	0.97

Film Crystallinity. The crystallinity of titania determined by XRD method was defined as the percentage of crystalline with size above 1 nm. (crystalline with size above 1 nm can be sensitized by X-ray diffraction). The crystallinity of the precipitated titania at 50, 100 and 200°C for the different deposition times are shown in Fig. 2-21, with the maximum 90% crystallinity observed for material grown at 200°C for 90 min, while 75% crystallinity

Figure 2-21 Crystallinity of titania material precipitated at 50, 100 and 200°C for different reaction periods

was attained at 50°C after 600 min. At all temperatures, crystallinity increased with deposition time. This is because the temperature in the reactors took approximately 90 min to reach the set values so the material precipitated for shorter periods would have done so at temperatures lower than the set temperatures of 50 or 200°C. However after 40 min at 200°C, the reaction temperature reached ~130°C and the crystallinity of the titania was already 85%. This does not change the fact that the crystallinity of titania increased with increasing reaction temperature when referred to the actual solution temperature listed in Appendix IV. At 50°C, the crystallinity was still increasing even after 4 hours (the solution temperature reached 50°C after 2 h) because the lower crystallinity material precipitated before the set temperature of 50°C was attained.

Figure 2-22 FTIR spectra of the titania powder synthesized at 200 and 50°C with different reaction time.
(The TGA weigh loss is in bracket)

In LPD process, the hexafluorotitanate ion first undergoes hydrolysis, followed by dehydration, before titania is finally formed as shown in equation (2.14).

It is believed that higher growth temperatures accelerate the hydrolysis reaction, thereby promoting higher crystallinity [110]. It should be pointed out that even if the hydrolysis and dehydration reactions were complete, the titania need not necessarily be crystalline. This is because anatase is formed when pairs of the octahedral titanium complexes $[\text{TiF}_{6-x}(\text{OH})_x]^{2-}$ repeatedly connect through shared edges in a periodic fashion to form skewed chains via dehydration reaction. A consequence of incomplete dehydration is that protons can be incorporated in the lattice either as hydroxyl groups (e.g. Ti-OH-Ti and Ti-OH) and/or water molecules (e.g. Ti-O $\cdots$ H₂O). In the case of hydrothermally synthesized perovskite and pyrochlore material, it has been reported that such proton incorporation can reduce the long-range Coulombic attractive forces significantly enough to cause lattice expansion [111]. Thermogravimetry analysis of the powder synthesized at 200°C and 50°C for different timings provides the total weight loss, including physically adsorbed surface water, water loss during the crystallization, and removal of other chemicals such as NH₃ (Fig. 2-22). The bending vibration of H₂O at $\sim 1630 \text{ cm}^{-1}$ significantly decreases with increasing temperature. As the powders were dried at 100°C, the physically absorbed surface water had been removed. Hence the result indicates the water is trapped inside the powder, and is most abundant for shorter reaction times, meaning there are more protons in the powder synthesized for shorter times. The dehydration reactions would conceivably be less complete at lower growth temperatures and this would translate to lower crystallinity.

2.4.3 Film Cracking

Cracking of the deposited films. Cracking of anatase films is common [36], and the films grown in this work are no exception, as shown in Fig. 2-23 for films prepared at 50°C. The films displayed a ‘mud cracking’ type pattern, which is consistent with biaxial tensile stresses. Some previous publications attributed the cracking to ‘drying stresses’ but do not elaborate how these stresses are generated. In this study, the reasons for film cracking were further explored. First, observations by optical microscopy (Fig. 2-23) showed that the films did not crack after cooling and washing with deionised water. This confirms that the films did not crack during cooling due to mismatch in their coefficients of thermal expansion (CTE) [113]. Second, the cracking only appeared after a drying process such as in an oven (at 50°C), in a dry box (30% relative humidity at 25°C) or under vacuum. Since the films cracked even after drying at room temperature (in a dry box 30% relative humidity at 25°C), there can be no generation of ‘drying stresses’ from shrinkage due to crystallization

Figure 2-23 Film with above and below critical thickness under drying at 50°C for 24 hours. (A) film deposited at 50°C for 180 minutes with 388nm; (A1) optical images of the 388nm film after drying; (A2) SEM images of the 388nm film after drying; (B) film deposited at 50°C for 120 minutes with 218nm; (B1) optical images of the 218nm film after drying; (B2) SEM image of the 218nm film after drying

of amorphous phases in the film. Furthermore, unlike sol-gel deposition, no volatile organic solvents are utilized and therefore film shrinkage due to the evaporation of such solvents is not an issue here.

As a result, it is believed that capillary stresses were generated by the meniscus of the wash solvent (water in this case) as it receded into pores in the film. The capillary stress develops as the result of the pressure difference (ΔP) across the liquid vapor interface of the wash solvent in a pore according to the Laplace equation,

$$\left| \Delta P = \frac{2\gamma_{LV} \cdot \cos\alpha}{r} \right| \quad (2.15)$$

where γ is the surface tension and r is the pore radius. When the pore size is less than 10 nm, the capillary stresses that tend to shrink the film can be very significant.

In this study, it was also found that cracking appears whenever the film thickness

Table 2-3 Film critical thicknesses in drying process

Sample	Critical Thickness (nm)
Film deposited at 50 °C	~276
Film deposited at 80 °C	~245
Film deposited at 100 °C	~227
Film deposited at 150 °C	~294
Film deposited at 200 °C	~238

exceeds a critical value (~225 to 295 nm) (Table 2-3). How is the film thickness related to film cracking? A simple model is presented and allows us to understand the occurrence of cracking mechanisms. This interaction between the titania film and liquid is an important problem since the titania film is first formed in aqueous medium. First, the mechanical properties of titania can be treated in the same way as for classical cellular foam with open cells [114]. It is well known that for cellular materials, the Young's modulus E_p and the brittle collapse stress σ^* are related to the porosity p and to the bulk properties of the dense

material according to the relationships: $E_p = E_{\text{TiO}_2} (1-p)^2$ and $\sigma^* = 0.65\sigma_{\text{TiO}_2} (1-p)^{3/2}$, where E_{TiO_2} and σ_{TiO_2} are corresponding to bulk titania and these relations have been proven in porous silicon by nanoindentation [115-118]. According to the Laplace equation, during drying the elastic energy per unit area can be written as $\Delta P^2 h / 2E_p$. When this energy is higher than that necessary to break the interface between the film and substrate or film, cracking occurs. This energy can be calculated according to the two new surfaces that appear (titania surface and glass surface). Hence, the energy is: $(1-p)\gamma_{\text{TiO}_2} + \gamma_{\text{glass}}$. This equation tells us that when porosity increases, cracking will be more severe. Substituting $\Delta P^2 h / 2E_p \geq (1-p)\gamma_{\text{TiO}_2} + \gamma_{\text{glass}}$ into this equation when the cracking appears leads to:

$$h_c = \frac{E_{\text{TiO}_2} (1-p)^2 \times r^2 [(1-p)\gamma_{\text{TiO}_2} + \gamma_{\text{glass}}]}{2\gamma_{\text{LV}}^2} \quad (2.16)$$

Cracking strongly correlates with porous film thickness and only appears for thicknesses $> h_c$, which is expressed by the surface tension γ_{LV} of the drying liquid, porosity P , and pore size r .

2.4.4 Film Aperiodic Mesoporous Structure

Nitrogen adsorption-desorption analysis. Pore characterization can be achieved by three techniques: nitrogen adsorption-desorption analysis, TEM, and small-angle XRD. The trend of pore size and porosity was investigated by nitrogen adsorption analysis of the films and powders (scratched from substrate surface). The surface area of an ideal non-porous anatase powder of 1 μm diameter and a density of 3.8 g/cm^3 can be calculated to be 0.19 m^2/g . However, the observed surface area of the powder is much larger, which indicates high porosity in the powder (Table 2-4). Comparing the surface area of powder to that of film, it was found that film surface area is much larger than the powder precipitated in the same reaction solution. In addition, pore volume of the film is also higher than that of the respective powder.

Table 2-4 Pore diameter and surface area of the film and powder synthesized at 50°C, 100°C and 200°C

	50°C 4 H		50°C 12 H	
	Powder	Film	Powder	Film
Surface area (m ² /g)	6.2	113.4	3.5	50.6
Pore diameter (nm)	3.6	3.5	3.9	2.1
Pore Volume (cm ³ /g)	0.023	0.13	0.016	0.029
	100°C 45 M		100°C 120 M	
	Powder	Film	Powder	Film
Surface area (m ² /g)	16.4	77.3	2.9	35.6
Pore diameter (nm)	3.6	2.8	3.5	3.5
Pore Volume (cm ³ /g)	0.05	0.27	0.007	0.033
	200°C 20 M		200°C 40 M	
	Powder	Film	Powder	Film
Surface area (m ² /g)	67.2	87.3	35.7	16.5
Pore diameter (nm)	3	3	3.2	3.5
Pore Volume (cm ³ /g)	0.052	0.06	0.015	0.034

Figure 2-24 Isotherm (A) and BJH pore size distribution (B) of the film at 50°C.

Obviously, nitrogen adsorption-desorption isotherms confirm that the films are porous, as shown in Fig. 2-24 for films grown at the 50°C oven temperature. The hysteresis loop observed in Fig. 2-24 (A) is due to capillary condensation in cylindrical pores but the abrupt

drop in the desorption branch is indicative of constrictions between connecting pores. The hysteresis loop of the adsorption and desorption isotherms is consistent with network-percolation belonging to IUPAC type IV (Fig.2-24). The hysteresis loops at successive reaction times close gradually as void space is reduced. This result is also consistent with the decrease of pore volume with longer reaction time (Table 2-4). It is presumed these pores were filled gradually during film growth. The isotherm figures of films and powders synthesized at higher temperatures were listed in Appendix VI.

Calculations using BJH method showed that most of the pores in the thinner film (4 hours growth time) are centered around 3.5 nm. As the film becomes thicker (12 hours growth time), there is a significant decrease in the volume of the nano-sized pores, which leads to the decrease of crack density as the film thickness increases. Since the film is still growing thicker by continuous nucleation after 4 hours, this means that the supersaturation is sufficient to cause precipitation of titania in the existing pores, causing the decrease in pore volume. In addition, if the precipitation occurs at the constrictions of the cylindrical pores, this could seal off some pores so that the internal surfaces are no longer accessible,

Figure 2-25 TEM images of the pores in the film with 450 nm deposited at 50°C.

therefore adding to the decrease in open pore volume.

TEM. It was not easy to observe directly 1-dimensional mesoporosity by TEM because they may be covered, twisted or partially-filled. TEM observations of the film did indeed show the presence of pores (Fig. 2-25), but these pores did not show long range order (Fig. 2-25 B). Pores 3~5 nm in diameter which may be indicative of unfilled pores were apparent between the anatase domains, and are consistent with the pore distribution determined by adsorption-desorption analysis.

Table 2-5 Film cracking spacing

Reaction Temperature & Time		Film Thickness (nm)	Crack Spacing (μm)
50°C	4 h	427	17.88
	7 h	669	24.06
	12 h	1100	32.27
100°C	45 min	452	12.92
	60 min	657	16.04
	120 min	1080	21.87
200°C	20 min	446	4.95
	30 min	600	14.01
	40 min	1140	18.95

Crack spacing. The pore size distribution in both the films and powders ranges from ~2 nm to 4 nm. According to the discussion in 2.4.3, severe cracking would be expected in thinner films as higher porosity will result in serious cracking, and this was also observed experimentally where cracking is more obvious in thinner films (400 nm) as compared to thicker films with (600 nm ~ 1100 nm) (Table 2-5). It was concluded that the pores gradually fill as the film grows thicker.

2.5 Photocatalytic Activity of Liquid Phase Deposited Film

The photodegradation of methylene orange by titania films of various thicknesses grown at 50 and 200°C was a pseudo-first-order reaction. UV illumination of aqueous methylene orange solutions in the absence of titania resulted in an apparent rate constant (blank constant) of $0.15 \times 10^{-4} \text{ min}^{-1}$. However, in the presence of titania films, the apparent rate constants were two orders of magnitude higher (Fig. 2-26 A, Table 2-6). The photodegradation rates are normalized by the volume of the respective films (Fig. 2-26 B). While the crystallinity increases with film thickness (i.e. with longer deposition times), the volume area normalized apparent rate constant decreases with film thickness increasing, especially for the 200°C material. Therefore, it appears that for crystallinity between 60 and 90%, it is the surface area that controls photocatalytic activity.

Nevertheless, it was found that after normalizing film surface area, titania photocatalytic activity increases with crystallinity (Fig. 2-27). However, it is strange photocatalytic activity is lower in 70% and 75% crystallinity of deposited film at 50°C than 64% crystallinity film deposited at 200°C. This can be explained by the small crystallite size at 50°C (~3 nm for 4 hours and ~5.6 nm for 12 hours), which is not in the best range of crystallite size for photocatalytic performance of titania (7~20 nm) [79, 80]. However, crystallite size at 200°C was ~8 nm for 20 mins to ~16 nm for 40 mins. Crystallite size in

Figure 2-26 Photocatalytic activities of the films deposited at 50°C (white bars) and 200°C (black bars) as characterized by the (A) photodegradation rate, k , and (B) Volume normalized degradation rate.
(Percentages in brackets above each column denote the crystallinity of each film)

this range is good enough to exhibit photocatalytic activity but still not large enough to induce the size effect that decreases photocatalytic activity as we discussed in 2.1.6.

Figure 2-27 Surface area normalized apparent rate constant k_1

In a similar study, Yu et. al. [110] reported a maximum degradation rate, k , of $18.5 \times 10^{-4} \text{ min}^{-1}$ for titania films that were deposited on glass substrates (80 cm^2) at room temperature. The film then was subjected to various annealing temperatures to induce crystallinity. Films annealed at 700°C , with a film thickness of 250 nm, displayed the highest degradation rate in methyl orange solutions under UV irradiation with an intensity of $112 \mu\text{W}/\text{cm}^2$. In order to compare this rate with the results obtained in this study, the rate was normalized by the volume of film under UV irradiation, giving a surface area normalized degradation rate of $0.925 \text{ min}^{-1}\text{cm}^{-2}$. This is still three times lower than the lowest rate of $2.94 \text{ min}^{-1}\text{cm}^{-2}$ obtained in this study for a film grown at 50°C for 12 hours that is 1020 nm thick. The highest surface areas normalized degradation rate obtained in this work is $0.77 \text{ min}^{-1}\text{cm}^{-2}$ for a film 604 nm thick grown at 200°C for 30 minutes. Yu and co-workers did not measure the crystallinity of their material, but it is reasonable to assume

that their films were of high crystallinity (at least higher than the lowest crystallinity of 64% examined in this study) due to the annealing at 700°C. Therefore, it is most likely that the surface area of the films in this work was much larger which resulted in the higher degradation rate.

Although there appears to be no study on the effect of UV intensity on the photodegradation of methyl orange by titania, Chen and Ray [69] observed that the rate increases with the square root of intensity in the photodegradation of 4-nitrophenol by titania. If this dependence on the UV intensity is assumed to be true for the photodegradation of methyl orange, then the adjusted volume normalized degradation rate works out to be $1.28 \text{ min}^{-1} \text{ cm}^{-3}$, which is still more than 2 times lower than the minimum rate obtained in this study.

Table 2-6 Information regarding film thickness, crystallinity and specific surface area for growth at 50 and 200°C and various reactions periods

Temperature	Reaction time	Film thickness (nm)	Crystallinity (%)	Apparent rate constant, k ($\times 10^{-4} \text{ min}^{-1}$)
50°C	4 hours	475	70	20
	6 hours	591	72	17.9
	12 hours	1020	75	29
200°C	20 minutes	455	64	32.4
	30 minutes	604	78	38.3
	40 minutes	1100	85	34.2

2.6 Conclusions

Both heterogeneous nucleation (film formation on a substrate) and homogeneous nucleation (powder formation in solution) take place during liquid phase deposition of anatase thin films. During heterogeneous nucleation, fewer islands appear on the substrate at higher reaction temperatures because the degree of supersaturation decreases rapidly as a result of homogeneous nucleation. A convenient method for diagnosing the kinetics of

isothermal solid-state reactions developed by Hancock and Sharp suggests that a diffusion-controlled mechanism is governing grain growth in the top layer of the film, while continuous nucleation is dominant in the lower portion. Moreover, the degree of supersaturation changes during the reaction, leading to the transition of phase-boundary-controlled nucleation to diffusion-controlled grain growth in both films and powders. Crystallization is promoted at higher temperatures, and thick films display considerable texture with z-axis perpendicular to the substrate. The crystallites occur as columnar clusters that also increase in size with film thickness. The crystallinity increased with deposition time but saturated at 75 and 90% for the lower and higher growth temperatures respectively. It is believed that defects due to incomplete hydrolysis and dehydration reactions inhibited and disrupted the periodic ordering that is required for complete crystallization.

Film cracking arising from capillary stresses induced by solvent evaporation from the mesopores was studied. The 200°C films were more porous, but the specific surface area decreased more significantly with deposition time than the 50°C films due to crystal growth. Porosity in both the films and powders decreased as a result of crystallite growth. Filled pores of 2~4 nm in diameter observed by TEM were consistent with the size determined by adsorption-desorption analysis.

It was observed that crystallinity did have a significant effect on the photodegradation of methyl orange. But for crystallinity above 60%, it is the surface area that has a more significant effect. The highest photodegradation rate of $38.8 \times 10^{-4} \text{ min}^{-1}$ was achieved in the present work for a 604 nm thick film deposited at 200°C for 30 min.

2.7 References

- [1] T. P. Niesen, M. R. De Guire, (2001). Review: deposition of ceramic thin films at low temperatures from aqueous solutions, *Journal of Electroceramics*, 6, 169.
- [2] S. Deki, Y. Aoi, O. Hiroi, A. Kajinami, (1996). Titanium (IV) oxide thin films prepared from aqueous solution, *Chem. Lett.*, 433.

- [3] A. Dutschke, C. Diegelmann, P. Löbmann, (2003). Nucleation and growth of TiO₂ thin films on modified polystyrene surface, *Chem. Mater.*, 15, 3501.
- [4] K. Shimizu, H. Imai, H. Hirashima, K. Tsukuma, (1999). Low-temperature synthesis of anatase thin films on glass and organic substrates by deposition from aqueous solutions, *Thin Solid Film*, 351, 220.
- [5] S. Deki, H. Y. Y. Ko, T. Fujuta, K. Akamatsu, M. Mizuhata, A. Kajinami, (2001). Synthesis and microstructure of metal oxide thin films containing metal nanoparticles by liquid phase deposition (LPD) method, *Eur. Phys. J. D16*, 325.
- [6] A. Dutschke, C. Diegelmann, P. Löbmann, (2003). Preparation of TiO₂ thin films on polystyrene by liquid phase deposition, *J. Mater. Chem.*, 13, 1085.
- [7] M. Wu, G. Lin, D. Chen, G. Wang, D. He, S. Feng, R. Xu, (2002). Sol-hydrothermal synthesis and hydrothermally structure evolution of nanocrystal titanium dioxide, *Chem. Mater.*, 14, 1974.
- [8] C. Wang, Z. X. Deng, Y. Li, (2001). The synthesis of nanocrystalline anatase and rutile titania in mixed organic media, *Inorg. Chem.*, 40, 5210.
- [9] S. D. Burnside, V. Shklover, C. Barbé, P. Comte, F. Arendse, K. Brooks, M. Grätzel, (1998). Self-organization of TiO₂ nanoparticles in thin film, *Chem. Mater.*, 10, 2419.
- [10] H. Yin, Y. Wada, T. Kitamura, S. Kambe, S. Murasawa, H. Mori, T. Sakata, S. Yanagida, (2001). Hydrothermal synthesis of nanosized anatase and rutile TiO₂ using amorphous phase TiO₂, *J. Mater. Chem.*, 11, 1694.
- [11] R. L. Penn, J. F. Banfield, (1999). Morphology development and crystal growth in nanocrystalline aggregates under hydrothermal conditions: insights from titania, *Geochim. Cosmochim. Acta*, 63, 1549.
- [12] S. Yin, R. Li, Q. He, T. Sato, (2002). Low temperature synthesis of nanosize rutile titania crystal in liquid media, *Mater. Chem. Phys.*, 75, 76.
- [13] Y. Zheng, E. Shi, S. Cui, W. Li, X. Hu, (2000). Hydrothermal preparation and characterization of brookite-type TiO₂ nanocrystallites, *Journal of Materials Science Letters*, 19, 1445.
- [14] Q. Chen, Y. Qian, Z. Chen, Y. Jia, G. Zhou, X. Li, Y. Zhang, (1996). Low-temperature deposition of ultrafine rutile TiO₂ thin films by hydrothermal method, *Phys. Stat. Sol.*, (a)156, 381.
- [15] J. M. Wu, S. Hayakawa, K. Tsuru, A. Osaka, (2002). Soft solution approach to prepare crystalline titania films, *Scr. Mater.*, 46, 705.
- [16] Q. Zhang, L. Gao, J. Guo, (2001). Effect of hydrolysis conditions on morphology and crystallization of nanosized TiO₂ powder, *J. Eur. Ceram. Soc.*, 20, 2153.
- [17] H. Yin, Y. Wada, T. Kitamura, T. Sumida, Y. Hasegawa, S. Yanagida, (2002). Novel synthesis of phase-pure nano-particulate anatase and rutile TiO₂ using TiCl₄ aqueous solutions, *J. Mater. Chem.*, 12, 378.
- [18] H. Hayashi, K. Torii, (2002). Hydrothermal synthesis of titania photocatalyst under subcritical and supercritical water conditions, *J. Mater. Chem.*, 12, 3671.
- [19] S. Deki, Y. Aoi, Y. Asaoka, A. Kajinami, M. Mizuhata, (1997). Monitoring the growth of titanium oxide thin films by the liquid-phase deposition method with a quartz crystal microbalance, *J. Mater. Chem.*, 7, 733.
- [20] Y. Zheng, E. Shi, Z. Chen, W. Li, X. Hu, (2001). Influence of solution concentration on the hydrothermal preparations of titania crystallites, *J. Mater. Chem.*, 11, 1547.
- [21] Y. Li, T. J. White, S. H. Lim, (2004). Low-temperature synthesis and microstructural of titania nano-particles, *J. Solid State Chem.* 177, 1372.
- [22] W. J. Li, E. W. Shi, Z. W. Yin, (2000). Growth habit of rutile and α -Al₂O₃ crystals, *Journal of Crystal Growth*, 208, 546.

- [23] H. Pizem, C. N. Sukenik, (2002). Effects of substrate surface functionality on solution-deposited titania films, *Chem. Mater.*, 14, 2476.
- [24] N. Ozawa, Y. Kumazawa, T. Yao, (2002). Effect of seed crystal and composition of solution on the formation of TiO₂ thin film from aqueous solution, *Thin Solid Film*, 418, 102.
- [25] S. Yamabi, H. Imai, (2001). Fabrication of rutile TiO₂ foils with high specific surface area via heterogeneous nucleation in aqueous solution, *Chem. Lett.*, 3, 220.
- [26] S. Yamabi, H. Imai, K. Awazu, (2002). Biomimetic approach for exact control of TiO₂ periodic microstructures, *Chem. Lett.*, 7, 714.
- [27] T. P. Niesen, J. Bill, F. Aldinger, (2001). Deposition of titania thin films by a peroxide route on different functionalized organic self-assembled monolayer, *Chem. Mater.*, 13, 1552.
- [28] D. Huang, Z. D. Xiao, J. H. Gu, N. P. Huang, C. W. Yuan, (1997). TiO₂ thin films formation on industrial glass through self-assembly processing, *Thin Solid Films*, 305, 110.
- [29] S. Baskaran, L. Song, J. Liu, Y. L. Chen, G. L. Graff, (1998). Titanium oxide thin films on organic interfaces through biomimetic processing, *J. Am. Ceram. Soc.*, 81, 401.
- [30] Z. Xiao, L. Su, N. Gu, Z. Lu, Y. Wei, (1998). The growth of TiO₂ thin films on mixed self-assembly monolayers from solution, *Thin Solid Film*, 333, 25.
- [31] K. Koumoto, S. Seo, T. Sugiyama, W. S. Seo, (1999). Micropatterning of titanium dioxide on self-assembled monolayers using a liquid-phase deposition process, *Chem. Mater.*, 11, 2305.
- [32] N. Ozawa, H. Yabe, T. Yao, (2003). Formation of titania submicrometer patterns by the combination of synthesis from an aqueous solution and transcription of a resist pattern, *J. Am. Ceram. Soc.*, 86, 1976.
- [33] Y. Masuda, N. Saito, R. Hoffmann, M. R. De Guire, K. Koumoto, (2003). Nano/micro-patterning of anatase TiO₂ thin film from an aqueous solution by site-selective elimination method, *Science and Technology of Advanced Materials*, 4, 461.
- [34] R. J. Collins, H. Shin, M. R. DeGuire, A. H. Heuer, (1996). Low temperature deposition of patterned TiO₂ thin films using photopatterned self-assembled monolayers, *Appl. Phys. Lett.*, 69, 860.
- [35] Y. Masuda, S. Ieda, K. Koumoto, (2003). Site-selective deposition of anatase TiO₂ in aqueous solution using a seeding layer, *Langmuir*, 19, 4415.
- [36] Q. Chen, Y. Qian, Z. Chen, (1995). Hydrothermal epitaxy of high oriented TiO₂ thin film on silicon, *Appl. Phys. Lett.*, 66, 1608.
- [37] H. G. Yang, H. G. Zeng, (2003). Control of nucleation in solution growth of anatase TiO₂ on glass substrate, *J. Phys. Chem. B*, 107, 12244.
- [38] H. Shin, R. J. Collins, M. R. De Guire, A. H. Heuer, C. N. Sukenik, (1995). Synthesis and characterization of TiO₂ thin films on organic self-assembled monolayers: Part II. film formation via an organometallic route, *J. Mater. Res.*, 10, 699.
- [39] Y. Masuda, T. Sugiyama, W. S. Seo, K. Koumoto, (2003). Deposition mechanism of anatase TiO₂ on self-assembled monolayers from an aqueous solution, *Chem. Mater.*, 15, 2496.
- [40] S. Yamabi, H. Imai, (2003). Synthesis of rutile and anatase films with high surface areas in aqueous solutions containing urea, *Thin Solid Films*, 434, 86.
- [41] S. Yamabi, H. Imai, (2002). Crystal phase control for titanium dioxide films by direct deposition in aqueous solutions, *Chem. Mater.*, 14, 609.
- [42] H. Cheng, J. Ma, Z. Zhao, L. Qi, (1995). Hydrothermal preparation of uniform nanosized rutile and anatase particles, *Chem. Mater.*, 7, 663.

- [43] Y. Qian, Q. Chen, Z. Chen, C. Fan, G. Zhou, (1993). Preparation of ultrafine powders of TiO_2 by hydrothermal H_2O_2 oxidation starting from metallic Ti, *J. Mater. Chem.*, 3, 203.
- [44] Q. Chen, Y. Qian, Z. Chen, G. Zhou, Y. Zhang, (1995). Preparation of TiO_2 powders with different morphologies by an oxidation-hydrothermal combination method, *Mater. Lett.*, 22, 77.
- [45] S. M. Klein, J. H. Choi, (2003). Synthesis of rutile titania powders: agglomeration, dissolution, and reprecipitation phenomena, *J. Mater. Res.*, 18, 1457.
- [46] S. T. Aruna, S. Tirosh, A. Zaban, (2000). Nanosize rutile titania synthesis via hydrothermal method without mineralizers, *J. Mater. Chem.*, 10, 2388.
- [47] S. H. Lee, M. Kang, S. M. Cho, G. Y. Han, B. W. Kim, K. J. Yoon, C. H. Chung, (2001). Synthesis of TiO_2 photocatalyst thin film by solvothermal method with a small amount of water and its photocatalytic performance, *J. Photochem. Photobiol. A: Chem.*, 146, 121.
- [48] G. K. L. Goh, S. K. Donthu, P. K. Pallathadka, (2004). Cracking and orientation of solution-deposited rutile TiO_2 films, *Chem. Mater.*, 16, 2857.
- [49] M. D. Donohue, G. L. Aranovich, (1998). Classification of Gibbs adsorption isotherms, *Advances in Colloid and Interface Science*, 76-77, 137.
- [50] K. S. W. Sing, (1998). Adsorption methods for the characterization of porous materials, *Advances in Colloid and Interface Science*, 76-77, 3.
- [51] P. I. Ravikovitch, A. V. Neimark, (2001). Characterization of nanoporous materials from adsorption and desorption isotherms”, *Colloids and Surface A: Physicochemical and Engineering Aspects*, 187-188, 11.
- [52] J. M. Thomas, O. Terasaki, P. L. Gai, W. Zhou, J. Gonzalez-Calbet, (2001). Structural elucidation of microporous and mesoporous catalysts and molecular sieves by high-resolution electron microscopy, *Acc. Chem. Res.*, 34, 583.
- [53] P. I. Ravikovitch, S. C. Ó Domhnaill, A. V. Neimark, F. Schüth, K. K. Unger, (1995). Capillary hysteresis in nanoporous: theoretical and experimental studies of nitrogen adsorption on MCM-41, *Langmuir*, 11, 4765.
- [54] U. Ciesla, F. Schüth, (1999). Ordered mesoporous materials, *Microporous and Mesoporous Materials*, 27, 131.
- [55] A. L. Linsebigler, G. Lu, J. T. Yates, Jr., (1995). Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected Results, *Chem. Rev.*, 95, 735.
- [56] M. Grätzel, J. Moser, (1983). Multielectron storage and hydrogen generation with colloidal semiconductors, *Proc. Natl. Acad. Sci.*, 80, 3129.
- [57] H. Kato, A. Kudo, (1998). New tantalate photocatalysts for water decomposition into H_2 and O_2 , *Chem. Phys. Lett.*, 295, 487.
- [58] M. Mohseni, A. David, (2003). Gas phase vinyl chloride (VC) oxidation using TiO_2 -based photocatalysis, *Appl. Catal. B*, 46, 219.
- [59] M. L. Hitchman, F. Tian, (2002). Studies of TiO_2 thin films prepared by chemical vapor deposition for photocatalytic and photoelectrocatalytic degradation of 4-Chlorophenol, *J. Electroanal. Chem.*, 538-539, 165.
- [60] G. Al-Sayyed, J. C. D'Oliveira, P. Pichat, (1991). Semiconductor-sensitized photodegradation of 4-chlorophenol in water, *J. Photochem. Photobiol. A: Chem.*, 58, 99.
- [61] J. C. D'Oliveira, G. Al-Sayyed, P. Pichat, (1990). Photodegradation of 2- and 3-chlorophenol in TiO_2 aqueous suspensions, *Environ. Sci. Technol.*, 24, 990.
- [62] K. Tanaka, W. Luesaiwong, T. Hisanaga, (1997). Photocatalytic degradation of mono-, di- and trinitrophenol in aqueous TiO_2 suspension, *J. Mol. Catal. A: Chem.*, 122, 67.

- [63] H. Kishimoto, K. Takahama, N. Hashimoto, Y. Aoi, S. Deki, (1998). Photocatalytic Activity of Titanium Oxide Prepared by Liquid Phase Deposition, *J. Mater. Chem.*, 8, 2019.
- [64] Y. İnel, A. N. Ökte, (1996). Photocatalytic degradation of malonic acid in aqueous suspensions of titanium dioxide: an initial kinetic investigation of CO₂ photogeneration, *J. Photochem. Photobiol. A: Chem.*, 96, 175.
- [65] A. Mills, J. Wang, (1999). Photobleaching of methylene blue sensitised by TiO₂: an ambiguous system? *J. Photochem. Photobiol. A: Chem.*, 127, 123.
- [66] J. H. Lee, W. Nam, M. Kang, G. Y. Han, K. J. Yoon, M. S. Kim, K. Ogino, S. Miyata, S. J. Choung, (2003). Design of two types of fluidized photo reactors and their photo-catalytic performance for degradation of methylene orange, *Appl. Catal. A*, 244, 49.
- [67] Y. Yang, Y. Guo, C. Hu, E. Wang, (2003). Lacunary keggins-type polyoxometalates-based macroporous composite films: preparation and photocatalytic activity, *Appl. Catal. A*, 252, 305.
- [68] M. C. Lu, G. D. Roam, J. N. Chen, C. P. Huang, (1993). Factors affecting the photocatalytic degradation of dichlorvos over titanium dioxide supported on glass, *J. Photochem. Photobiol. A: Chem.*, 76, 103.
- [69] L. C. Chen, T. C. Chou, (1993). Kinetics of photodecolorization of methylene orange using titanium dioxide as catalyst, *Ind. Eng. Chem. Res.*, 32, 1520.
- [70] D. Chen, A. K. Ray, (1998). Photodegradation kinetics of 4-nitrophenol in TiO₂ suspension, *Wat. Res.*, 32, 3223.
- [71] R. Fretwell, P. Douglas, (2001). An active, robust and transparent nanocrystalline anatase TiO₂ thin film- preparation, characterisation, and the kinetics of photodegradation of model pollutants, *J. Photochem. Photobiol. A: Chem.*, 143, 229.
- [72] V. Augugliaro, M. J. López-Muñoz, L. Palmisano, J. Soria, (1993). Influence of pH on the degradation kinetics of nitrophenol isomers in a heterogeneous photocatalytic system, *Appl. Catal. A*, 101, 7.
- [73] G. Balasubramanian, D. D. Dionysiou, M. T. Suidan, I. Baudin, J. M. Laine, (2004). Evaluating the activities of immobilized TiO₂ powder films for the photocatalytic degradation of organic contaminants in water, *Appl. Catal. B*, 47, 73.
- [74] R. I. Bickley, T. Gonzalez-Carreno, J. S. Lees, L. Palmisano, R. J. D. Tilley, (1991). A structural investigation of titanium dioxide photocatalysts, *J. Solid. State. Chem.*, 92, 178.
- [75] B. Sun, P. G. Smirniotis, (2003). Interaction of anatase and rutile TiO₂ particles in aqueous photooxidation, *Catalysis Today*, 88, 49.
- [76] R. R. Bacsa, J. Kiwi, (1998). Effect of rutile phase on the photocatalytic properties of nanocrystalline titania during the degradation of p-coumaric acid, *Appl. Catal. B*, 16, 19.
- [77] T. Kawahara, T. Ozawa, M. Iwasaki, H. Tada, S. Ito, (2003). Photocatalytic activity of rutile-anatase coupled TiO₂ particles prepared by a dissolution-reprecipitation method, *J. Colloid. Interface. Sci.*, 276, 377.
- [78] T. Ohno, K. Sarukawa, K. Tokieda, M. Matsumura, (2001). Morphology of a TiO₂ photocatalyst (Degussa, P-25) consisting of anatase and rutile crystalline phases, *J. Catal.*, 203, 82.
- [79] L. Gao, Q. Zhang, (2001). Effects of amorphous content and particle size on the photocatalytic properties of TiO₂ nanoparticles, *Scripta mater.*, 44, 1195.
- [80] K. Tanaka, M. F. V. Capule, T. Hisanaga, (1991). Effect of crystallinity of TiO₂ on its photocatalytic action, *Chem. Phys. Lett.*, 187, 73.

- [81] J. C. Yu, J. Yu. W. Ho, Z. Jiang, L. Zhang, (2002). Effects of F⁻ doping on the photocatalytic activity and microstructures of nanocrystalline TiO₂ powder, *Chem. Mater.*, 14, 3808.
- [82] H. Luo, T. Takata, Y. Lee, J. Zhao, K. Domen Y. Yan, (2004). Photocatalytic activity enhancing for titanium dioxide by co-doping with bromine and chlorine, *Chem. Mater.*, 16, 846.
- [83] B. Sun, A. V. Vorontsov, P.G. Smirniotis, (2003). Role of platinum deposited on TiO₂ in phenol photocatalytic oxidation, *Langmuir*, 19, 3151.
- [84] I. M. Arabatzis, T. Stergiopoulos, M. C. Bernard, D. Labou, S. G. Neophytides, P. Falaras, (2003). Silver-modified titanium dioxide thin films for efficient photodegradation of methyl orange, *Appl. Catal. B*, 42, 187.
- [85] P. Cheng, W. Li, T. Zhou, Y. Jin, M. Gu, (2004). Physical and photocatalytic properties of zinc ferrite doped titania under visible light irradiation, *J. Photochem. Photobiol. A: Chem.*, 168, 97.
- [86] R. L. Sheldrick, (1993). *Analytic Profile Fitting of X-Ray Powder Diffraction Profiles in Rietveld Analysis*, Oxford University Press, (pp.111-131).
- [87] C. V. Thompson, (2000). Structure evolution during processing of polycrystalline films, *Annu. Rev. Mater. Sci.*, 30, 159.
- [88] Q. Zhang, L. Gao, J. Guo, (2000). Effect of hydrolysis conditions on morphology and crystallization of nanosized TiO₂ powder, *Journal of European Ceramic Society*, 20, 2153.
- [89] R. W. Thompson, (1992). Analysis of zeolite crystallizations using avrami transformation methods, *Zeolites*, 12, 680.
- [90] M. Avrami, (1939), Kinetics of phase change. I*, *J. Chem. Phys.*, 7, 1103.
- [91] M. Avrami, (1940). Kinetics of phase change. II, *J. Chem. Phys.*, 8, 212.
- [92] M. Avrami, (1941). Granulation, phase change, and microstructure, *J. Chem. Phys.*, 9, 177.
- [93] J. D. Hancock, J. H. Sharp, (1972). Method of comparing solid-state kinetic data and its application to the decomposition of kaolinite, brucite, and BaCO₃, *J. Amer. Ceram. Soc.*, 55, 74.
- [94] B. Ma, G. K. L. Goh, J. Ma, (2006). Crystallinity and photocatalytic activity of liquid phase deposited TiO₂ film, *J. Electroceram.*, 16, 441.
- [95] M. Yoshimura, W. Suchanek, (1997). In situ fabrication of morphology-controlled advanced ceramic materials by soft solution processing, *Solid State Ionics*, 98, 197.
- [96] G. Yu, Y. K. L. Lai, (1995). Kinetics of transformation with nucleation and growth mechanism: fundamentals of derivation and one-dimensional model", *J. Appl. Phys.*, 78, 5965.
- [97] O. Söhnel, J. Garside, (1991). *Precipitation: Basic Principles and Industrial Applications*, Butterworth-Heinemann, Oxford,
- [98] A. M. Fogg. S. J. Price, R. J. Francis, S. O'Brien, D. O' Hare, (2000). Determination of the kinetics of crystallisation of Gibbsite using time resolved in situ energy dispersive powder X-ray diffraction, *J. Mater. Chem.*, 10, 2355.
- [99] A. M. Beale, G. Sankar, (2003). In situ study of the formation of crystalline bismuth molybdate materials under hydrothermal conditions, *Chem. Mater.*, 15, 146.
- [100] G. A. Rossetti, D. J. Watson, R. E. Newnham J. H. Adair, (1992). Kinetics of the hydrothermal crystallization of the pervoskite, *Journal of Crystal Growth*, 116, 251.
- [101] R. A. Gardner, (1974). The kinetics of silica reduction in hydrogen, *Journal of Solid State Chemistry*, 9, 336.
- [102] R. I. Walton, F. Millange, R. I. Smith, T. C. Hansen, D. O'Hare, (2001). Real time observation of the hydrothermal crystallization of barium titanate using in situ neutron powder diffraction, *J. Am. Chem. Soc.*, 123, 12547.

- [103] G. Yu, Y. K. L. Lai, W. Zhang, (1997). Kinetics of transformation with nucleation and growth mechanism: diffusion-controlled reactions, *J. Appl. Phys.*, 82, 4270.
- [104] K. Byrappa, M. Yoshimura, (2001). *Handbook of Hydrothermal Technology*, William Andrew Publishing.
- [105] D. V. Bavykin, E. N. Savinov, P.G. Smirniotis, (2003). Kinetics of the TiO₂ films growth at the hydrothermal hydrolysis of TiOSO₄, *React. Kinet. Catal. Lett.*, 79, 77.
- [106] J. Moon, E. Suvaci, A. Morrone, S. A. Costantino, J.H. Adair, (2003). Formation mechanisms and morphological changes during the hydrothermal synthesis of BaTiO₃ particles from a chemically modified, amorphous titanium (hydrous) oxide precursor, *Journal of the European Ceramic Society*, 23, 2153.
- [107] J. Moon, E., M. L. Carasso, H.G. Krarup, J.A. Kerchner, (1999). Particle-shape control and formation mechanisms of hydrothermal derived lead titania, *J. Mater. Res.*, 14(3), 866.
- [108] M. M. Lencka, R. E. Riman, (1995). Thermodynamics of the hydrothermal synthesis of calcium titanate with reference to other alkaline-earth titanates, *Chem. Mater.*, 7, 18.
- [109] F. K. Lotgering, (1959). Topotactical reactions with ferrimagnetic oxide having hexagonal crystal structures-I, *J. Inorg. Nucl. Chem.*, 9, 113.
- [110] J. G. Yu, H. G. Yu, B. Cheng, X. J. Zhao, J. C. Yu, W. K. Ho, (2003). The effect of calcination temperature on the surface microstructure and photocatalytic activity of TiO₂ thin films prepared by liquid phase deposition, *J. Phys. Chem. B*, 107, 13871.
- [111] G. K. L. Goh, S. M. Haile, C. G. Levi and F. F. Lange, (2002). Hydrothermal synthesis of perovskite and pyrochlore powders of potassium tantalite, *J. Mater. Res.*, 17[12], 3168.
- [112] E. Olsson, A. Gupta, M. D. Thouless, A. Segmüller, (1999). Crack formation in epitaxial [110] thin films of YBa₂Cu₃O_{7-δ} and PrBa₂Cu₃O_{7-x} on [110] SrTiO₃ substrates, *Appl. Phys. Lett.*, 58, 1682.
- [113] J. S. Park, M. V. Streltsina, T. P. S. Shvaikoskaya, (1983). *Handbook of Glass Data, Part A and Part B*, Elsevier, New York.
- [114] L. J. Gibson, M. F. Ashby, (1999). *Cellular Solids: Structure and Properties*. Pergamon, New York.
- [115] D. Bellet, P. Lamagnère, A. Vincent, Y. Brèchet. (1999). Nanoindentation investigation of the Young's modulus of porous silicon, *J. Appl. Phys.*, 80(7), 3772.
- [116] D. Bellet, L. Canham, (1998). Controlled drying: the key to better quality porous semiconductor, *Advanced Materials*, 10(6), 487-490.
- [117] O. Belmont, D. Bellet Y. Brèchet, (1996). Study of the cracking of highly porous P+ type silicon during drying, *J. Appl. Phys.*, 79(10), 7586-7591.
- [118] H. Namatsu, K. Kurihara, M. Nagase, K. Iwadate, K. Murase, (1995). Dimensional limitation of silicon nanolines resulting from pattern distortion due to surface tension of tinse water, *Appl. Phys. Lett.*, 66(20), 2655.

CHAPTER 3

AAO TEMPLATED MACROPOROUS TITANIA MEMBRANES

In this chapter, in order to control the pore configuration in LPD, anodized aluminium oxide (AAO) was used to template and fabricate self-supporting macroporous anatase membranes. Ammonium hexafluorotitanate $(\text{NH}_4)_2\text{TiF}_6$ (AHFT) was employed as the precursor. The alumina eliminates F^- in solution and forces the precipitation of titania instead of boric acid. Alumina in a porous AAO template was replaced by titania via dissolution of H_3AlF_6 . It is noted that the in-situ growth of titania preserves the macroporous structure of the AAO template. Moreover, mesoporosity at the tubular titania walls is controlled by the same pore formation mechanism in LPD discussed in previous chapter. The microstructure and composition are studied as functions of reaction time, temperature, precursor concentration and heat treatment process. The photocatalytic activity of the membranes is evaluated by decolorisation of aqueous methylene blue (MB) under UV irradiation. It was found to be optimal for material fabricated by immersion of the AAO for 5 h in AHFT without subsequent heat treatment and observed to have the best combination of titania content, surface area and effective pore diameter trapped MB molecules. Titania membranes are potentially effective for filtration and purification of liquid and gaseous waste streams.

3.1 State of the Art

Both soft and hard templates have been used to fabricate nanostructured titania. Soft templates include block copolymers and ionic surfactants widely used in sol-gel synthesis

of ordered mesoporous materials such as mesoporous titania film. On the other hand, anodic aluminium oxide (AAO) is usually used as a hard template for the molding of titania nanotubes and nanofibers. Through using AAO templates with channels of different diameters, various nanotubes and nanowires have been directly deposited inside the channels. In this work, highly ordered macroporous titania membranes were synthesized for the first time by AAO templating. This titania structure has attracted further attention because they possess the bi-functional features of photocatalytic and filtration properties [1-4].

3.1.1 Anodized Aluminium Oxide (AAO)

The growth of oxide coatings and protecting shells by the anodization technique constituted was attempted during the last century. Masuda and Fukuda [5] obtained highly ordered porous anodized aluminium oxide (AAO) using anodization processes. The interesting characteristic of AAO is the growth of well-ordered hexagonal arrays of cells with central pores parallel to each other. The macroporous channels also possess a symmetry axis perpendicularly oriented to the substrate surface. Since then, AAO became an important material in nanotechnology development and research fields such as optoelectronic, self-assembly and magnetic storage devices. Much attention has been paid to the use of AAO templates in nanostructure synthesis (Fig. 3-1, AAO template).

Figure 3-1 Commercial AAO template (A) plan view (B) cross-section.

3.1.2 Nanostructured Titania Directed by AAO

Although titania nanotubes have been fabricated by various hydrothermal processes without templates, their applications are limited by poor alignment [6-14]. It is noted that well-organized macroporous titania nanotube arrays can also be fabricated by the molding of AAO template in sol-gel or direct anodization. Nevertheless, in anodic oxidation of titanium, the underlying impermeable substrate renders the assemblage unsuitable for filtration [15-20] (Fig. 3-2). Anodized titania nanotube arrays were found to exhibit high efficiency in solar cell.

Figure 3-2 Titania nanotube arrays by anodization. [18]

Figure 3-3 Various nanostructured titania by AAO template [24, 26, 28].

The major problem is that the well-ordered structure is destroyed after the removal of AAO template. Therefore, AAO is usually kept in the structure if it has no effect on properties. Without a removal process, AAO is still a good template widely used to

fabricate aligned fibers, nanotubes and pillars via techniques such as MBE, CVD and ion beam lithography (Fig. 3-3).

Successful syntheses for obtaining nanowire arrays and nanotubes using AAO template include: (1) self-assembly of one material in the roughness or relief present on the solid surface of the template [21], and (2) self-organization within the template channels and cavities [22-23]. The direct replication of morphological features from AAO have also been identified as a part of the nano-imprint lithography technique [24]. With this novel technology, linewidths of 5 nm to 200 nm in SiC, HA, titania and TiN have been successfully controlled and synthesized [25-28] (Fig. 3-3).

3.1.3 Titania Formation Mechanism

Self-aligned titania nanotubes can directly deposit on alumina surfaces of an AAO template by hydrolysis of TiF_4 through Route A (Fig. 3-4) [29-31]. Alternatviely, titania

Figure 3-4 Schematic of titania growth mechanism by (A) directly deposited on surface of AAO template (B) liquid phase deposited titania.

can grow in-situ by hydrolysis of AHFT, while, AAO dissolves and reacts as a precursor through Route B (Fig. 3-4) [32]. In route A, the well-organized titania nanotubes will lose periodicity after removal of the AAO template. Therefore, to overcome this problem, route B is recommended by Yamanaka et al. [32]. They reported the use of porous AAO templates in LPD to fabricate titania self-aligned nanotubes. However, the amorphous titania nanotubes arrays were fragile and not photocatalytic at 30°C.

The effect of alumina in LPD is considered to be the same as that of boric acid. During LPD, the reaction equilibrium could be forced to the right by the addition of boric acid that consumes fluoride via the formation of $[\text{BF}_4]^-$. The same effect can also be achieved by alumina or aluminium via the formation of $[\text{AlF}_6]^{3-}$ as shown in equation (3.1). It is evident mechanism is operative from the increase of the pH of the solution after reaction.

3.2 Experimental Procedure

3.2.1 Synthesis of Titania Membranes

The precursor solution was prepared by dissolving $(\text{NH}_4)_2\text{TiF}_6$ (Aldrich) in distilled water to a concentration of 0.1 M. As a structure director (hard template) and a starting material, commercial ~50 µm thick porous AAO disc (anodic 47, WHATMAN Inc.) with straight macroporous channels ca. ~250 nm in diameter (Fig. 3-1) was immersed in 25 ml of the precursor solution with molar ratio Al/Ti=1 and maintained at 323 K for 1, 3, 5, 7, 12, and 24 hours respectively. To analyze the composition of the resultant material, titania membranes were also fabricated by varying the molar ratio Al/Ti to 2, 0.5 and 0.3 and the reaction temperature to 293K and 373K. After reaction, the samples were removed from the solution and washed with distilled water, then dried at 323 K for 24 hours before characterization. Subsequent heat treatment of the fabricated membranes was carried out by

soaking at 400oC in air for 10 hours. Sample notations and synthesis conditions are listed in Table 3-1.

Table 3-1 Sample synthesis conditions

Sample notation	Molar ration of Ti/Al	Reaction Temperature	Reaction time (hour)	Heat treatment (400oC 10 h)
A0	0	50°C/323K	0	no
A1	1	50°C/323K	1	no
AH1	1	50°C/323K	1	yes
A3	1	50°C/323K	3	no
AH3	1	50°C/323K	3	yes
A5	1	50°C/323K	5	no
AH5	1	50°C/323K	5	yes
A7	1	50°C/323K	7	no
AH7	1	50°C/323K	7	yes
A12	1	50°C/323K	12	no
AH12	1	50°C/323K	12	yes
A24	1	50°C/323K	24	no
AH24	1	50°C/323K	24	yes
A3-T1	1	20°C/293K	3	no
A3-T2	1	50°C/323K	3	no
A3-T3	1	100°C/373K	3	no
A3-C1	0.1	50°C/323K	3	no
A3-C2	0.2	50°C/323K	3	no
A3-C3	1	50°C/323K	3	no
A3-C4	2	50°C/323K	3	no

3.2.2 Characterization

The surface and cross-section morphologies of the membranes were studied by secondary electron imaging (JEOL JSM 6300F, Japan). The crystal phases were identified

by powder X-ray diffraction (XRD, Shimadzu) using Cu K α radiation (50 kV, 40 mA) and a scan speed of 0.5° /min in θ -2 θ mode. The divergence, anti-scatter and receiving slits were fixed at 1°. The crystallite size of AlF_n(OH)_{3-n} (n=1.5, 1.62 and 1.65) was calculated from the (111) peak based on Scherrer's formula. Energy dispersive X-ray (EDX) spectroscopy coupled with scanning electron microscopy (JEM-6360) confirmed the composition of the membranes. The anatase nanocrystallines in the nanotubes were studied by transmission electron microscopy (TEM) using a Jeol JEM 2010 electron microscope operating at 200 kV after dispersing the samples in ethanol using an ultrasonic bath for 30 minutes and collecting the fragments on holey carbon copper-supported grids. Nitrogen adsorption and desorption isotherms were recorded at 77 K using an Accelerated Surface Area and Porosimetry System (ASAP 2020) after the membranes were vacuum dried at 373 K for 12 hours to remove surface moisture to obtain the mesopore size distribution using the Barrett-Joyner-Halenda (BJH) method.

3.2.3 Photocatalytic Activity Test

The photocatalytic activity of the fabricated membranes was evaluated by degradation of aqueous methylene blue (MB) dye. An ultraviolet (UV) reaction chamber (RPR-100) was used to irradiate a glass vessel (the glass having 98% transmittance in the UV range). The intensity at 365 nm in the center of the container was 213 $\mu\text{W}/\text{cm}^2$. Prior to catalytic testing, 6 $\pm$ 0.15 mg titania membranes were washed with distilled water and soaked in 50ml distilled water for 24 hours to equilibrate surficial hydroxyl groups. After drying at 323 K for 24 hours, the membranes were immersed in 15 ml MB solution (3.7×10^{-5} M) in the glass reaction vessel. The adsorption equilibrium of the dye by the membranes was established by keeping the container in the dark for 24 hours until the concentration of MB stabilized. The concentration of MB was then monitored by UV-Vis-NIR scanning spectrophotometer. The container was then exposed to UV irradiation and the discoloration of MB monitored by a UV-Vis-NIR scanning spectrophotometer (Shimadzu UV-3101PC) at a wavelength of

664 nm, which is nearly centered at a strong adsorption band of MB and its decomposition products. To provide a baseline, the photocatalytic activity of a porous AAO template was measured under identical conditions.

3.3 Microstructural Evolution

3.3.1 Composition

The EDX results from the surface of samples have shown that the alumina has been completely replaced by titania after 1 hour of reaction (Fig. 3-5). There is no Al incorporation in the titania when the reaction is completed on the surface. It is also observed that alumina has not been entirely displaced at the internal part of the templates from a EDX spectra of Al cross sections (Fig. 3-6). The results suggest that reaction takes place layer by layer in the AAO template. It is important to consider the supersaturation of the

Figure 3-5 EDX spectra of the surface of AAO, 1-h and 5-h immersed membranes.
(The presence of Au should be attributed to the coatings on the samples for SEM observation)

Figure 3-6 EDX spectra of the cross-section in 1-h immersed membranes.
(The presence of Pt should be attributed to coatings on the samples for SEM observation)

solution may account for this layer-by-layer reaction.

It is observed that the reaction rate decreases with reaction time (Fig. 3-7). According to equation (3.1), the weight of the titania membrane will increase after reaction. Hence, the increase of AAO weight indicates the content of titania precipitation and reaction rate. The decrease of reaction rate indicates that the degree of supersaturation decreases as reaction proceeds.

Compared with B^{3-} in traditional LPD, Al^{3+} is more capable of eliminating the F^- in the reaction solution through forming $[AlF_6]^{3-}$. The alumina in AAO surface reacted almost immediately (less than one hour) and results in the decrease of supersaturation of solution (Fig.3-7 A). Hence, the reaction rate decreases. When the supersaturation decreases below the level that titania can continuously precipitate, the increase of weight tended to be saturated (Fig. 3-7 D). Decrease of supersaturation can adequately explain the layer-by-layer reaction in AAO templates, as the decrease of supersaturation prevents the solution diffusion from entering into the membranes.

Figure 3-7 The weight increment of AAO template with reaction time.

3.3.2 Macroporous Titania Membranes

The AAO template consists of nearly hexagonal macroporous arrays (240~250 nm diameter) with wall thickness ~50 nm. After 1-h immersion, self-aligned titania nanotube arrays with ~250 nm diameter were deposited by replacing the alumina through in-situ titania growth. The titania nanotube arrays retained their integrity by bonding to the residual alumina in the middle of the AAO initially, which probably were protected from the layer by layer reaction (Fig. 3-8 A1). The length of titania nanotube arrays are ~6 μm, which is only about 1/10 the thickness of AAO template. At this stage, separated titania nanotubes will fall apart without the remaining template (Fig. 3-9 A1).

With the increase of reaction time, the diameter of pore decreases to ~ 100 nm in A5 (Fig. 3-8 A3, A5) and the wall thickness also increases to ~ 100 nm. This is attributed to titania continuously growing on the surface of the nanotubes in A1, which also may cause the walls of the nanotubes to merge together. Therefore, titania membranes formed after 5 hours of reaction (Fig. 3-8 A5). The inner topography of the titania membranes (A5) was little changed from the AAO template (Fig. 3-9 A5). The thickness of these titania membranes are ~ 10 μm . The well ordered macropores with diameter of ~ 100 nm parallel to each other are orientated perpendicular to surface in the titania membranes for the A5 sample. After a 5 h reaction, further growth of titania on the top of AAO forms a $1\sim 2$ μm thin layer that covers the macropores after 12-h reaction. According to these observations, the thickness of AAO template can be modified to ~ 10 μm . Hence, well-ordered macroporous titania membranes without residual alumina can be expected.

Figure 3-8 Micrographs of porous AAO membrane templates immersed for different reaction times.

Figure 3-9 Cross-section of A1 and A5.

The thickness of the titania layer increases with reaction time: $\sim 6 \mu\text{m}$ for 1 hour, $\sim 10 \mu\text{m}$ for 5 hours and $\sim 12 \mu\text{m}$ for 12 hours. Clearly, the increase in thickness after 5 hours is not apparent because the layer covered on the A5 sample prevents solution from penetrating into AAO. The densification in this layer after 12 hours is the result of the remaining Ti^{4+} species.

The structure evolution tells us that the template structure is preserved as the dissolution and precipitation of Ti^{4+} ions occurs almost simultaneously due to its low solubility. The kinetics constant K_{sp} was finite and this limited the mobility of Ti^{4+} , which in turn, resulted the ionic migration over the membrane surfaces or the neighboring tubes in the initial reaction (Fig. 3-7 A). With increasing reaction time, more Ti^{4+} ions appear in the solution, and the ionic migration to neighboring tubes is released, which results in the merging of tubes and formation of membranes (Fig. 3-7 B). But after 5 hours, the mobility of Ti^{4+} was further increased, Ti^{4+} ions started to migrate farther to the surface of templates and the dense layer on top was then formed (Fig. 3-7 C).

3.3.3 Mesoporosity in Titania Membranes

In theory, the surface area of the titania nanotubes with 200 nm diameter and 50 nm wall thickness will be $11.4 \text{ m}^2/\text{g}$ (anatase density is 3.84 g/cm^3). In the present work, more

than 100 times higher surface area was observed for the 1-h fabricated titania from adsorption analysis (Table 3-2). Obviously, the walls of the titania nanotubes are believed to be porous (Fig. 3-10). Moreover, the N_2 adsorption and desorption isotherms obtained for the samples (Fig. 3-11) were typical IUPAC types IV. The hysteresis loop in the isotherm curve indicates a mesoporous structure. The average mesopore size distribution is ~ 4 nm (Table 3-2).

Figure 3-10 Surface area of fabricated titania with different reaction time.

The dramatic increase in surface area after immersion can be attributed to the replacement of dense alumina by porous titania, but further reaction causes particle growth, resulting in a reduction of surface area (Fig. 3-10). The pore diameter (~ 4 nm) suggests that the mesopores are not located between the titania nanotube arrays, which should be ~ 39 nm. Moreover, the pores between titania nanotube arrays may become smaller when the walls of tubes start to merge together. These pores will be located in the titania walls.

Figure 3-11 Isotherms and BJH pore size distribution of the fabricated membranes immersed for different reaction times

Calcination at 400°C leads to a decrease in surface area and an increase in pore size distribution (Fig. 3-10, Fig. 3-11). This implies that the grain growth during heat treatment process destroys the mesoporous structure. These pores cannot trap MB molecules in a photocatalytic test due to the increase of pore diameter, and the adsorption ability of the annealed sample decreases dramatically. (This will be shown later in the photocatalytic

Figure 3-12 Micrographs of the titania membranes calcined at 400°C for 10 h. (The upper and bottom parts of each micrograph are original and cross-section respectively)

Table 3-2 Surface area and pore diameter of membranes

	Surface area (m ² /g)		Pore Diameter (nm)	
	as-fabricated	after annealing	as-fabricated	after annealing
A0	7.8	--	250	--
A1	137.8	81.3	3.5	3.5, 4.5
A3	123.84	70.6	3.9	4.0, 9.08
A5	72.9	55.5	4	4.0, 9.1
A7	65.5	48.5	3.3	3.6, 12.6
A12	51.7	40.6	3.8	3.6, 9
A24	38.1	20.3	4	3.5

results). The macroporous structure after 1~5 hours immersion remained open after the annealing process (Fig. 3-12 a). However, for membranes immersed for longer durations (>7 h), heat-treatment unevenly densifies the top titania layer (Fig. 3-12 b) and results in a closed macroporous structure. This, in turn, significantly decreased photocatalytic activity by blocking the entry of MB to the tubes (as shown in photocatalytic results later).

Direct observation of these pores by TEM confirmed an aperiodic structure with a pore size of 4 ± 0.8 nm (Fig. 3-13 a, b), which is consistent with average pore size obtained in BET analysis (Table 3-2).

Figure 3-13 TEM images of single anatase nanotube reacted for 1 h
(a, b: mesoporous wall; c: nanocrystallite titania in the wall)

3.4 Crystal Phases

AAO templates are amorphous. Immersion for 1 hour in AHFT leads to the formation of both poorly crystallized anatase and large crystals of $\text{AlF}_n(\text{OH})_{3-n}$ ($n=1.5, 1.62$ or 1.65) (Fig. 3-14). For example, anatase has an average crystallite size of < 5 nm as compared to

Figure 3-14 X-ray Diffraction patterns of the porous AAO templates immersed for different reaction times.

(a: A0, b: A1, c: A3, d: AH3 and e: A24)

~45 nm for $\text{AlF}_n(\text{OH})_{3-n}$ in the A1. However, the stoichiometry of $\text{AlF}_n(\text{OH})_{3-n}$ ($n=1.5, 1.62$ or 1.65) could not be determined by XRD due to the similar X-ray scattering power of F^- and OH^- , and it is possible that a range of compounds may co-exist. $\text{AlF}_n(\text{OH})_{3-n}$ phases locate principally between the titania layer and residual AAO template, specifically on the inner membrane surfaces attached to partially reacted alumina with a grain size of ~30-50 nm. Moreover, fluoride can only be detected where $\text{AlF}_n(\text{OH})_{3-n}$ was detected (Fig. 3-13 b and d). The number of $\text{AlF}_n(\text{OH})_{3-n}$ crystals observed by SEM is quite small as compared with anatase, but these crystals diffracted X-rays strongly as a result of their high crystalline size and crystallinity (Fig. 3-15). From the location of the $\text{AlF}_n(\text{OH})_{3-n}$, the formation mechanism was probably explained by the decrease of supersaturation such as the insufficiency of the fluoride with reaction time as indicated by equation (3.2)

Figure 3-15 Cross-section morphology of the 5-h immersed membrane before (a: A1) and after (b: AH1) heat-treatment at 400°C.
(White arrows indicate the location of $\text{AlF}_n(\text{OH})_{3-n}$ and black arrows refer to partially reacted alumina)

After heating to 400°C, anatase is well developed, but the reflections of $\text{AlF}_n(\text{OH})_{3-n}$ disappear due to its decomposition and volatilization at 400°C to amorphous Al_2O_3 and AlF_3 as shown in equation (3.3). The same observation was evident when $\text{AlF}_n(\text{OH})_{3-n}$ disappeared after heat-treatment at 400°C (Fig. 3-15 a and b).

$\text{AlF}_n(\text{OH})_{3-n}$ phase could not be detected from XRD for the room temperature reaction (Fig. 3-16 a), but was found at > 50°C (Fig 3-16 b, c). However, EDX analysis (not shown) suggests that even at room temperature, a small amount of fluoride was incorporated in the inner membranes (crash membranes) due to the presence of poorly crystalline $\text{AlF}_n(\text{OH})_{3-n}$. Yamanaka et. al. [32] did not report $\text{AlF}_n(\text{OH})_{3-n}$ at 20°C according to their XRD results probably because its was amorphous at ambient temperature.

Figure 3-17 XRD patterns of AAO templates immersed for 3 h at different temperatures in the solutions with atomic ratio of Al/Ti=1.0 (a: 20°C, b: 50°C, c: 100°C)

Figure 3-16 XRD patterns of the AAO templates immersed at 50°C for 3 h in the solution with atomic ratios of Ti/Al equal to (a)0.1, (b)0.2, (c)1.0 and (d)2.0 respectively.

Higher concentrations of titanium precursor solution suppresses $\text{AlF}_n(\text{OH})_{3-n}$ formation and it is barely detectable by XRD at the ratio of $\text{Ti}/\text{Al}=2.0$ (Fig. 3-17). This is consistent with EDX analysis where no fluoride was detected on the surface of fabricated membranes when supersaturation is still high (Fig. 3-5). However, with increasing immersion time, more $(\text{NH}_4)_2\text{TiF}_6$ was consumed, leading to a lower degree of supersaturation and the obvious precipitation of $\text{AlF}_n(\text{OH})_{3-n}$ on the inner membrane walls.

3.5 Photocatalytic activity of titania membranes

When titania is illuminated by UV light, the photons raise electrons from the band gap into the conduction band to create a vacancy in the valence band. These energetic electrons react with water to produce hydroxyl radicals that oxidize the dye, during which methylene blue discolors [33-36].

3.5.1 Adsorption Ability

It can be understood that the adsorption increases with titania content. The increase of pore size and the decrease of hydroxyl groups chemically trapped onto the surface of the membranes after heat treatment at 400°C significantly reduced the adsorption of MB onto

Figure 3-18 Adsorption of MB onto the titania membranes after adsorption equilibrium

the membranes. (Fig. 3-18) [37]. Both factors prohibit trapping the MB molecules (15 Å diameter) in the solution.

3.5.2 Photocatalytic Activity

The degradation of MB by the titania membrane catalyst obeys pseudo first order reaction kinetics as we mentioned in Chapter 2 [35] (Fig. 3-19, Table 3-3). The apparent rate constant of the template is the same as that of blank MB solution under UV irradiation (Table 3-3), which confirms AAO does not contribute to photocatalytic activity.

Table 3-3 Apparent rate constant

Sample	Apparent rate constant k (min⁻¹)	R²
blank	0.0006	0.9935
A0	0.0006	0.9887
A1	0.0046	0.9653
AH1	0.0045	0.9939
A3	0.007	0.9933
AH3	0.0062	0.9976
A5	0.0146	0.9932
AH5	0.0016	0.9789
A12	0.0045	0.9963
AH12	0.0034	0.997

Photocatalytic activity of the anatase is dominated by titania content, surface area and crystallinity. In our experiment, the titania membrane microstructures including pore size and architectures are also important for its performance. The apparent rate constant of as-fabricated titania membranes increases with reaction time (for A1 to A5) because titania content increases. However, for these membrane architectures undergoing further reaction (A12), the most significant factor is the thin titania layer that covers the tubes and blocks MB from entering the inner membrane surfaces and hence decreases accessibility to the matrix of the titania membranes. The photocatalytic activity of A12 is only determined by surface of the top layer. More importantly, the 5-h immersed membranes have the best combination of titania content, surface area, pore size and architectures, and so exhibit the

highest apparent rate constants. On the other hand, reduced photocatalytic activity is observed for membranes with heat treatment, though higher crystallinity of titania was achieved, as the adsorption ability decreases during annealing and can not trap the MB molecules.

(A)

(B)

Figure 3-19 (A) The decolorisation of MB under UV irradiation (B) First order linear relation

The normalization of photocatalytic test was carried out considering the following factors that influence the apparent rate constant: titania content, MB dye content in each test, the ratio of titania surface area to MB content, the ratio of titania weight to MB content, the light intensity of UV source and pH of MB solution. After normalization of the photocatalytic test conditions [36-38], the rate constant ($k=0.0146 \text{ min}^{-1}$) for the 5-h immersed sample without heat treatment was much higher than that reported for Al-containing porous titania networks derived from sol-gel methods ($0.0023/\text{min}$) [39] and Degussa P-25 ($0.0008/\text{min}$) [35], but much lower than sol-gel mesoporous titania films ($0.56/\text{min}$) [40]. These results suggest that self-supporting titania membranes have the potential to be applied as water filters with a self-cleaning function.

Figure 3-20 Working scheme of bi-functional titania membranes

3.6 Conclusions

Self-supporting macroporous membranes with walls composed of mesoporous anatase were successfully synthesized by liquid phase deposition over porous AAO templates. A $\sim 10 \mu\text{m}$ thick well-ordered macroporous titania membrane was obtained after 5-h reaction. After that, the penetration of macroporous structure was inhibited by a titania layer covering the surface. This also leads to degradation in photocatalytic activity due to the

blocking of the MB entry into the membranes. The by-product $\text{AlF}_n(\text{OH})_{3-n}$ ($n=1.5, 1.62$ or 1.65), which precipitated within the membranes, could be eliminated by adjusting the atomic ratio of Ti/Al in the precursors. The membrane, which is fabricated by 5-h immersion in $(\text{NH}_4)_2\text{TiF}_6$ without heat treatment, has the highest rate constant ($k=0.015/\text{min}$). The self-supporting titania membranes in this work may serve as multifunctional filters that are self-cleaning and suitable for the separation of liquid or gaseous waste streams. (Fig. 3-20).

3.7 References

- [1] M. A. Anderson, M. J. Gieselmann, Q. Xu, (1988). Titania and alumina membranes, *Journal of Membrane Science*, 39, 243.
- [2] T. V. Gestel, C. Vandecasteele, A. Buekenhoudt, C. Dotremont, J. Luyten, R. Leysen, B. V. der Bruggen, G. Maes, (2002). Alumina and titania multilayer membranes for nanofiltration: preparation, characterization and chemical stability, *Journal of Membrane Science*, 207, 73.
- [3] T. V. Gestel, C. Vandecasteele, A. Buekenhoudt, C. Dotremont, J. Luyten, R. Leysen, B. V. der Bruggen, G. Maes, (2003). Corrosion properties of alumina and titania NF membranes, *Journal of Membrane Science*, 214, 21.
- [4] M. Miyauchi, H. Tokudome, (2006). Low-reflective and super-hydrophilic properties of titanate or titania nanotube thin films via layer-by-layer assembly, *Thin Solid Film*, 515, 2091.
- [5] H. Masuda, K. Fukuda, (1995). Highly ordered nanochannel-array architecture in anodic alumina, *Science*, 268, 1466.
- [6] Y. Q. Wang, G. Q. Hu, X. F. Duan, H. L. Sun, Q. K. Xue, (2002). Microstructure and formation mechanism of titania dioxide nanotubes, *Chem. Phys. Lett.*, 365, 427.
- [7] Z. Y. Yuan, W. Z. Zhou, B. L. Su, (2002). Hierarchical interlinked structure of titanium dioxide nanofibers, *Chem. Comm.*, 1202.
- [8] Y. J. Lin, L. Wang, W. Y. Chiu, "Preparation and Characterization of Titania Nanotubes and Hybrid Materials Derived from Them, *J. Vac. Sci. B*, 23, 2398, 2005.
- [9] L. D. Gao, Y. Le, J. X. Wang, J. F. Chen, (2006). Preparation and characterization of titania nanotubes with mesostructured walls, *Mater. Lett.*, 60, 3882.
- [10] V. P. Godbole, Y. S. Kim, G. S. Kim, M. A. Dar, H. S. Shin, (2006). Synthesis of titanate nanotubes and its processing by different methods, *Electrochemical Act*, 52, 1781.
- [11] C. C. Tsai, J. N. Nian, H. Teng, (2006). Mesoporous nanotube aggregates obtained from hydrothermally treating TiO_2 with NaOH, *Appl. Surf. Sci.*, 253, 1898.
- [12] L. Q. Weng, S. H. Song, S. Hodgson, A. Baker, J. Yu, (2006). Synthesis and characterisation of nanotubular titanates and titania, *Journal of the European Ceramic Society*, 26, 1405.
- [13] Z. Y. Yuan, B. L. Su, (2004). Titanium dioxide nanotubes, nanofibers and nanowires, *Colloids Surf., A*, 241, 173.
- [14] D. S. Seo, J. K. Lee, H. Kim, (2001). Preparation of nanotube-shaped TiO_2 powder, *J. Crystal Growth*, 229, 428.

- [15] Y. X. Zhang, G. H. Li, Y. X. Jin, Y. Zhang, J. Zhang, L. D. Zhang, (2002). Hydrothermal synthesis and photoluminescence of TiO₂ nanowires, *Chem. Phys. Lett.*, 365, 300.
- [16] T. Kasuga, (2006). Formation of titanium oxide nanotubes using chemical treatments and their characteristic properties, *Thin Solid Film*, 496, 141.
- [17] G. K. Mor, O. K. Varghese, M. Paulose, K. Shankar, C. A. Grimes, (2006). A review on highly ordered, vertically orientated TiO₂ nanotube arrays: fabrication, material properties, and solar energy application, *Solar Energy Material & Solar Cells*, 90, 2011.
- [18] J. Zhao, X. Wang, T. Sun, L. Li, (in press). Crystal phase transition and properties of titanium oxide nanotube arrays prepared by anodization, *Journal of Alloys and Compounds*.
- [19] D. Gong, C. A. Grimes, O. K. Varghese, (2001). Titanium oxide nanotube arrays prepared by anodic oxidation, *J. Mater. Res.*, 16, 3331.
- [20] N. Wang, H. Lin, J. Li, X. Yang, B. Chi, (2006). Electrophoretic deposition and optical properties of titania nanotubes films, *Thin Solid Film*, 496, 649.
- [21] D. G. Shchukin, R. A. Caruso, (2004). Template synthesis and photocatalytic properties of porous metal oxide spheres formed by nanoparticle infiltration, *Chem. Mater.* 16, 2287.
- [22] D. Zhao, P. Yang, B. F. Chmelka, G. D. Stucky, (1999). Multiphase assembly of mesoporous-macroporous membranes, *Chem. Mater.*, 11, 1174.
- [23] S. Ngamsinlapasathian, S. Sakulkaemaruehai, S. Pavasupree, A. Kitiyanan, T. Sreethawong, Y. Suzuki, S. Yoshikawa, (2004). Highly efficient dye-sensitized solar cell using nanocrystalline titania containing nanotube structure, *J. Photochem. Photobiol. A*, 164, 145.
- [24] M. Hernández-Vélez, (2006). Nanowire and 1D arrays fabrication: an overview, *Thin Solid Film*, 495, 51.
- [25] A. Kar, K. S. Raja, M. Misra, (2006). Electro deposition of hydroxyapatite onto nanotubular TiO₂ for implant application, *Surface & Coatings Technology*, 201, 3723.
- [26] M. S. Sander, M. J. Côté, W. Gu, B. M. Kile, C. P. Tripp, (2004). Template-assisted fabrication of dense, aligned arrays of titania nanotubes with well-controlled dimensions on substrates, *Adv. Mater.*, 22, 2052.
- [27] S. Liu, K. Huang, (2005). Straightforward fabrication of highly ordered TiO₂ nanowire arrays in AAM on aluminium substrate, *Solar Energy Materials & Solar Cells*, 85, 125.
- [28] A. Michailowski, D. AIMawlawi, G. Chen, M. Moskovits, (2001). Highly regular anatase nanotubule arrays fabricated in porous anodic templates, *Chem. Phys. Lett.*, 349, 1.
- [29] H. Imai, M. Matsuta, K. Shimitu, H. Hirashima, N. Negishi, (2000). Preparation of TiO₂ fibers with well-organized structures, *J. Mater. Chem.*, 10.
- [30] H. Imai, M. Matsuta, K. Shimitu, H. Hirashima, N. Negishi, (1999). Direct preparation of TiO₂ nanotubes in porous alumina membranes, *J. Mater. Chem.*, 9.
- [31] S. M. Liu, L. M. Gan, L. H. Liu, W. D. Zhang, H. C. Zeng, (2002). Synthesis of single -crystalline TiO₂ nanotubes, *Chem. Mater.* 14, 1391.
- [32] S. Yamanaka, T. Hamaguchi, H. Muta, K. Kurosaki, M. Uno, (2004). Fabrication of oxide nanohole arrays by a liquid phase deposition method, *Journal of Alloys and Compounds*, 373, 312.
- [33] T. Hamaguchi, M. Uno, K. Kurosaki, S. Yamanaka, (2005). Study on the formation process of titania nanohole arrays, *Journal of Alloys and Compounds*, 386, 265.

- [34] J. J. Shyue, R.E. Cochran, N.P. Padture, (2006). Transparent-conducting, gas-sensing nanostructures (nanotubes, nanowires, and thin films) of titanium oxide synthesized at near-ambient conditions, *J. Mater. Res.*, 21,2894.
- [35] T. Zhang, T. Oyama, A. Aoshima, H. Hidaka, J. Zhao, N. Serpone, (2001). Photooxidative N-demethylation of methylene blue in aqueous TiO₂ dispersions under UV irradiation, *J. Photochem. Photobiol. A*, 140, 163.
- [36] S. Lakshmi, R. Renganthan, S. Fujita, (1995). *J. Photochem. Photobiol. A:Chem*, 88, 163.
- [37] L. C. Chen, T. C. Chou, (1993). *Ind. Eng. Chem. Res.*, 32, 1520.
- [38] T. Zhang, T. Oyama, A. Aoshima, H. Hidaka, N. Serphone, (2001). *J. Photochem. Photobiol. A:Chem*, 140, 163.
- [39] F. Huang, M. Zhou, Y.B. Cheng, R.A. Caruso, (2006). *Chem. Mater.*, 18, 5835.
- [40] Y. Zhang, J. Li, J. Wang, (2006). Substrate-assisted crystallization and photocatalytic properties of mesoporous TiO₂ thin films, *Chem. Mater.* 18, 2917.

CHAPTER 4

BLOCK COPOLYMER DIRECTED PERIODIC MESOPOROUS TITANIA FILM

F127 ($\text{PEO}_{106}\text{PPO}_{70}\text{PEO}_{106}$) and PS-*b*-PEO block copolymer templated mesoporous titania thin films with ~12 nm and ~30 nm pore diameters are discussed in this chapter. The pore formation mechanism in this sol-gel system employs an evaporation induced self-assembly (EISA) method. The mesoporous structure in the films forms after removal of F127 at 400°C. For the F127 templated mesoporous titania films, the crystallinity and surface area were improved by adjusting the proton concentration and F127 content in the titania precursor. Photocatalytic activity was twice as effective in the aperiodic structure with higher crystallinity compared to the ordered mesoporous film with low crystallinity. Photocatalytic activity of the low crystallinity film with larger surface areas remained constant.

The ordered mesoporous structure of F127 templated titania film was found to be destroyed during titania crystallization at 400°C. To increase the thermal stability of the titania mesoporous structure during crystallization, the PS-*b*-PEO block copolymer, which completely decomposes at 600°C (higher than F127 decomposition temperature ~350°C), was employed to template titania mesoporous films. The PS-*b*-PEO block copolymer allowed the mesoporous structure to be maintained as titania crystallized. The mesopore diameter was twice the size of the material templated by F127. Various nanostructures of titania, such as islands and network of nanowires, can be developed by adjusting the concentration of TTIP, HCl and the volume fraction of the PEO block in PS-*b*-PEO. The photocatalytic activity of the PS-*b*-PEO titania mesoporous films also proved higher than

the catalyst produced by F127 templating. These results indicate that at low film crystallinity, photocatalytic activity is controlled primarily by crystal perfection, rather than surface area.

4.1 State of the Art

4.1.1 Titania Formation Mechanism during Sol-Gel Processing

The sol-gel process is a classical chemical method used to synthesize dispersed material through the growth of inorganic polymer in a solvent. Recently, the technique was further developed to tailor the structure of oxides in the mesoscale by adding polymer or surfactant [1].

Titania formation mechanism. Titania sol is generated from titanium-organic precursors (titanium oxopolymers, such as titanium n-butoxide and isopropoxide) or titanium tetrachloride in acid alcohol. Titanium oxopolymers are hydrolyzed into monomers which carry four reactive functional groups through nucleophilic addition of water (equation 4.1). This first hydrolysis does not increase the coordination of the titanium. Therefore, the hydrolyzed oligomers, which consist of several monomers, remain reactive. This hydrolysis process can happen because (1) the titanium atom carries a positive partial charge which attracts the negative partial charge of water, (2) the presence of H^+ facilitates the -OR groups to stabilization, and (3) ROH is a low energy solvent material.

Theolation reaction proceeds when the OH group from one Ti atom is added to the coordinated sphere of a neighboring Ti atom. At this stage, the coordination of Ti increases from 4 to 5 or 6,

Continuation of polymerization occurs through a set of nucleophilic substitution reactions as shown in equation (4.3), where residual OR groups are substituted with OH [2].

A titania skeleton forms from the condensation reactions. However, the overall condensation reaction can be inhibited by H^+ which prevents the attack on a Ti atom by the O atom from another TiOH (TiOH is protonated to TiOH_2^+). The dense structure of titania grows from a process where a few large polymers grow first then densify through the capture of unused monomers. This growth only occurs in solutions with higher acidities. Eventually, the resultant titania phase is amorphous, which is evident by the broad peak in FTIR spectra indicating Ti-O-Ti bonding [3-5].

Crystallization of titania. The titania crystallization occurs during the annealing process. Previous studies on the titania powders synthesized from sol-gel methods show that anatase crystallizes around 400°C and rutile appears around 600°C [6]. Anatase (21-1272) is completely transforms to rutile (21-1276) at 800°C . The anatase crystallite size increases continuously from ~ 9 nm to 38 nm, while rutile crystallites grow beyond 42 nm as the annealing temperature increases. The crystallization of titania films is slower than bulk titania due to limited diffusion in the two-dimensional film. The endothermic peak shown from 50°C to 120°C in DSC-TGA analysis was attributed to vaporization of water and oxidative elimination of organic residue. The phase transformation temperature and crystallization temperature relies on the concentration of HCl [7-10].

It was reported that the grain boundaries of titania crystallites can create a porous structure in titania films without using template, but this is not stable and decreases considerably when titania crystallites grow.

4.1.2 Evaporation Induced Self-assembly

A common definition of self-assembly is spontaneous organization of materials through noncovalent interactions (hydrogen bonding, Van der Waals forces, electrostatic forces, π - π interactions, etc.) without external intervention. Generally, they are induced by amphiphilic surfactant molecules or block copolymers composed of hydrophilic and hydrophobic parts [11]. Evaporation induced self-assembly (EISA) through block polymer micelle-assisted templating is also a well established method to tailor the internal topology of ceramics. Introduced by Huo et al [12] for periodic mesoporous silica, this technique has

Figure 4-1 Illustration of (A) cubic and (B) hexagonal or lamellar asymmetry micelle structure formation mechanism in evaporation self-assembly process [13, 14].

been extended to the synthesis of titania as photocatalysts, gas sensors, optical devices, solar cells and filters, in which high surface areas are essential to enhance functionality. During EISA, organic-inorganic hybrids are developed by solvent evaporation, and the organic phase organizes on a mesoscopic scale to serve as a template for the inorganic framework. Non-disruptive solvent evaporation prior to template removal is the key step to obtain highly ordered mesohybrids consisting of interlinked amorphous titania (Fig. 4-1).

4.1.3 Mesophase Formation Mechanism

Surfactant. Classification by ionic type is a convenient way to systematize the organic surfactants based on whether surfactants ionize (Fig. 4-2) [15-17].

Figure 4-2 Classification of surfactant

Figure 4-3 (A) Monotailed surfactant molecules and micelles (B) Schematic phase diagram for CTAB in water [11, 15]

In aqueous solutions, above the critical micelle concentration (c. m. c), block copolymer or surfactant molecules assemble into spherical or cylindrical micelles that maintain the hydrophilic parts in contact with water while shielding the hydrophobic parts interior (Fig. 4-3 A). The size of the micelles, and sphere to rod transformation, are strongly dependent on temperature, anion, and surfactant chain length. Further increases in the concentration of block copolymer or surfactant (in evaporation of solvent or addition of surfactant) results in periodic hexagonal, cubic, or lamellar mesophases (Fig. 4-3 B). However, surfactant self-assembly conducted in aqueous solution of solvable silica species results in spontaneous co-assembly of a silica-surfactant hybrid mesophase. Periodic mesoporous solids can then be created after the removal of the surfactant. The interaction between ionic surfactant and inorganic species is mainly through electrostatic forces. The organic/inorganic interface chemistry uses four synthesis routes with (S^+T), (S^-T), ($S^+X^-T^+$) and (S^-M^+T) directly. Hybrid mesophases are mediated by a combination of surfactant (cationic S^+ , anionic S^-) and soluble inorganic (cationic I^+ , anionic I^-) molecular species. Various mesostructure geometries can be generated by adjusting the charge density matching between the surfactant micelles and inorganic species (Fig. 4-4).

Block copolymer. Block copolymers are macromolecule, produced by joining two or more chemically distinct polymer blocks, each consists of a linear series of identical monomers that may be thermal dynamically incompatible [18, 19]. Their complex structure can give rise to block copolymers with many useful and desirable properties, especially the ability to form regular nanometer-scale patterns. The micelle of the block copolymer can

<p>Surfactant</p> <p>→</p>	<div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> <p>Cationic</p> </div> <div style="text-align: center;"> <p>Anionic</p> </div> </div> <p style="text-align: center;"> C_nH_{2n+1} $n = 8 - 22$ </p>	
	<p>Soluble Inorganic Species</p> <p>↓</p> <p>a. $R'=R=CH_3, C_2H_5, C_3H_7$ b. $R=CH_3, R'=H, (CH_2)_3SO_3^-, OH$ C_2H_5, C_2H_4OH, CH_2 c. $(NR, R') =$ $,$ $,$ C_2H_5N </p> <p style="text-align: right;"> $X = O,$ $, CH_2$ </p>	
<p>Cationic</p>	<p style="text-align: center;">$S^+X^-I^+$</p> <p>Silica (hexagonal, cubic Pm3n, lamellar) Zinc Phosphate (lamellar)</p>	<p style="text-align: center;">S^-I^+</p> <p>Lead Oxide (hexagonal, lamellar) Mg, Al, Ga, Mn, Fe, Co, Ni and Zn Oxide (lamellar)</p>
<p>Anionic</p>	<p style="text-align: center;">S^+I^-</p> <p>Antimony(V) Oxide (hexagonal, cubic Ia3d) Tungsten(VI) Oxide (hexagonal) MCM-41 (hexagonal) MCM-48 (cubic Ia3d), Silicate (lamellar)</p>	<p style="text-align: center;">$S^-M^+I^-$</p> <p>Zinc Oxide (lamellar) Aluminium Oxide (lamellar)</p>
<p>Observed Phases</p>	<p style="text-align: center;">Hexagonal</p>	<p style="text-align: center;">Cubic (Ia3d)</p>
	<p style="text-align: center;">Cubic (Pm3n)</p>	<p style="text-align: center;">Lamellar</p>

Figure 4-4 General scheme for the synthesis pathways for combination of different surfactant and soluble inorganic species [13]

Figure 4-5 Diblock copolymers are predicted to self-assemble according to self-consistent mean field theory [19].

form a variety of ordered structures via the repulsion of the immiscible blocks such as polystyrene (PS), polypropylene oxide (PPO), poly isoprene (PI), poly ethylene-co-butylene (PHB), and poly atactic-poly methyl methacrylate (PMMA). In a simpler case of diblock copolymer AB, the micelle formation behavior can be controlled by the degree of polymerization (N), the composition (f) and the AB Flory-Huggins interaction parameter (χ). The Flory-Huggins equation describes approximately free energy ΔG_{mix} of a blend as shown in equation (4.4).

$$\frac{\Delta G_{\text{mix}}}{k_b T} = \frac{1}{N_A} \ln(f_A) + \frac{1}{N_B} \ln(f_B) + f_A f_B \chi \quad (4.4)$$

The first two items on the right correspond to the configurational entropy of the system, and can be regulated via the polymerization chemistry to vary the relative lengths of the chains with fractions of A versus B polymer. In the third item, χ is associated with the non-ideal penalties of A-B monomer contacts as $\chi = \frac{a}{T} + b$. Below the ODT (Order-Disorder Temperature), when the volume fraction of block A (f_A) is quite small, it forms a sphere in

a body-centered cubic (BCC) configuration surrounded by a matrix of B. As f_A is increased towards 0.5, the minority nanodomains will first form cylinders in hexagonal lattices, then a bicontinuous double gyroid structure, and eventually lamellae (Fig. 4-5).

The S-I interaction is particularly important in block copolymer- metal oxide hybrids, especially in PEO-based system. Studies show that only at a higher concentration of block copolymer, the PPO/PPO (S-S) attractions take over the S-I interactions and microsegregation takes place, and results in a periodic mesophase formation. Especially in titania-based EISA derived systems, addition of water not only promotes hydrolysis, but also assists in phase separation [20-22].

4.1.4 Characterization Techniques

Three reliable characterization techniques are used to characterize the ordered mesoporous structure: small angle X-ray diffraction (SAXS); transmission electron microscopy (TEM) and adsorption analysis (discussed in Chapter 2).

Figure 4-6 The X-ray diffraction patterns and proposed structures of MCM-41, MCM-48, and MCM-50 [20].

Small Angle XRD (SAXS). The symmetry of the mesoporous structure can be identified by small angle X-ray diffraction. At low angle ($2\theta < 5^\circ$), X-ray diffraction is caused by the larger d-spacing (mesophase) in the materials instead of the d-spacing of the lattice. The materials can be treated as a two-phase system: pores and oxide matrix. If the mesopores are three dimensionally ordered and the wall thickness can be neglected comparing with the pore size, a family of peaks appears in the low angle according to Bragg's Law and the peak positions can reflect the asymmetry of the domain in the sample [23-25]. The typical SAXS data recorded from mesoporous silica has been successfully indexed to cubic, hexagonal and lamellar symmetries (Fig. 4-6).

Figure 4-7 Structural Elucidation of the pore structure and the HRTEM of the MCM-48 [26]

TEM. Transmission electron microscopy (TEM) or high resolution transmission electron microscopy (HRTEM) is an effective technique to directly observe the porous structure. It is instructive to summarize the three ways in which HRTEM has elucidated the structures of micro- and mesoporous solids. An image produced by HRTEM corresponds to a map of projected electrostatic potential of electrons along the direction of incident beam. Since atomic scattering amplitudes of electrons are approximately 10^4 - 10^5 times as large as they are for X-rays and neutrons, it follows that, with electrons as probes, structural information may be retrieved from single crystals. Three-dimensional images of the unit cells of the mesoporous silica structure (called MCM-48) were observed by HRTEM, because the porous structure of MCM-48 is well-ordered over a large area, but the walls are amorphous and follow a so-called gyroid surface (a minimal surface) [26] (Fig. 4-7).

It is not straightforward to obtain structural information from TEM for three dimensional mesoporous structure as the images are the projected structural information of the materials along the direction of incidence. For example, the projection of (001) in hexagonal and (111) projection of body centered cubic will result in the same image. The symmetry of mesopores can only be determined by X-ray diffraction. Nevertheless, the structures of 3-D periodic mesostructured silica have been solved successfully by careful studying the TEM images and their Fourier diffractograms [27].

4.1.5 Ordered Mesoporous Materials

Silica. Ordered mesoporous silica is the first but most successful attempt using micelle-assistant self-assembly method. Ionic surfactants (CTAB, CTAC) [28-35], nonionic PEO-based surfactant (Brij-76, tergitol 15-S-12, igepal CA-720) [36-42] and block copolymer (P123, F127 and F108) [43-50] have been used to template ordered mesoporous silica films and powders in last decade. Widely reported are the synthesis of three M41S mesophases, namely, MCM-41(2-D hexagonal), MCM-48 (3-D $Ia\bar{3}d$ cubic), and MCM-50 (Lamellar) (Fig. 4-6). So far, numerous new ordered mesophases have been also discovered such as

SBA-1/SBA-6 ($P6\bar{3}m$), SBA-2/ SBA-12 ($P6\bar{3}/mmc$), SBA-11 ($P6\bar{3}m$), SBA-16 ($Im\bar{3}m$), SBA-8; and some disordered mesoporous structures such as HMS, MSU-n, MSU-V and KIT-I [52-61]. However, it is difficult to control the mesoporous structure on a macroscopic scale. The local ordered porous structure has limited application in special optical and electronic devices. Miyata et. al. [62] introduced a full alignment control of tubular mesopores in mesoporous silica films on the macroscale, in which the symmetry of the mesopores can be identified as single crystalline three dimensional hexagonal ($P6\bar{3}/mmc$). In addition, the pore size was controlled from 2 nm to 20 nm. The most important applications of mesoporous silica reported in the literature remain in the fields of catalysis and environmental remediation [63].

Non-silica materials. The great success in development of mesoporous structures in silica is because of this material thermal stable. However, surfactant and block copolymer templating can hardly be used in the fabrication of non-silica mesoporous materials, although they may find promising applications with electron transport and transfer or magnetic interactions involved. Generally, thermal stability of mesoporous non-silica is of great concern following aspects: susceptibility to hydrolysis; redox reactions; or phase transition and crystallizations that accompany collapse of mesoporous integrity. Even

Figure 4-8 TEM images of ordered non-silica mesoporous materials [65].

though, diverse strategies have been developed to synthesize mesoporous MnO_2 [65, 66], Al_2O_3 [67, 68], TiO_2 [69-72], Nb_2O_5 [73,74], Ta_2O_5 [65], ZrO_2 [65], HfO_2 [74], SnO_2 [65], WO_3 [65], PbS , ZnS [75, 76], GeS , Ge [77, 78], Pt [79] and C [80], using block copolymers or surfactants in the past few years at low temperature (Fig. 4-8), the thermal stability of these mesostructures remains unsatisfactory.

4.1.6 Mesoporous Titania Films

The application of EISA to the synthesis of ordered mesoporous titania is difficult due to the rapid condensation of the precursor and collapse of framework during crystallization. First, it is found that rapid condensation of titania precursor could be decreased by adding acid and by using a dehydrating solution, which inhibits hydrolysis and condensation, improves the quality of micelle-assembly. Second, it is evident that thin-walled mesoporous titania can crystallize rapidly to the detriment of structural integrity, such as the frameworks formed by ionic surfactant templating in the order of 1 nm thick. Early efforts using ionic surfactants have led to poor thermal stability and low crystallinity of the mesostructures [82-86]. Nevertheless, a promising alternative is to use polyethylene oxide (PEO) based block polymers such as F127 and P123 as structure directing reagents [87]. The block copolymer route yields thicker titania walls that are robust towards crystallization (>10nm) [88-92], together with the desirable properties of higher porosity, larger pore diameters, greater order, and lower synthesis cost.

Grain growth during sintering titania may change the mesoporous symmetry. For example, Sanchez et al. [93] reported that a titania mesoporous film with $p6mm$ plane symmetry transformed to $c2mm$ at 350°C due to unidirectional contraction. A range of three dimensionally periodic mesoporous structures including cubic ($Ia\bar{3}d$, $Im\bar{3}m$) and hexagonal ($P6_3/mmc$) forms have also been reported [94-100]. Some recent attempts to increase crystallinity without collapse of the framework include incremental heat treatments

[101], delayed rapid crystallization (DRC) [102], and substrate-assisted crystallization [103].

It is noted that the thermal stability of the F127 templated mesoporous titania film is still unsatisfactory. It was proposed to develop versatile micelle structures of polystyrene-block-polyethylene oxide (PS-*b*-PEO) diblock copolymer in EISA. Compared with F127 and P123, PS-*b*-PEO has higher decomposition temperature ($\sim 600^{\circ}\text{C}$), which can sustain the mesostructures in the titania crystallized at $\sim 350^{\circ}\text{C}$. This polymer was first used for precipitation of titania nanoparticles formed in a geometric pattern on a silicon substrate [104-108]. Only recently, it was found that the cylindrical microdomains of symmetric PS-*b*-PEO diblock copolymer micelles, could facilitate the synthesis of titania crystals aligned perpendicular to the substrate surface [109-115]. Therefore, mesostructured titania templated by PS-*b*-PEO is seldom reported [116].

Nanocrystalline anatase films have been investigated extensively during last decade as ultraviolet (UV) photocatalysts dependent on crystallinity and surface area. As UV transmission and chemical adsorption can be enhanced by producing mesoporous titania as thin films on transparent glass substrates, the present study was directed towards the fabrication of highly crystalline coatings with high photocatalytic efficiency for the oxidation of methylene blue (MB), a model pollutant. In this work, a new approach for enhancing the crystallinity and surface area of mesoporous titania by adjusting proton concentration and F127 template content of the precursor solution is reported. On the other hand, crystallinity is also increased by higher annealing temperature. Homogeneous mesoporous titania film templated by PS-*b*-PEO block copolymer was annealed at 600°C . In addition, various mesostructured titania film morphologies were observed by adjusting the concentration parameters in the solution and PS volume fraction.

4.2 Experiment Procedures

4.2.1 Mesoporous Titania Film Templated by F127

The primary reagent was a mixture of titanium isopropoxide $\text{Ti}[(\text{CH}_3)_2\text{CHO}]_4$ (TTIP) and acetylacetone (AcAc) in a 1:0.5 molar ratio, which was slowly added to ethanolic solutions containing the template F127 ($\text{PEO}_{106}\text{-PPO}_{70}\text{-PEO}_{106}$), hydrochloric acid (HCl, 37%) and distilled water (Table 4-1). Mesoporous films were fabricated by spin-coating (3000 rpm for 1 minute) these mixtures on commercial silica glass slides, followed by sequential solvent evaporation at 24°C for 2 days, 50°C for 2 days, 120°C for 1 day, 200°C for 12 h and 300°C for 4 h, and finally sintering at 400°C for 12 h to burn away the template. The baseline materials were fabricated through the solvent evaporation of the solution. The powder was finally annealed at 400°C for 12 h.

Table 4-1 F127 Templated film properties and synthesis conditions

Sample		Ft0/Fh0	Ft1	Ft2	Ft3	Fh1	Fh2
Composition molar ration in solution	EtOH	40	40	40	40	40	40
	TTIP	1	1	1	1	1	1
	AcAc	0.5	0.5	0.5	0.5	0.5	0.5
	HCl	0.5	2	3	3	0.5	0.5
	H ₂ O	15	15	15	20	15	15
	F127	0.005	0.005	0.005	0.005	0.01	0.015
Crystal size (nm)		< 2	3.5	6.1	< 2	< 2	< 2
Surface area (cm ³ /g)		110	88	89	137	185	223
Pore volume (cm ³ /g)		0.243	0.232	0.208	0.295	0.379	0.476
Pore diameter (nm)		6	6	6	6.4	7.3	9.4
Film thickness (nm)		128±5	-	124±8	141±9	-	295±5
Apparent rate constant k (min ⁻¹)		0.0009	-	0.0018	0.0009	-	0.0021
R ²		0.9886	-	0.9902	0.9816	-	0.9979
Volume normalized k ₀ (min ⁻¹ cm ⁻³)		0.938	-	1.94	0.85	-	0.95

4.2.2 Mesoporous Titania Film Templated by PS-*b*-PEO

Two kinds of PS-*b*-PEO block copolymer with PEO volume fractions of 0.25 (P25) and 0.35 (P35), having molecular weights of 25400 and 90000 respectively, were dissolved in 1,4-dioxane, which is a good solvent for PS and PEO blocks. Titanium isopropoxide $\text{Ti}[(\text{CH}_3)_2\text{CHO}]_4$ (TTIP, 99.9%, Aldrich) and hydrochloric acid (HCl, 37%, Honeywell) were then slowly added into the solution with molar ratio of 1,4-dioxane: TTIP: HCl: H_2O : P35=45.4: 3: 1: 3.7: 0.44×10^{-3} and 1,4-dioxane: TTIP: HCl: H_2O : P25=45.4: 1: 1: 3.7: 1.58×10^{-3} , respectively. Films were spin-coated on a silicon substrate at 2000 rpm for 1 min, and named as TP35 and TP25 respectively. The effects of TTIP and HCl content on mesostructures were studied, as listed in Table 4-2. After that, the films were aged in evaporation induced self-assembling process at 80°C for 48 h, and the template was removed at 400°C for 4 h and at 600°C for 2 h.

Table 4-2 Gel composition in PS-*b*-PEO template system

Sample notation	PS- <i>b</i> -PEO (P35) $\times 10^{-3}$	PS- <i>b</i> -PEO (P25) $\times 10^{-3}$	1,4-dioxane	HCl	H_2O	TTIP
TP35	0.44	0	45.4	1	3.7	3
TP35-T	0.44	0	45.4	1	3.7	2
TP35-H	0.44	0	45.4	2	3.7	2
TP25	0	1.58	45.4	1	3.7	1
TP25-T	0	1.58	45.4	1	3.7	2

Different thermal treatments were adopted in F127 templated titania and PS-*b*-PEO templated titania based on the fact that the two templates decompose at different temperature. For F127 templated titania, there is no difference in crystal size and decomposition of templates when the films were annealed at 400°C for 2 h to 12 h (F127 template was completely removed by annealing for longer time). For PS-*b*-PEO templated titania, annealing at 400°C for 4 h aims to remove the PEO block in the template and further solidifies the titania matrix. Finally, in order to remove the PS in PS-*b*-PEO template, films was annealing at 600°C for 2 h. TGA results showed that the templates was completely removed at 600°C for 2 h.

4.2.3 Characterization

The surface morphology of the mesostructured titania films was observed using a field emission scanning electron microscope (SEM, JEOL JSM 6300F, Japan). The mesoporous films were studied by transmission electron microscopy (TEM) using a Jeol JEM 2010 electron microscope operating at 200 kV by scratching the films into ethanol, dispersing the suspension in an ultrasonic bath for 5 min, and collecting fragments on a holey-carbon film supported by a copper grid. Pore configurations of the titania films were studied by small angle X-ray diffraction (SAXS) from 0.15° to 3° with Cu K α radiation ($\lambda=1.54 \text{ \AA}$, 45 kV, 35 mA) using a Bruker AXA Nanostar system. Powder X-ray diffraction (XRD-6000, Shimadzu) patterns were obtained with CuK α radiation (50 kV, 40 mA) and a scan speed of $0.5^\circ/\text{min}$ in θ - 2θ mode. The divergence, anti-scatter and receiving slits were fixed at 1° . Nitrogen adsorption and desorption isotherms were collected at 77K using an Accelerated Surface Area and Porosimetry System (Micrometics 2000) after the delaminated films from the glass substrate were vacuum dried at 300°C for 4 h to remove surface moisture. The pore diameter distribution and pore volume were calculated from the nitrogen desorption isotherm using the Barrett-Joyner-Halenda (BJH) method. The temperature at which the template decomposed was studied by thermal gravimetric and differential thermal analysis (TG-DTA) (PerkinElmer, SDT 2960). The solution was put in a glass plate and heated at $50\sim 80^\circ\text{C}$. After solvent evaporation, the gel was solidified, then put 5 mg sample in the TG-DTA, ramping $10^\circ\text{C}/\text{min}$ from room temperature to 900°C at air atmosphere.

4.2.4 Photocatalytic Activity Test

Mesoporous films on glass (2 pieces $\times$ 1.5 cm $\times$ 2.5 cm) were washed and stored in distilled water (100 ml) for 24 h to equilibrate hydroxyl groups on the titania surface. After drying at 50°C for 24 h, the films were immersed in 15 ml of MB solution with an initial concentration of $3.6\times 10^{-5} \text{ M}$, which had been prepared by dissolving 13.5 mg methylene blue ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}\cdot 3\text{H}_2\text{O}$, SIGMA) in 1 L of distilled water with stirring for 24 h. Aging in

the dark was carried out in a glass container (the glass having 98% transmittance in the UV range). A UV reaction chamber (RPR-100) was used to irradiate the glass container, with an intensity of $213 \mu\text{W}/\text{cm}^2$ peaking at 365 nm at the center of the vessel. The adsorption and desorption equilibrium of MB over the films was established by keeping the glass container in the dark for several hours before UV irradiation. Photocatalytic activity was monitored by tracking the decolorisation of MB using a UV-Vis-NIR scanning spectrophotometer (Shimadzu UV-3101PC) at the absorption band centered at 664 nm. The contribution from photolysis pristine glass and silicon substrates was monitored in a similar way.

4.3 Ordered Mesoporous Titania Film Templated by F127

4.3.1 Thermal Analysis of F127 and Titania Hybrids

Mesoporous titania films formed from complete removal of the F127 template were also thermally analyzed. The pure polymer decomposes exothermically at 247°C in air (Fig. 4-9), however, for hybrid materials, decomposition is delayed to $\geq 284^\circ\text{C}$ especially those

Figure 4-9 TG-DTA curves obtained for hybrid titania films with various F127 contents (solid line) and pure F127 (dotted line)

with higher F127 contents (up to 70 w% in titania matrix). This can be attributed to higher coordination between the PEO and titania (Fig. 4-9). A similar trend was also reported for P123-titania hybrid materials [88,117]. Higher proton concentrations in the gel do not retard decomposition as it does not modify interaction between polymer and titania. In all hybrid films, the F127 template was completely removed when calcined at $\geq 350^{\circ}\text{C}$. On this basis, the mesostructures were studied at 200°C prior to template removal, while titania crystallization was investigated at 400°C after oxidation of the polymer.

4.3.2 Effect of Proton Concentration

After annealing, the titania film with highest crystallinity was prepared from solutions with higher proton concentrations (Fig. 4-10). The size of the crystals was determined from the width of the (101) anatase reflection in the XRD patterns using the Scherrer method (Table 4-1). The same trend was also observed in titania powders synthesized by heating gels at 300°C for 12 h, suggesting that, in general, higher proton concentrations decrease the temperature of crystallization. It is well accepted that protons control TTIP hydrolysis and condensation by facilitating the initial hydrolysis reaction but inhibiting the overall

Figure 4-10 XRD patterns of film synthesized from solutions with different proton concentrations.

(The crystalline size calculated from (101) peak centered at $\sim 25^{\circ}$ is shown in brackets).

condensation reaction. In this case, it is believed that titania oligomers consisting of several monomers are produced from the initial hydrolysis and condensation of a stable solution. However, Kallala et al. [118] found that dense growth of titania oligomers proceeded only at higher proton concentrations. It is proposed that during EISA condensation, large numbers of dense oligomers resultant from solvent evaporation of high proton concentration solutions formed a titania framework. More numerous homogeneous nucleation sites gave rise to high crystallinity during annealing (Fig. 4-10).

Figure 4-11 Bright field transmission electron micrographs of mesostructure titania films synthesized from various proton concentrations and heating to 200°C (A: a, B: a, C: a) and 400°C (A: bc, B: bc, C: bc). The diffraction patterns reflecting the crystal size of anatase were taken from b images in each group; A: Ft0 synthesized from the solution with HCl/Ti=0.5/1, B: Ft1 synthesized from the solution with HCl/Ti=1/1, B: Ft2 synthesized from the solution with HCl/Ti=2/1.

Although protons control the formation of the hybrid mesophase by inducing hydrogen bonding between the nonionic block polymer and the titania oligomers [88], increasing the content above a critical level (pH=1.2, Ti/HCl=1/0.5) has no effect on the mesostructures heated at 200°C (Fig. 4-11). However, crystallization and template removal at 400°C for 12 h in Ft0 (lowest proton concentration) yielded a well ordered mesoporous structure, whereas, poor periodicity was observed in the Ft1 film (4×proton concentration), and a completely disrupted film was formed in Ft2 (6×proton concentration) (Fig. 4-11).

Figure 4-12 SAXS patterns of the mesoporous thin films synthesized at various HCl concentrations and heated at (a) 200°C for 8 h annealed at (b) 400°C for 12 h.

TEM showed that the combination of pore size and wall thickness in the film was ~ 122 Å after annealing, and is consistent with SAXS results where the strongest diffraction peak occurs at 127 ± 4 Å. Nevertheless, the determination of mesopore symmetry by TEM imaging is ambiguous as the $(111)_{\text{cubic}}$ plane projection cannot be differentiated from the $(001)_{\text{hex}}$ planes (Fig. 4-11A). After annealing at 400°C , mesopore ordering was uncorrelated three dimensionally as a family of diffraction peaks in SAXS was absent. This is in contrast to other reports where a body centered cubic structure ($Im\bar{3}m$) was obtained using the F127 template and TiCl_4 in the molar ratio of $\text{F127/Ti}=0.005/1$ [89]. According to the F127-water phase diagram [119], the most likely mesostructure symmetry after heating at 200°C in the current experiment will be primitive cubic such as $Pm\bar{3}m$ with a cell edge of ~ 120 Å obtained by indexing the d-spacing at ~ 120 Å as (100). The broad peak at ~ 85 Å was assigned as (110) (Fig. 4-12a). Annealing at 400°C removes the template and crystallization destroys a three-dimensionally ordered mesoporous structure recognizable by SAXS in the films. One- or two-dimensional order was observed from Ft0 and Ft1 in TEM images. The Ft2 film annealed at 400°C was completely disrupted and order was not apparent by X-ray diffraction or electron microscopy. It is evident that proton concentration directly affects the stability of mesopore order towards sintering in titania films.

Water content regulates the interaction between the block copolymer and titania during aging, which in turn controls micelle formation in EISA [92]. The present results show that increasing the $\text{H}_2\text{O/Ti}$ ratio to 20 in the Ft3 sample yields superior mesoporous order after sintering (Fig. 4-13a). SAXS contained two strong peaks for the 200°C sample that could be indexed to a primitive cubic unit cell with a ~ 120 Å (Fig. 4-13b). Although higher water content did increase the order of the titania-polymer hybrid film, the removal of F127 at 400°C led to poorer crystallinity as the proton concentration had been diluted (Fig. 4-13).

(A) Ft3

(B)

Figure 4-13 The ordered mesoporous titania with water assistant (A) TEM images of mesostructure titania film Ft3 after annealing at 400°C for 12h (B) SAXRD patterns of the Ft3 mesoporous thin film heating at 200°C and annealing at 400°C.

Figure 4-14 SAXS patterns of the mesoporous thin films synthesized with various F127 concentrations (a) Heating at 200°C for 8 h; (b) annealing at 400°C for 12 h.

4.3.3 Influence of F127 Template

As template concentration increases, the d-spacings observed by SAXS and TEM dilated in tandem with the pore size (Fig. 4-14). However, a sponge-like mesoporous structure, rather than three dimensional order, was observed (Fig.4-15). This is in contrast with earlier investigations where increasing template content during EISA resulted in hexagonal and lamellar mesostructures after heat treatment [105]. These different outcomes probably occur due to the fact that fast evaporation during spin-coating limits micelle

Figure 4-15 TEM images of mesostructure titania film synthesized from various F127 concentration solution. (The diffraction pattern is taken from b in each group).

packing perfection for the F127 block polymer. The single reflection in the SAXS pattern indicates a uniform pore size and wall thickness in one dimension. It is noted that the surface area of the film increased with template content (Table 4-1), but the crystallinity and crystal size were poorly developed and remained constant irrespective of template content according to powder XRD.

Figure 4-16 Isotherms of physical adsorption and desorption of nitrogen for films synthesized with different proton, template and water content in the solution.

4.3.4 Pore Volume and Diameter

The physical adsorption and desorption isotherms of nitrogen by the films were typically type IV and consistent with a mesoporous structure (Fig. 4-16). The pore diameter, pore volume and surface area all increased with polymer content (Table 4-1). The order of mesopores was disrupted in high concentrations of HCl, but the pore volumes of

the films decreased slightly from 0.24 to 0.21 cm³/g (Table 4-1) after annealing at 400°C. In summary, pore volume can be enlarged by increasing the template content. The pore diameter distribution was consistent with the TEM images (~10 nm), and dilated marginally after annealing due to the wall shrinkage.

4.4 Mesostructured Titania Film Templated by PS-*b*-PEO

4.4.1 Thermal Analysis of PS-*b*-PEO

To increase the thermal stability of the mesoporous structure of titania, PS-*b*-PEO was used considering its higher decomposition temperature. Thermal analysis of mesophase hybrid titania and PS-*b*-PEO shows that PEO block is decomposed at around 260°C (Fig. 4-17), however, the PS block is found to decompose around 440°C after titania crystallization in air, which can later serve as a scaffold to titania crystallization in the mesophase.

Figure 4-17 TG-DTA curve obtained for TP35 mesostructured titania film.

4.4.2 Mesoporous Titania Film Templated by PS-*b*-PEO

Mechanism. First, hexagonal micelle formation is induced by addition of HCl and water in the PS-*b*-PEO solution (Fig. 4-18 a). After that, titania was formed in the hydrophilic PEO domain through hydrogen bonding provided by HCl (Fig. 4-18 b). Finally, the mesostructured titania hybrid film was formed by evaporation of solvent (Fig. 4-18 c, d). Moreover, it worthy of note that the inverse micelle is formed if the volume fraction of PEO block decreases in PS-*b*-PEO. This results in mesostructured titania islands formed on the PEO block inside micelle and isolated by PS block.

Figure 4-18 The formation mechanisms of TP35 and TP25 mesostructured titania by PS-*b*-PEO diblock copolymer.

Figure 4-19 FESEM images of TP35 mesoporous titania film after annealing at 600°C for 2 h.

Mesoporous Titania Films. Up to now, the pore diameter in titania films templated by PEO-based block polymer was controlled in the range of 8~20 nm. In this work, large scale ($>1 \text{ mm}^2$) mesoporous titania with homogeneous pore diameter ($\sim 30 \pm 3 \text{ nm}$) was formed after annealing TP35 film at 600°C for 2 hours (Fig. 4-19). These nearly hexagonal packed mesopores were perpendicular to substrate surface. In the TP35 film, the orientation of these hexagonal PEO domains was explained by the micelle formation mechanism in PS-*b*-PEO films with absence of titania by EISA method [113]. However, by careful control of the parameters in the solution, the formation of titania in hydrophilic PEO domain was subsequently formed with the same mesostructure. Interestingly, the TP25 film consisting of hexagonally packed titania islands was observed. The diameters of the titania islands were $440 \pm 10 \text{ nm}$ at 80°C and decreased to $330 \text{ nm} \pm 10 \text{ nm}$ due to shrinkage when annealed at 600°C (Fig. 4-22). This structure is a result of the inverse micelle structure in TP35 film.

4.4.3 Versatile Mesostructured PS-*b*-PEO Templated Titania Film

It is interesting to note that various mesostructured titania film can be observed by adjusting the TTIP and HCl content. In this section, several structures will be discussed .

Figure 4-20 FESEM images of TP25 mesoporous titania film (b) after heating at 80°C and (a) annealing at 600°C for 2 hours

Figure 4-21 SEM images of morphology in TP25-T film

Titania islands in TP25. According to micelle structure of P25, titania islands can be aligned on the substrate surface (Fig. 4-20). Moreover, the size of the titania island in TP25 film can be controlled by adjusting the TTIP content in the solution. Increasing TTIP content of TP25 results in an increase of the titania island size in TP25-T sample (Fig. 4-21). Decreasing the TTIP content in the solution decreases the titania island [111]. Therefore, TTIP content is the dominant factor which controls the titania nanoparticle size and arrangement on the substrate surface.

Figure 4-22 SEM images of morphologies in TP35 with (a) TP35-T and (b) TP35-H.

Titania Nanowires in TP35. For TP35 film, decreasing TTIP content in the solution changes the mesoporous structure to nanowires. This may be attributed to the incomplete formation of a mesoporous structure, which is the result of lack in titania source (Fig. 4-22 a). With the increase of the titania source, the mesoporous structure can be formed in TP35 films. Therefore, the thickness of the titania wall in TP35 could be further increased by increasing TTIP content. It is also observed that the HCl content could affect the length of

titania nanowires (Fig. 4-22 b). The HCl content in the TP35 titania mesostructure are hence responsible for the width and length of the nanowires, and the TTIP content controls the titania mesoporous structure integrity.

This result indicates that the volume fraction of the PEO block in the PS-*b*-PEO is responsible for the formation of titania both outside and inside the micelle. It further determines the titania film matrix structure to be porous or island-like.

4.4.4 Crystallinity and Crystalline Size

The properties of mesoporous titania are commonly limited by its low crystallinity. The novelty of the mesostructured titania synthesized by PS-*b*-PEO block polymer is that the structure remains thermally stable up to 600°C with the help of the PS block (that serves as a scaffold to support the titania during crystallization at higher temperature). XRD patterns of the TP35 and TP25 films showed the crystallinity and titania crystalline size (~20 nm) are both high (Fig. 2-23). This could be attributed to the thicker wall in the mesoporous TP35 film and titania crystallization at 600°C. The crystal size is consistent with that observed TEM (Fig. 2-24 a). However, after annealing at 700°C for 2 h, rutile appears in TP35 film and shrinkage caused the cracking of mesoporous structure.

Figure 4-23 (a) XRD patterns of mesostructured titania film TP25 and TP35 after annealing at 600°C for 2h. (b) XRD patterns of the powder of TP35 after annealing at various temperatures.

Figure 4-24 High resolution transmission electron microscopy (HRTEM) images of TP35 mesoporous titania film

4.5 Photocatalytic Activity of Mesoporous Titania Films

4.5.1 The Influence of Surface Area and Crystallinity of F127 Templated Film

Previous studies of photocatalytic activity in mesoporous films focused on the increase in crystallinity from firing at higher temperatures (600°C), since amorphous titania is reported a less effective catalyst. However, these methods are constrained by the selection of substrates that should have high thermal stability and are UV transparent (e.g. quartz). This study overcame these limitations by using protons to modify titania crystallization, so as to simultaneously retain a higher surface area after sintering at 400°C on a glass substrate. Moreover, the surface area can be enlarged by increasing the F127 polymer content.

Photocatalytic activities of mesoporous films modified by adjusting these parameters were evaluated by monitoring the rate of degradation of MB. It was found that Ft2 and Fh2 mesoporous films decolorized MB rapidly (Fig. 4-25), obeying pseudo-first-order kinetics

initially (Table 4-1). The ordered mesoporous titania film Ft0 showed low photocatalytic activity ($k=0.0009 \text{ min}^{-1}$), which is attributed to its low crystallinity. Conversely, the heavily disrupted mesoporous structure of Ft2 had a slightly lower surface area, but gave a higher rate constant (0.0018 min^{-1}). When crystallization was inhibited by water in Ft3, photocatalytic activity decreased to that of Ft0. It is evident that mesoporous films with higher surface area and constant crystallinity do not show enhanced photocatalysis, suggesting that crystallinity is the dominant factor for photocatalytic activity, especially when the crystalline content is low [120]. However, when crystallinity is $>60\%$ (with 40% amorphous content), surface area becomes the major contributing factor influencing photocatalysis. Therefore, there exists a critical compromise for crystallinity and surface area in optimizing photocatalytic activity of titania.

Figure 4-25 MB degradation as a function of irradiation time

(a)

(b)

Figure 4-26 (a) Adsorption and degradation of MB by TP35 mesoporous titania film and reference pure silicon substrate as function of time (b) First order linear relation and the determination of the apparent first order degradation rate constant, k

4.5.2 Photocatalytic Activity of PS-*b*-PEO Templated Film

The photocatalytic activity of the mesoporous titania film TP35 was evaluated by degradation of MB in aqueous solution. The reference test was carried out on a silicon substrate in the absence of titania. Adsorption and desorption equilibrium was established in the dark. Through the comparison of the adsorption ability between mesoporous films and

silicon substrate, it is noted that the MB molecules were trapped in the titania walls (Fig. 4-26 a). It clearly showed that MB in the solution decomposed faster by the TP35 titania mesoporous film than by silicon substrate (Fig. 4-26 a). Since the MB degradation by titania obeys pseudo-first-order kinetics in initial period, the apparent rate constant can be determined by the slope of a straight line plotting $\ln(C_0/C)$ against irradiation time (Fig. 4-26 b). This apparent rate constant of TP35 film (thickness=130 nm) is 2.5 times higher than that of reference. Moreover, the normalized (according to respective conditions) rate constant of the TP35 mesoporous film on silicon substrate is twice higher than that of the mesoporous titania films with ~12 nm pore diameter templated by F127 block polymer laminated from silicon substrate, and the crystallinity of the F127 templated mesoporous had been improved by substrate effect.

4.6 Conclusions

The evolution of mesostructured titania films up to 400°C was studied in an EISA fast evaporation process as a function of proton concentration, water content and proportion of polymer template. It was found that protons control the density of titania oligomers in solution, mesophase formation and thermal crystallization. Higher proton concentrations in the precursor improve crystallization and create a dense titania framework condensed from titania oligomers. Excessive shrinkage during sintering at 400°C destroys the ordered mesoporous structure with negligible change in film surface area, while raising water content contributes to enhanced order through decreasing the proton concentration in the solution. Both pore size and porosity increase with template content, despite that only aperiodic structures were formed due to the rapid evaporation. Highly crystalline films synthesized at higher proton concentrations were found to be more effective photocatalysts. Spongy mesoporous titania films produced at high template contents enhanced photodegradation of MB as a result of the deposition of thicker films.

Mesostructured titania film was templated by PS-*b*-PEO block copolymer. Through adjusting the TTIP and HCl concentration in the solution, homogeneous and nearly hexagonal ~30 nm pore diameter mesoporous titania film perpendicular to substrate surface was fabricated by spin-coating on silicon wafer. However, with the volume fraction of PEO block decreasing, inversed hexagonal packed titania islands were formed. The effects of TTIP and HCl content on the mesostructured titania film were also discussed through micelle formation mechanism of PS-*b*-PEO block copolymer. The fabricated high crystallinity mesostructure anatase film was thermally stabilized at 600°C with the assistance of the PS block of PS-*b*-PEO. Although the surface area of the mesoporous titania is lower than that of the film templated by PEO-PPO-PEO block copolymer due to its larger diameter of mesopores, it still exhibits higher photocatalytic activity with decomposing MB in aqueous solution.

4.7 References

- [1] H. Lin, H. Kozuka, T. Yoko, (1998). Preparation of TiO₂ films on self-assembled monolayers by sol-gel method, *Thin Solid Film*, 315, 111.
- [2] M. Kallala, C. Sanche, B. Cabane, (1999). Structure of inorganic polymers in sol-gel processes based on titanium oxide, *Phys. Rev. E*, 48, 3692.
- [3] M. J. Alam, D. C. Cameron, (2002). Preparation and characterization of TiO₂ thin films by sol-gel method, *J. Sol-Gel. Sci. Technol.*, 25, 137.
- [4] H. Okudera, Y. Yokogawa, (2001). Formation of TiO₂ thin films by hydrolysis of Ti-tetraethoxide in ethanol: kinetics, surface morphology, constituent phases and their formation mechanism, *Thin Solid Film*, 401, 124.
- [5] B. E. Yoldas, (1986). Hydrolysis of titanium alkoxide and effects of hydrolytic polycondensation parameters, *J. Mater. Sci.*, 21, 1087.
- [6] Y. U. Ahn, E. J. Kim, H. T. Kim, S. H. Hahn, (2003). Variation of structural and optical properties of sol-gel TiO₂ thin films with catalyst concentration and calcination temperature, *Mater. Lett.*, 57, 4660.
- [7] S. Qiu, S. J. Kalita, (2006). Synthesis, processing and characterization of nanocrystalline titanium dioxide, *Mater. Sci. Eng. A*, 435-436, 327.
- [8] A. Verma, A. Basu, A. K. Bakhshi, S. A. Agnihotry, (2005). Structural, optical and electrochemical properties of sol-gel derived TiO₂ films: annealing effects, *Solid State Ionics*, 176, 2285.
- [9] D. J. Kim, S. H. Hahn, S. H. Oh, E. J. Kim, (2002). Influence of calcination temperature on structural and optical properties of TiO₂ thin films prepared by sol-gel dip coating, *Mater. Lett.*, 57, 355.
- [10] Y. Zhang, A. Weidenkaff, A. Reller, (2002). Mesoporous structure and phase transition of nanocrystalline TiO₂, *Mater. Lett.*, 54, 375.

- [11] C. J. Brinker, Y. Lu, A. Sellinger, H. Fan, (1999). Evaporation-induced self-assembly: nanostructures made easy, *Adv. Mater.*, 11, 579.
- [12] O. Huo, D. I. Margolese, G. D. Stucky, (1996). Surfactant control of phases in the synthesis of mesoporous silica-based materials, *Chem. Mater.*, 8, 1147.
- [13] E. L. Crepaldi, G. J. de A. A. Soler-Illia, D. Grosso, F. Cagnol, F. Ribot, C. Sanchez, (2003). Controlled formation of highly organized mesoporous titania thin films: from mesostructured hybrids to mesoporous nanoanatase TiO₂, *J. Am. Chem. Soc.*, 125, 9770.
- [14] D. Grosso, F. Babonneau, C. Sanchez, G. J. de A. A. Soler-Illia, E. L. Crepaldi, (2003). A first insight in the mechanisms involved in the self-assembly of 2D-hexagonal templated SiO₂ and TiO₂ mesostructured films during dip-coating, *J. Sol-Gel. Sci. Technol.*, 26, 561.
- [15] Q. Huo, D. I. Margolese, U. Ciesla, D. G. Demuth, P. Feng, T. E. Gier, P. Sieger, A. Firouzi, B. F. Chemelka, F. Schüth, G. D. Stucky, (1994). Organization of organic molecules with inorganic molecular species into nanocomposite biphase arrays, *Chem. Mater.*, 6, 1176.
- [16] T. Fjuimoto, (1985). *New Introduction to Surface Active Agents*, Sanyo Chemical Industries, LTD.,
- [17] L. L. Schramm, (2000). *Surfactants: Fundamentals and Applications in the Petroleum Industry*, Cambridge University Press,
- [18] F. S. Bates, G. H. Fredrickson, (1999). Block copolymers-designer soft materials, *Physics Today*, 2, 32.
- [19] R. A. Segalman, (2005). Patterning with block copolymer thin films, *Mater. Sci. Eng. R*, 48, 191.
- [20] T. J. Barton, L. M. Bull, W. G. Klemperer, D. A. Loy, B. McEnaney, M. Misono, P. A. Monson, G. Pez, G. W. Scherer, J. C. Vartuli, O. M. Yaghi, (1999). Tailored porous materials, *Chem. Mater.*, 11, 2633.
- [21] G. J. de A. A. Soler-Illia, E. L. Crepaldi, D. Grosso, C. Sanchez, (2003). Block copolymer-templated mesoporous oxides, *Current Opinion in Colloid and Interface Science*, 8, 109.
- [22] J. Patarin, B. Lebeau, R. Zana, (2002). Recent advances in the formation mechanism of organized mesoporous materials, *Current Opinion in Colloid and Interface Science*, 7, 107.
- [23] P. A. Albouy, A. Ayrat, (2002). Coupling X-ray scattering and nitrogen adsorption: an interesting approach form the characterization of ordered mesoporous materials. application to hexagonal silica, *Chem. Mater.*, 14, 3391.
- [24] M. L. Lavčević, A. Turković, (2002). Small-angle X-ray scattering and wide-angle X-ray diffraction on thermally annealed nanostructured TiO₂ films, *Thin Solid Films*, 419, 105.
- [25] D. Grosso, P. A. Albouy, H. Amenitsch, A. R. Balkenende, F. Babonneau, (2000). Time-resolved in-situ X-ray diffraction study of the formation of 3D-hexagonal mesoporous silica films, *Mat. Res. Soc. Symp. Proc.*, 628, CC6.17.1.
- [26] J. M. Thomas, O. Terasaki, P. L. Gai, W. Zhou, J. Gonzalez-Calbet, (2001). Structural elucidation of microporous and mesoporous catalysts and molecular sieves by high-resolution electron microscopy, *Acc. Chem. Res.*, 34, 583.
- [27] Y. Sakamoto, M. Kaneda, O. Terasaki, D. Y. Zhao, J. M. Kim, G. Stucky, H. J. Shin, R. Ryoo, (2000). Direct imaging of the pores and cages of three-dimensional mesoporous materials, *Nature*, 408, 449.
- [28] M. Grün, K. K. Unger, A. Matsumoto, K. Tsutsumi, (1999). Novel pathways for the preparation of mesoporous MCM-41 materials: control of porosity and morphology, *Microporous and Mesoporous Materials*, 27, 207.

- [29] A. C. Vogetlin, F. Ruch, J. L. Guth, J. Patarin, L. Huve, (1997). F^- mediated synthesis of mesoporous silica with ionic-and non-ionic surfactant. a new templating pathway, *Microporous Materials*, 9, 95.
- [30] A. Monnier, F. Schuth, Q. Huo, D. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke, B. F. Chmelka, (1993). Cooperative formation of inorganic-organic interfaces in the synthesis of silicate mesostructures, *Science*, 261, 1299.
- [31] G. S. Attard, J. C. Glyde, C. G. Göltner, (1995). Liquid-crystalline phases as templates for the synthesis of mesoporous silica, *Nature*, 378, 366.
- [32] M. Trau, N. Yao, E. Kim, Y. Xia, G. M. Whitesides, I. A. Aksay, (1997). Microscopic patterning of orientated mesoscopic silica through guided growth, *Nature*, 390, 674.
- [33] Q. Huo, D. I. Margolese, G. D. Stucky, (1996). Surfactant control of phases in the synthesis of mesoporous silica-based materials, *Chem. Mater.*, 8, 1147.
- [34] J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J.B. Higgins, J. L. Schlenker, (1992). A new family of mesoporous molecular sieves prepared with liquid crystal templates, *J. Am. Chem. Soc.*, 114, 10834.
- [35] M. Klotz, A. Ayril, C. Guizard, L. Cot, (2000). Synthesis condition for hexagonal mesoporous silica layers, *J. Mater. Chem.*, 10, 663.
- [36] S. A. Bagshaw, E. Prouzet, T. J. Pinnavaia, (1995). Templating of mesoporous molecular sieves by nonionic polyethylene oxide, *Science*, 29, 1242.
- [37] R. Richer, L. Mercier, (2001). Direct synthesis of functional mesoporous silica by neutral pH nonionic surfactant assembly: factors affecting framework structure and composition, *Chem. Mater.*, 13, 2999.
- [38] P. T. Tanev, T. J. Pinnavaia, (1995). A neutral templating route to mesoporous molecular sieves, *Science*, 267, 865.
- [39] Y. Lu, H. Fan, N. Doke, D. A. Loy, R. A. Assink, D. A. LaVan, C. J. Brinker, (2000). Evaporation-induced self-assemble of hybrid bridged silsesquioxane film and particulate mesophases with integral organic functionality, *J. Am. Chem. Soc.*, 122, 5258.
- [40] C. Boissière, A. Larbot, A. van der Lee, P. J. Kooyman, E. Prouzet, (2000). A new synthesis of mesoporous MSU-X silica controlled by two-step pathway, *Chem. Mater.*, 12, 2902.
- [41] B. Smarsly, S. Polarz, M. Antonietti, (2001). Preparation of porous silica materials via sol-gel nanocasting of nonionic surfactant: a mechanistic study on the self-aggregation of amphiphiles for the precise prediction of the mesopore size, *J. Phys. Chem. B*, 105, 10473.
- [42] B. Tian, X. Liu, Z. Zhang, B. Tu, D. Zhao, (2002). Syntheses of high-quality mesoporous materials directed by blends of nonionic amphiphiles under nonaqueous condition, *Journal of Solid State Chemistry*, 167, 324.
- [43] M. A. U. Martinez, E. Yeong, A. Larbot, E. Prouzet, (2004). Temperature dependence in the synthesis of hexagonal MSU-3 type mesoporous silica synthesized with Pluronic P123 block copolymer, *Microporous and Mesoporous Materials*, 74, 213.
- [44] D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, (1998). Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores, *Science*, 279, 548.
- [45] D. Zhao, P. Yang, N. Melosh, J. Feng, B. F. Chmelka, G. D. Stucky, (1998). Continuous mesoporous silica films with highly ordered large pore structures, *Adv. Mater.*, 10, 1380.

- [46] C. Yu, Y. Yu, D. Zhao, (2000). Highly ordered large caged mesoporous silica structures templated by triblock PEO-PPO-PEO copolymer, *Chem. Comm.*, 17, 575.
- [47] O. Muth, C. Schellbach, M. Fröba, (2001). Triblock copolymer assisted synthesis of periodic mesoporous organosilicas (PMOs) with large pores, *Chem. Comm.*, 23, 2032.
- [48] J. Yao, H. Wang, K. Y. Chan, L. Zhang, N. Xu, (2005). Incorporating organic polymer into silica walls: a novel strategy for synthesis of templated mesoporous silica with tunable pore structure, *Microporous and Mesoporous Materials*, 82, 183.
- [49] C. Yu, B. Tian, J. Fan, G. D. Stucky, D. Zhao, (2002). Nonionic block copolymer synthesis of large-pore cubic mesoporous single crystals by use of inorganic salts, *J. Am. Chem. Soc.*, 124, 4556.
- [50] N. A. Melosh, P. Davidson, B. F. Chmelka, (2000). Monolithic mesophase silica with large ordering domains, *J. Am. Chem. Soc.*, 122, 823.
- [51] M. Kruk, M. Jaroniec, (2000). Characterization of the porous structure of SBA-15, *Chem. Mater.*, 12, 1961.
- [52] D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, (1998). Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermal stable, mesoporous silica structures, *J. Am. Chem. Soc.*, 120, 6024.
- [53] D. Grosso, A. R. Balkenende, P. A. Albouy, A. Ayral, H. Amenitsch, F. Babonneau, (2001). Two-dimensional hexagonal mesoporous silica thin films prepared from block copolymers: detailed characterization and formation mechanism, *Chem. Mater.*, 13, 1848.
- [54] M. Impérator-Clerc, P. Davidson, A. Davidson, (2000). Existence of a microporous corona around the mesopores of silica-based SBA-15 materials templated by triblock copolymers, *J. Am. Chem. Soc.*, 122, 11925.
- [55] C. G. Göltner, S. Henke, M. C. Weissenberger, M. Antonietti, (1998). Mesoporous silica from lyotropic liquid crystal polymer templates, *Angew. Chem. Int. Ed.*, 37, 613.
- [56] F. Kleitz, L. A. Solovyov, G. M. Anilkumar, S. H. Choi, R. Ryoo, (2004). Transformation of highly ordered large pore silica mesophases (Fm3m, Im3m and p6mm) in a ternary triblock copolymer-butanol-water system, *Chem. Comm.*, 2, 1536.
- [57] G. J. A. A. Soler-Illia, E. L. Crepaldi, D. Grosso, D. Durand, C. Sanchez, (2002). Structural control in self-standing mesostructured silica oriented membranes and xerogels, *Chem. Comm.*, 19, 2298.
- [58] J. M. Kim, G. D. Stucky, (2000). Synthesis of highly ordered mesoporous silica materials using sodium silicate and amphiphilic block copolymer, *Chem. Comm.*, 22, 1159.
- [59] J. M. Kim, Y. J. Han, B. F. Chmelka, G. D. Stucky, (2000). One-step synthesis of ordered mesocomposites with non-ionic amphiphilic block copolymers: implications of isoelectric point, hydrolysis rate and fluoride, *Chem. Comm.*, 7, 2437.
- [60] S. S. Kim, T. R. Pauly, T. J. Pinnavaia, (2000). Non-ionic surfactant assembly of ordered, very large pore molecular sieve silicas from water soluble silicates, *Chem. Comm.*, 4, 1661.
- [61] M. Klotz, N. Idrissi-Kandri, A. Ayral, C. Guizard, (2000). Porous oxide thin layers using mesophase templating, *Mat. Res. Soc. Symp. Proc.*, 628, CC7.4.1.
- [62] H. Miyata, T. Suzuki, A. Fukuoka, T. Sawada, M. Watanabe, T. Noma, K. Takada, T. Mukaide, K. Kuroda, (2004). Silica films with a single-crystalline mesoporous structure, *Nature Materials*, 3, 651.
- [63] A. Sayari, S. Hamoudi, (2001). Periodic mesoporous silica-based organic-inorganic nanocomposite materials, *Chem. Mater.*, 13, 3151.

- [64] M. E. Davis, (2002). Ordered porous materials for emerging applications, *Nature*, 417, 813.
- [65] P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka, G. D. Stucky, (1999). Block copolymer templating syntheses of mesoporous metal oxides with large ordering lengths and semicrystalline framework, *Chem. Mater.*, 11, 2831.
- [66] F. Schüth, (2001). Non-siliceous mesostructured and mesoporous materials, *Chem. Mater.*, 13, 3184.
- [67] M. Templin, A. Franck, A. D. Chesne, H. Leist, Y. Zhang, R. Ulrich, V. Schadler, U. Wiesner, (1975). Organically modified aluminosilicate mesostructures from block copolymer phases, *Science*, 278, 5344.
- [68] N. Idrissi-Kandri, A. Ayrat, M. Klotz, P. A. Albouy, A. E. Mansouri, A. V. der Lee, C. Guizard, (2001). Porous alumina thin layers using mesophase templating, *Mater. Lett.*, 50, 57.
- [69] D. Grosso, G. J. de A. A. Soler Illia, E. L. Crepaldi, B. Charlesux, C. Sanchez, (2003). Nanocrystalline transition-metal oxide spheres with controlled multi-scale porosity, *Adv. Funct. Mater.*, 13, 37.
- [70] L. Kavan, J. Rathouský, M. Grätzel, V. Shklover, A. Zukal, (2000). Surfactant-templated TiO₂ (anatase): characteristic features of lithium insertion electrochemistry in organized nanostructures, *J. Phys. Chem. B*, 104, 12012.
- [71] D. Grosso, F. Cagnol, A. Coupé, N. Baccile, C. Boissière, G. J. de A. A. Soler Illia, E. Crepaldi, C. Sanchez, (2003). Amorphous and crystalline mesoporous materials prepared via evaporation, *Mat. Res. Soc. Symp. Proc.*, 775, P4.3.2.
- [72] J. Du, Z. Liu, Z. Li, B. Han, Y. Huang, Y. Gao, (2005). Mesoporous TiO₂ with wormlike structure synthesized via interfacial surfactant assisted route, *Microporous and Mesoporous Materials*, 83, 19.
- [73] D. Grosso, C. Boissière, L. Nicole, C. Sanchez, (2006). Preparation, treatment and characterisation of nanocrystalline mesoporous ordered layers, *J. Sol-Gel Sci. Techn.*, 40, 141.
- [74] P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka, G. D. Stucky, (1998). Generalized syntheses of large-pore mesoporous metal oxides with semicrystalline frameworks, *Nature*, 396, 152.
- [75] P. V. Braun, P. Osenar, V. Tohver, S. B. Kennedy, S. I. Stupp, (1999). Nanostructure templating in inorganic solid with organic lyotropic liquid crystals, *J. Am. Chem. Soc.*, 121, 7302.
- [76] K. K. Rangan, S. J. L. Billinge, V. Petkov, J. Heising, M. G. Kanatzidis, (1999). Aqueous mediated synthesis of mesostructured manganese germanium sulfide with hexagonal order, *Chem. Mater.*, 11, 2629.
- [77] G. S. Armatas, M. G. Kanatzidis, (2006). Mesostructured Germanium with cubic pore symmetry, *Nature*, 441, 1122.
- [78] D. Sun, A. E. Riley, A. J. Cadby, E. K. Richman, S. D. Korlann, S. H. Tolbert, (2006). Hexagonal nanoporous Germanium through surfactant-driven self-assembly of Zintl clusters, *Nature*, 441, 1126.
- [79] G. S. Attard, P. N. Bartlett, N. R. B. Coleman, J. M. Elliott, J. R. Owen, J. H. Wang, (1997). Mesoporous platinum films from lyotropic liquid crystalline phase, *Science*, 278, 838.
- [80] R. Ryoo, S. H. Joo, M. Kruk, M. Jaroniec, (2001). Ordered mesoporous carbons, *Adv. Mater.*, 13, 677.
- [81] C. M. Yang, C. Weidenthaler, B. Spliethoff, M. Mayanna, F. Schüth, (2005). Facile template synthesis of ordered mesoporous carbon with polypyrrole as carbon precursor, *Chem. Mater.*, 17, 355.
- [82] M. M. Yusuf, H. Imai, H. Hirashima, (2001). Preparation of mesoporous TiO₂ thin films by surfactant templating, *Journal of Non-Crystalline Solids*, 285, 90.

- [83] Q. Dai, Z. Zhang, N. He, P. Li, C. Yuan, (1999). Preparation and characterization of mesostructured titanium dioxide and its application as a photocatalyst for the wastewater treatment, *Materials Science and Engineering C*, 8-9, 417.
- [84] L. Zhang, Y. Zhu, Y. He, W. Li, H. Sun, (2003). Preparation and performances of mesoporous TiO₂ films photocatalyst supported on stainless steel, *Appl. Catal. B*, 40, 287.
- [85] D. M. Antoneli, J. Y. Ying, (1995). Synthesis of hexagonally packed mesoporous TiO₂ by a modified sol-gel method, *Angew. Chem. Int. Ed. Engl.*, 34, 2014.
- [86] R. L. Putnam, N. Nakagawa, K. M. McGrath, N. Yao, I. A. Aksay, S. M. Gruner, A. Navrotsky, (1997). Titanium dioxide-surfactant mesophases and Ti-TMS1, *Chem. Mater.*, 9, 2690.
- [87] G. Q. Liu, Z. G. Jin, X. X. Liu, T. Wang, Z. F. Liu, (2006). Anatase TiO₂ porous thin films prepared by sol-gel method using CTAB surfactant, *J. Sol-Gel. Sci. Techn.*, 9.
- [88] H. S. Yun, K. Miyazawa, I. Honma, H. Zhou, M. Kuwabara, (2003). Synthesis of semicrystallized mesoporous TiO₂ thin films using triblock copolymer template, *Materials Science and Engineering C*, 23, 487.
- [89] P. C. A. Alberius, K. L. Frindell, R. C. Hayward, E. J. Kramer, G. D. Stucky, B. F. Chmelka, (2002). General predictive syntheses of cubic, hexagonal, and lamellar silica and titania mesostructured thin films, *Chem. Mater.*, 14, 3284.
- [90] F. Bosc, A. Ayrat, P. A. Albouy, L. Datas, C. Guizard, (2004). Mesostructure of anatase thin films prepared by mesophase templating, *Chem. Mater.*, 16, 2208.
- [91] H. S. Yun, K. Miyazawa, H. Zhou, I. Honma, M. Kuwabara, (2001). Synthesis of mesoporous thin TiO₂ films with hexagonal pore structures using triblock copolymer templates, *Adv. Mater.*, 13, 1377.
- [92] F. Bosc, A. Ayrat, P. A. Albouy, C. Guizard, (2003). A simple route for low-temperature synthesis of mesoporous and nanocrystalline anatase thin films, *Chem. Mater.* 15, 2463.
- [93] D. Grosso, G. J. de A. A. Soller-Illia, F. Babonneau, C. Sanchez, P. A. Albouy, A. Brunet-Brunet, A. Ruud Balkenende, (2001). Highly organized mesoporous titania films showing mono-orientated 2D hexagonal channels, *Adv. Mater.*, 13, 1085.
- [94] V. R. Koganti, D. Dunphy, V. Gowrishankar, M. D. McGehee, X. Li, J. Wang, S. E. Rankin, (2006). Generalized coating route to silica and titania films with orthogonally tilted cylindrical nanopore arrays, *Nano Letters*, 6, 2567.
- [95] C. W. Wu, T. Ohsuna, M. Kuwabara, K. Kuroda, (2006). Formation of highly ordered mesoporous titania films consisting of crystalline nanopillars with inverse mesospace by structural transformation, *J. Am. Chem. Soc.*, 128, 4544.
- [96] K. Liu, M. Zhang, K. Shi, H. Fu, Large-pore mesoporous nanocrystalline titania thin films synthesized through evaporation-induced self-assembly, *Mater. Lett.*, in press.
- [97] M. M. Yusuf, H. Imai, H. Hirashima, (2002). Preparation of porous titania film by modified sol-gel method and its application to photocatalyst, *J. Sol-Gel. Sci. Technol.*, 25, 65.
- [98] S. Nagamine, S. Takahashi, E. Sasaoka, (2004). Synthesis of transparent film of mesoporous TiO₂ by solvent evaporation, *J. Mater. Sci.*, 39, 3767.
- [99] M. Wark, J. Tschirch, O. Bartels, D. Bahnemann, J. Rathouský, (2005). Photocatalytic activity of hydrophobized mesoporous thin film of TiO₂, *Microporous and Mesoporous Materials*, 84, 247.
- [100] K. Liu, W. Zhou, K. Shi, L. Li, L. Zhang, M. Zhang, H. Fu, (2006). Influence of calcination temperatures on the photocatalytic activity and photo-induced hydrophilicity of wormhole-like mesoporous TiO₂, *Nanotechnology*, 17, 1363.

- [101] Y. Sakatani, D. Grosso, L. Nicole, C. Boissière, G. J. de A. A. Soler-Illia, C. Sanchez, (2006). Optimized photocatalytic activity of grid-like mesoporous TiO₂ films: effect of crystallinity, pore size distribution, and pore accessibility, *J. Mater. Chem.*, 16, 77.
- [102] D. Grosso, G. J. de A. A. Soler-Illia, E. L. Crepaldi, F. Cagnol, C. Sinturel, A. Bourgeois, A. Brunet-Bruneau, H. Amenitsch, P. A. Albouy, C. Sanchez, (2003). Highly porous TiO₂ anatase optical thin films with cubic mesostructure stabilized at 700°C, *Chem. Mater.*, 15, 4562.
- [103] Y. Zhang, J. Li, J. Wang, (2006). Substrate-assisted crystallization and photocatalytic properties of mesoporous TiO₂ thin films, *Chem. Mater.*, 18, 2917.
- [104] H. Schlaad, B. Smarsly, M. Losik, (2004). The role of chain-length distribution in the formation of solid-state structures of polypeptide-based rod-coil block copolymers, *Macromolecules*, 37, 2210.
- [105] Z. Liu, Z. Jin, X. Liu, Y. Fu, G. Liu, (2006). Fabrication of ordered TiO₂ porous thin films by sol-dipping PS template method, *J. Sol-Gel. Sci. Technol.*, 38, 73.
- [106] D. H. Kim, Z. Sun, T. P. Russell, W. Knoll, J. S. Gutmann, (2005). Organic-inorganic nanohybridization by block copolymer thin films, *Adv. Funct. Mater.*, 15, 1160.
- [107] X. Li, K. H. A. Lau, D. H. Kim, W. Knoll, (2005). High-density arrays of titania nanoparticles using monolayer micellar films of diblock copolymers as templates, *Langmuir*, 21, 5212.
- [108] Z. Sun, J. S. Gutmann, (2004). Synthesis of TiO₂ nanoparticles in ultrathin block copolymer films-an integral geometry study, *Physica A*, 339, 80.
- [109] K. Yu, C. Bartels, A. Eisenberg, (1999). Trapping of intermediate structure of the morphological transition of vesicles to inverted hexagonally packed rods in dilute solutions of PS-*b*-PEO, *Langmuir*, 15, 7157.
- [110] R. Ulrich, A. D. Chesne, M. Templin, U. Wiesner, (1999). Nano-objects with controlled shape, size, and composition from block copolymer mesophases, *Adv. Mater.*, 11, 141.
- [111] Z. Lin, D. H. Kim, X. Wu, L. Boosahda, D. Stone, L. LaRose, T. P. Russell, (2002). A rapid route to arrays of nanostructures in thin films, *Adv. Mater.*, 14, 1373.
- [112] S. H. Kim, M. J. Misner, T. Xu, M. Kimura, T. P. Russell, (2004). Highly oriented and ordered arrays from block copolymers via solvent evaporation, *Adv. Mater.*, 16, 226.
- [113] P. F. W. Simon, R. Ulrich, H. W. Spiess, U. Wiesner, (2001). Block copolymer-ceramic hybrid materials from organically modified ceramic precursors, *Chem. Mater.*, 13, 3486.
- [114] K. Yu, A. Eisenberg, (1998). Bilayer morphologies of self-assembled crew-cut aggregates of amphiphilic PS-*b*-PEO diblock copolymers in solution, *Macromolecules*, 31, 3509.
- [115] L. Zhu, P. Huang, W. Y. Chen, Q. Ge, R. P. Quirk, S. Z. D. Cheng, (2002). Nanotailored crystalline morphology in hexagonal perforated layers of a self-assembled PS-*b*-PEO diblock copolymer, *Macromolecules*, 35, 3553.
- [116] Y. J. Chen, J. S. Gutmann, (2006). Morphology phase diagram of ultrathin anatase TiO₂ films templated by a single PS-*b*-PEO block copolymer, *J. Am. Chem. Soc.*, 128, 4658.
- [117] B. Smarsly, D. Grosso, T. Brezesinski, N. Pinna, C. Boissière, M. Antonietti, C. Sanchez, (2004). Highly crystalline cubic mesoporous TiO₂ with 10-nm pore diameter made with a new block copolymer template, *Chem. Mater.*, 16, 2948.
- [118] G. J. de A. A. Soler-Illia, E. Scolan, A. Louis, P. A. Albouy, C. Sanchez, (2001). Design of meso-structured titania oxo based hybrid organic-inorganic networks, *New J. Chem.*, 25, 156.

- [119] V. M. Nace, (1996). *Nonionic Surfactant-Polyoxyalkylene Block Copolymers*, Marcel Dekker, Inc.,
- [120] X. You, F. Chen, J. Zhang, (2005). Effects of calcination on the physical and photocatalytic properties of TiO₂ powders prepared by sol-gel template method, *J. Sol-Gel. Sci. Technol.*, 38, 181.

CHAPTER 5

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions and Achievements

5.1.1 Conclusions

This thesis describes the fabrication and application of porous titania as a photocatalyst. Titania has a long history of use in the photocatalytic field, where high crystallinity and surface area are desirable. The purpose of this study was (1) to develop and control porous structured titania by chemical methods, (2) to study the titania and pore formation mechanism, and (3) to investigate the porous structured titania photocatalytic properties.

The present work starts from liquid phase deposited titania films without templates, with investigations of the spontaneous porous structures, film morphologies, crystallinity and growth kinetics at elevated reaction temperatures. First, film growth kinetics were found to transform from phase-boundary-controlled continuous nucleation to diffusion-controlled grain growth as the supersaturation of the reaction solution decreases. At elevated reaction temperatures, more rapid decrease in supersaturation resulted in the greater film thicknesses controlled by diffusion-controlled grain growth kinetics, which shows columnar morphology. Second, porous structure evolution as a function of film growth and reaction temperature was observed to be unstable and proceeds as pore-filling during reaction. The crystallinity of the film increases with the increase of reaction temperature. Therefore, as highest photodegradation rate was achieved by the film deposited at 200°C for 30 min, it is also concluded that surface area has a more significant effect on the photocatalytic performance than crystallinity when this exceeds 60%.

The application of AAO as a template to control the porous structure in macroporous range via LPD is also investigated. It is found that AAO not only serves as a template but also a starting material. Self-supporting macroporous membranes with walls composed of mesoporous anatase were successfully synthesized with macroporous AAO, where aluminium was displaced by titania. With increasing immersion time, the diameters of the macropores decreases. After 5 h immersion, a thin titania layer grows on the top surface of the membranes. This structure, however, becomes denser after heat treatment and leads to a decrease in photocatalytic activity due to the blocking of dye entry into the membranes. The membrane, fabricated by 5 hours of immersion without heat treatment, is noted to possess the highest rate constant, a value comparable to benchmark titania powders. The by-product $\text{AlF}_n(\text{OH})_{3-n}$ ($n=1.5, 1.62$ or 1.65) which precipitated within the membranes could be controlled by adjusting the atomic ratio of Ti/Al in the precursors or decomposed at 400°C . The self-supporting titania membranes reported may serve as multifunctional filters that are both self-cleaning and suitable for the separation of liquid or gaseous waste streams.

In LPD, the crystallinity of precipitated titania is above 60%. Under this condition, the surface area proved to control the photocatalytic efficiency. In the last part of this study, the crystallinity is the dominant factor controlling photocatalytic activity with low crystallinity, which is observed in the PEO-based block copolymer templated titania.

PEO-based block copolymer was used to synthesize ordered mesoporous structured titania film in sol-gel by EISA. The film surface area and crystallinity templated by F127 was improved by adjusting the parameters in the solution, such as proton concentration, template, and water content. It was found that protons control the density of titania oligomers in solution, mesophase formation and thermal crystallization. Higher proton concentrations in the precursor can improve crystallization and hence create a dense titania framework condensed from titania oligomers. Nevertheless, surface area and porosity are noted to increase with template content. Thermal stability of the mesoporous structure was

improved to 600°C by using PS-*b*-PEO block copolymer. Various nanostructured titania films are also observed by adjusting the PEO volume fraction in PS-*b*-PEO block copolymer, TTIP, and proton concentration in the solution. Highly crystalline films synthesized at higher proton concentrations and higher annealing temperatures are all found to be the most effective photocatalysts.

5.1.2 Achievements

The specific research and scientific contributions of this work are summarized below.

- The film growth kinetic in LPD was first analyzed using a modified solid-state Hancock and Sharp model, and the phase-boundary-controlled continuous nucleation mechanism and diffusion-controlled grain growth mechanisms are successfully represented by the model.
- The titania precipitation mechanism was studied in LPD using alumina as a fluoride scavenger, which is boric acid traditionally. The precipitation of pure titania is more strongly dependent on the molar ratio of Al and Ti. Lack of alumina will result in the formation of aluminium fluoride hydrates.
- The PEO-based block copolymer micelle assisted evaporation induced self-assembly process to produce mesoporous titania films with symmetries porous structures was established. The PS-*b*-PEO block copolymer micelle formation mechanism was studied. An inverse micelle structure can be achieved by increasing the PS volume fraction in the block copolymer.
- Film crystallinity was increased by increasing reaction temperature in LPD and determined to be 60% at 50°C to 90% at 200°C.
- Alumina replacing boric acid in the formation of titania in LPD was found to be useful. The macroporous titania membrane keeps the structure of the AAO template by in-situ growth. The self-supporting titania membranes reported may serve as

multifunctional filters that are both self-cleaning and suitable for the separation of liquid or gaseous waste streams

- Higher thermal stability was achieved with a PS-*b*-PEO block copolymer templated titania film. Although the pore size increased to ~30 nm, but the large scale homogeneous mesoporous structure was retained during crystallization at 600°C.
- Various nanostructured titania films including nanoparticle arrays, titania islands with different diameters, nanowires and mesopores were fabricated by adjusting solution parameters and PEO volume fraction in PS-*b*-PEO block copolymer.
- It was discovered that the photocatalytic activity of titania films is dependent on surface area when crystallinity is above 60%, while it is more strongly dependent on crystal perfection for poorly crystalline materials.

5.2 Future Work

The results of this research, and its limitations provide a possible scope for interesting future work.

- Film cracking: The liquid phase deposited film cracking is believed to arise from capillary stress when the solvent comes out of the pores. Hence, freezing-drying and washing with pentane is proposed to avoid this problem.
- Titania membranes: More dedicated control of macroporous structure in the AAO templated titania membranes can be achieved by using modified anodic alumina with various pore size, membrane thickness and different shapes of pore channels. It is promising in water purification and filtration.
- PS-*b*-PEO templated various nanostructured titania film: the PS block can be oriented in electric fields and also conductive polymer blocks. Hence, various nanostructured oxides can be templated by this copolymer in electric fields in an

oriented configuration. High crystallinity and large scale periodic mesostructure hybrids with this polymer can make titania attractive in solar cell applications.

PUBLICATION LIST

- ✧ **B. Ma**, Gregory K. L. Goh and J. Ma “Crystallinity and Photocatalytic Activity of Liquid Phase Deposited Film”, J. Electroceram., (2006) 16:441–445.
- ✧ **Bing Ma**, Gregory K. L. Goh, Jan Ma and Tim J. White “Growth Kinetics and Cracking of Liquid-Phase-Deposited Anatase Films”, Journal of The Electrochemical Society, (2007) 154(10): D577-D561.
- ✧ **Bing Ma**, Gregory K. L. Goh, T. J. White, T. S. Zhang and Jan Ma “Synthesis of Titania membrane by Anodic Oxidation Alumina Template” under revision, to be updated.
- ✧ **B. Ma**, Gregory K. L. Goh, T. J. White and J. Ma, “Enhanced Titania Film Crystallinity and Surface Area via a New Evaporation Induced Self-Assembly Approach”, Microporous and Mesoporous Materials, accepted.
- ✧ **B. Ma**, Gregory K. L. Goh and J. Ma, “High Thermal Stability Mesoporous PS-*b*-PEO Block Copolymer Templated Titania Film”, Journal of Materials Science, accepted.

APPENDIX I ADSORPTION INTENSITY AND CONCENTRATION OF MO/MB

Linear relation of adsorption intensity and concentration of methylene orange (A) and methylene blue (B) (I: the adsorption intensity; C: concentration)

APPENDIX II AFM IMAGES OF LIQUID PHASE DEPOSITED FILM

APPENDIX III XRD PATTERNS OF LIQUID PHASE DEPOSITED TITANIA

21-1272		Wavelength= 1.54056 *									
TiO ₂		2θ	Int	h	k	l	2θ	Int	h	k	l
Titanium Oxide		25.281	100	1	0	1	118.434	4	2	1	0
		38.948	10	1	0	3	120.088	2	2	2	8
		37.80	20	0	0	4	121.720	<2	4	1	3
		38.676	10	1	1	2	122.381	2	4	0	4
		48.048	35	2	0	0	131.028	2	4	2	0
		53.880	20	1	0	5	135.881	<2	3	2	7
		55.080	20	2	1	1	137.384	4	4	1	5
		62.119	4	2	1	3	143.879	2	3	0	9
		62.888	14	2	0	4	150.028	4	4	2	4
		68.780	8	1	1	6	152.822	2	0	0	12
		70.308	8	2	2	0					
		74.028	<2	1	0	7					
		75.028	10	2	1	5					
		78.017	4	3	0	1					
		80.725	<2	0	0	8					
		82.136	2	3	0	3					
		82.655	6	2	2	4					
		83.147	4	3	1	2					
		93.217	2	2	1	7					
		94.178	4	3	0	5					
		95.138	4	3	2	1					
		98.315	2	1	0	9					
		98.801	2	2	0	6					
		104.218	2	3	2	3					
		107.444	4	3	1	8					
		108.959	4	4	0	0					
		112.838	<2	3	0	7					
		113.857	2	3	2	5					
		114.904	2	4	1	1					
Sys.: Tetragonal S.G.: I4 ₁ /amd (141) a: 3.7852 b: c: 9.5139 A: C: 2.5134 c: β: γ: Z: 4 mp: Ref: Ibid. Dx: 3.893 Dm: SS/POM: F ₃₀ = 74(.0118 . 35) Color: Colorless Pattern taken at 25 C. Sample obtained from National Lead Co., South Amboy, NJ, USA. Anatase and another polymorph, brookite (orthorhombic), are converted to rutile (tetragonal) by heating above 700 C. Pattern reviewed by Holzer, J., McCarthy, G., North Dakota State Univ, Fargo, ND, USA, ICDD Grant-in-Aid (1980). Agrees well with experimental and calculated patterns. 02 Ti type. PSC: U12. Validated by calculated pattern. Mwt: 79.90. Volume[CD]: 136.81.											

APPENDIX IV SOLUTION TEMPERATURE IN LPD

Oven Temperature: 50°C		Oven Temperature: 80°C	
Reaction Time (min)	Solution Temperature (°C)	Reaction Time (min)	Solution Temperature (°C)
0	21	0	21
5	23.5	7	31
10	28.2	10	35.5
20	34.1	15	45.4
30	38.8	20	51.9
40	42.3	25	57.5
50	44.9	30	61.8
60	46.1	35	64
70	47.5	45	67.9
80	48.1	50	70
90	49.1	60	74.5
100	49.9	90	78.8
110	50.01	100	79
120	50	110	79.5
180	50	130	80

Oven Temperature: 100°C	
Reaction Time (min)	Solution Temperature (°C)
0	21
6	26
11	33
20	49.5
25	57.5
32	60.5
44	78
54	84.8
60	88.2
70	92.5
80	96.5
90	99
100	100

Oven Temperature: 150°C	
Reaction Time (min)	Solution Temperature (°C)
0	21
6	39.5
10	42.5
15	58.2
20	71.8
30	92.5
37	105.6
40	109.8

Oven Temperature: 200°C	
Reaction Time (min)	Solution Temperature (°C)
0	21
7	38.5
10	40.5
15	60
20	80
25	100
27	108
30	115

APPENDIX V LIQUID PHASE DEPOSITED FILM THICKNESS

Oven Temperature: 50°C				
Same Notation	Reaction Time (min)	Film Thickness (nm)	Err Bar (nm)	Err Bar (nm)
LPDF50H2	120	190.67	27.3333	-30.6667
LPDF50H3	180	300.33	13.6667	-15.3333
LPDF50H4	240	456.33	33.6667	-29.3333
LPDF50H5	300	582	34	-28
LPDF50H6	360	672.33	29.6667	-42.3333
LPDF50H7	420	716.67	15.3333	-18.6667
LPDF50H8	480	878.67	52.3333	-62.6667
LPDF50H9	540	941.33	14.6667	-16.3333
LPDF50H10	600	933	2.5	-2.5
LPDF50H11	660	1015.67	70.3333	-60.6667
LPDF50H12	720	1085.67	58.3333	-42.6667
LPDF50H24	1440	1393.6	41.8	-36.5
LPDF50H48	2880	1719.37	26.1333	-39.4667
LPDF50H96	4320	1811.43	30.4667	-27.5333
LPDF50H216	12960	2195	71.6667	-68.3333

Oven Temperature: 80°C				
Same Notation	Reaction Time (min)	Film Thickness (nm)	Err Bar (nm)	Err Bar (nm)
LPDF80M40	40	181.667	21.3333	-33.6667
LPDF80M50	50	280	33	-42
LPDF80M60	60	457.667	10.3333	-10.6667
LPDF80M70	70	529	24	-16
LPDF80M80	80	626.667	36.3333	-64.6667
LPDF80M90	90	782	6	-4
LPDF80M100	100	800	35	-22
LPDF80M120	120	910.333	32.6667	-43.3333
LPDF80M130	130	892	12	-20
LPDF80M140	140	1037.67	31.3333	-17.6667
LPDF80M150	150	1065.67	41.3333	-34.6667

Oven Temperature: 100°C				
Same Notation	Reaction Time (min)	Film Thickness (nm)	Err Bar (nm)	Err Bar (nm)
LPDF100M30	30	195	41	-67
LPDF100M40	40	390	38	-28
LPDF100M50	50	581	83	-61
LPDF100M60	60	608.667	33.667	-48.333
LPDF100M70	70	750.333	5.66667	-6.33333
LPDF100M80	80	802.333	9.66667	-8.33333
LPDF100M90	90	991	4	-4
LPDF100M100	100	989.333	6.66667	-7.33333
LPDF100M120	120	1123.33	36.6667	-16.667

Oven Temperature: 150°C				
Same Notation	Reaction Time (min)	Film Thickness (nm)	Err Bar (nm)	Err Bar (nm)
LPDF150M15	15	123.7	16.3	-14.67
LPDF150M20	20	298.33	26.7	-46.3
LPDF150M25	25	424.3	40.67	-41.33
LPDF150M30	30	522.3	25.7	-27.3
LPDF150M40	40	657.3	98.7	-59.3
LPDF100M50	50	954	3.3	-2.7
LPDF100M60	60	1220.33	150.7	-76.3

Oven Temperature: 200°C				
Same Notation	Reaction Time (min)	Film Thickness (nm)	Err Bar (nm)	Err Bar (nm)
LPDF100M15	15	249	16	-17
LPDF100M20	20	456.7	23.3	44.7
LPDF100M30	30	609	10	-7
LPDF100M40	40	1159.3	69.7	-54.3

APPENDIX VI ISOTHERMS AND BJH PORE SIZE DISTRIBUTION

Isotherms and BJH pore size distribution of films deposited by LPD

Isotherms and BJH pore size distribution of powder deposited by LPD