Hierarchical assembly of immobilized TiO₂-based nanostructured epitaxial films on Ti Substrates for photocatalytic water decontamination and hydrogen generation

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NANYANG
TECHNOLOGICAL
UNIVERSITY

**HIERARCHICAL ASSEMBLY OF IMMOBILIZED
TiO₂-BASED NANOSTRUCTURED EPITAXIAL
FILMS ON Ti SUBSTRATES FOR
PHOTOCATALYTIC WATER DECONTAMINATION
AND HYDROGEN GENERATION**

NG JIAWEI

SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

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2012

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ABSTRACT

World population is expected to hit 8.3 billion by 2030. This will cause a massive 30 percent increase in the global demand for drinking water that is already short in supply currently. Researchers have worked tirelessly over decades to develop advanced technologies for decontamination of used water and to increase the supply of fresh water. The emergence of heterogeneous TiO_2 photocatalysis has been a tremendous research milestone in water reclamation technologies.

This PhD thesis primarily involved the hierarchical assembly of immobilized TiO_2 -based epitaxial crystalline thin film photocatalysts that are anchored and grown directly from crystalline Ti substrates. The synthesized novel photocatalysts featuring various nanostructures presented herein include nanotubes, nanowhiskers, nanowires, nanofungus and nanocubes. The different morphologies have imparted various functionalities and also tailor surface- and shaped-induced properties of semiconductor nanocrystalline phase. The increased surface area and reactive sites also resulted in a consistently higher activity for surface-based processes such as heterogeneous photocatalysis.

Free-standing and self-organized TiO_2 nanotube arrays were synthesized via electrochemical anodization and demonstrated excellent photocatalytic disinfection of *E. coli* cells. Over 95% of the initial 10^6 cpu/mL *E. coli* cells were inactivated within 50 mins of UV-A photocatalytic disinfection, and influencing factors from different ionic species and organic compound were studied.

Progressive morphological and crystallographic evolution of the highly ordered anodic nanotubes to radially-aligned nanowhisker arrays was elucidated. Owing to its unique morphology and monocrystalline defect-free lattice structure, the nanowhisker sample exhibited excellent photodegradation of AO7, a common photostable dye used in textile industries.

An immobilized anatase TiO_2 thin film bearing a unique, mesoporous nanofungus-like morphology was developed for the photocatalytic degradation of BPA. The

mechanistic degradation pathway was elucidated using charge-trapping and interfering scavenging species as diagnostic tools and experimental evidence have manifested hydroxyl radicals ($\bullet\text{OH}$) to be the predominant active species in associated oxidation processes.

Coupling of TiO_2 and SrTiO_3 to develop a unique morphology of heterojunctioned $\text{TiO}_2/\text{SrTiO}_3$ photocatalyst was performed to achieve spatial delocalization of photogenerated electrons and holes. The enhanced photocatalytic H_2 generation is largely attributed to the efficient separation of photogenerated charges at heterojunctions of the 2 dissimilar semiconductors, as well as a negative redox potential shift in Fermi level which acted as potential traps for electrons and reinforced reduction of hydroxide ions present in water.

This PhD work embarked on the development of immobilized TiO_2 -based nanostructured epitaxial film photocatalysts to degrade recalcitrant, emerging contaminants and pathogens that are commonly present in water bodies (AO7, *E. coli* cells and BPA) via photogenerated holes and oxidative radicals. The free electrons produced from photocatalytic reduction half-reactions are harvested and utilized for the reduction of hydroxide ions present in the treated water to generate hydrogen gas, a source of clean energy. The photocatalysts will address the common shortcomings of conventional nanopowdered TiO_2 photocatalysts, by 1) enabling ease of catalyst recovery in scale-up engineering processes; 2) overcoming mass-transfer limitations present in micro- or mesoporous bulk particles; 3) promoting high performance photocatalysis by virtue of its high quantum efficiency, unique nanostructure morphology and surface defect-free crystal structure.

LIST OF PUBLICATIONS AND AWARDS

Awards:

1. **Ng, J.**, Sun, D. D. (2011). "Autumn's Drought" Awarded 1st Prize in the Materials Research Society (MRS) Annual "Science as Art" Competition 2011. Please refer to Appendix (I) for details.

Journal Papers:

1. **Ng, J.**, Pan, J. H., Sun, D. D. (2011). "Hierarchical assembly of anatase nanowhiskers and evaluation of their photocatalytic efficiency in comparison to various one-dimensional TiO₂ nanostructures". Journal of Materials Chemistry 21 (32): 11844-11853.
2. **Ng, J.**, Wang, X., Sun, D. D. (2011). "One-pot hydrothermal synthesis of a hierarchical nanofungus-like anatase TiO₂ thin film for photocatalytic oxidation of Bisphenol A". Applied Catalysis B: Environmental 110: 260-272.
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13. Zhang, T., Zhang, X., **Ng, J.**, Yang, H., Liu, J., Sun, D. D. (2011). "Fabrication of magnetic cryptomelane-type manganese oxide nanowires for water treatment". Chemical Communications 47 (6): 1890-1892.
14. Zhang, T., Zhang, X., Yan, X., **Ng, J.**, Wang, Y., Sun, D. D. (2011). "Removal of bisphenol A via a hybrid process combining oxidation on β -MnO₂ nanowires with microfiltration". Colloids and Surfaces A: Physicochemical and Engineering Aspects 392 (1): 198-204.
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2. Xu, S., **Ng, J.**, Du, A. J., Sun, D. D. (2011). Simultaneous Copper ions Removal and Hydrogen Production from Water over TiO₂ Nanotube Photocatalyst. IWA Water and Industry 2011, Valladolid, Spain, 1st – 4th May 2011.
3. Zhang, X., Zhang, T., **Ng, J.**, Sun, D. D. (2010). Superhydrophilic Manganese Oxide Nanowire Membrane for High Flux Water Filtration. Singapore International Water Week, Suntec City, Singapore, 28th June – 3rd July 2010.
4. Xu, S., **Ng, J.**, Zhang, X., Bai, H., Sun, D. D. (2010). Adsorption and Photocatalytic Degradation of Dye Pollutants over TiO₂ Nanotube Photocatalyst. 6th International Conference on Interfaces Against Pollution, Beijing, China, 16th – 19th May 2010.
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LIST OF SYMBOLS AND TERMS

Symbols	Terms
λ	Light wavelength
$(>\text{Ti}^{\text{III}}\text{OH})$	Surface-trapped conduction band electron
$\eta_{\text{app, in}}$	Apparent quantum efficiency
$(\text{Ti}^{\text{IV}}\text{OH}^{\bullet+})$	Surface-trapped valence band hole (or surface-bound $\bullet\text{OH}$)
$\bullet\text{OH}$	Hydroxyl radical
AO7	Acid orange 7
BE	Binding energy
BET	Brunauer-emmett-teller
BJH	Bopp-jancso-heinzinger
BPA	Bisphenol A
BQ	Benzoquinone
CB	Conduction band
CVD	Chemical vapor deposition
DBPs	Disinfection by-products
DMSO	Dimethyl sulfoxide
DOS	Densities of states
DSSCs	Dye-sensitized solar cells
E_{g}	Band gap energy
E_{cb}	Conduction band energy
EDX	Energy dispersive X-ray spectroscopy
E_{vb}	Valence band energy
FEG	Field-emission gun
FESEM	Field-emission scanning electron microscopy
FWHM	Full width at half maximum
GC	Gas chromatography
H_2O_2	Hydrogen peroxide
HPLC	High-performance liquid chromatograph

HRTEM	High-resolution transmission electron microscopy
ICDD	International Centre for Diffraction Data
LDA	Local density approximation
NaN ₃	Sodium azide
N _L	Avogadro number
O ₂ ^{•-}	Superoxide radicals
Ox	Oxidant
PDF	Powder diffraction file
PL	Photoluminescence
PVD	Physical vapor deposition
QSE	Quantum size effects
Red	Reductant
ROS	Reactive oxygen species
RSF	Relative sensitive factor
SAED	Selected area electron diffraction
SEM	Scanning electron microscopy
SSA	Specific surface area
TEM	Transmission electron microscopy
TiO ₂	Titanium dioxide
TOC	Total organic carbon
UHV	Ultrahigh vacuum
VB	Valence band
VOCs	Volatile organic compounds
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray diffraction

CHAPTER 1 INTRODUCTION

1.1 Background

Amidst global emphasis and deliberate policy and planning on sustainable development, water and energy crises remain the biggest challenges to mankind. World population is expected to hit 8.3 billion by 2030 and this will lead to a 50 and 30 percent respective increase in global energy and clean water demand. Climate change and industrialization will intensify this crisis even further in unpredictable ways. It is therefore critical to develop better and cleaner technologies now for the production of water energy and supplies.

Recycling and reuse of wastewater and desalination are the alternative solutions for conservation of potable water. Traditional treatment processes, such as adsorption, coagulation/flocculation and membrane technologies have been investigated and practised in the water treatment process. However, these treatment processes do not degrade or mineralize the contaminants, but merely transfer them from one matrix to another. They usually incur high operating costs and generate sludge or brines that require further treatment and disposal. Ozonation is effective in disinfection and oxidizing recalcitrant organic contaminants, but steep operating costs from high energy consumption limit its extensive potential. Membrane applications are, on the other hand, severely hampered by high propensity of biofouling, organic/inorganic fouling and scaling; while pressure-driven membranes are energy-intensive. There is thus an urgent need for alternative cost-effective technologies to overcome not only shortage of clean water, but explore clean energy generation from water as well.

Semiconductor-mediated heterogeneous photocatalysis has been a promising technology in environmental remediation due to the fact that they do not generate harmful by-products. Photocatalytic oxidation processes present significant advantages for disinfection, decontamination and membrane fouling control strategies, especially in rural areas where access to chemical oxidants is limited and

solar irradiation is readily available (Duffy et al. 2004, Gelover et al. 2006, Malato et al. 2009).

Since the discovery of photoelectrochemical decomposition of water under an irradiated titanium dioxide (TiO₂) photoelectrode by Fujishima and Honda in 1972 (Fujishima and Honda 1972), TiO₂ photocatalysis has spawned a tremendous amount of research work on the development of novel photocatalysts for industrial applications. The unique optical, electronic and chemical properties of TiO₂, renders it a remarkable yet uncostly material for a wide spectrum of practical applications. Recently, the design and construction of tunable nanostructured TiO₂ photocatalysts have drawn significant attention (Chen and Mao 2007a, Liu et al. 2010a, Testino et al. 2007). By precise manipulation of the nanostructures, it is possible to impart new functionalities, as well as control and tailor properties of semiconductor nanocrystals and biomolecular systems (West and Halas 2000, Xia et al. 2003). In the context of photocatalysis, consistently higher activity is also justified from the increased surface area and reactive sites. As an important wide bandgap semiconductor, various nanofeatures of TiO₂ have been explored to optimize properties and improve efficiencies. Among the wide array of nanostructures, nanowires (Ng et al. 2010, Wu et al. 2009a), nanotubes (Macak et al. 2007, Macak et al. 2005a), nanobelts (Fang et al. 2011), nanoflakes (Ho et al. 2005, Wang et al. 2010), nanospheres (Li and Zeng 2007, Yang and Zeng 2004) and nanorods (Wu et al. 2005a, Wu 2007), are some of the more commonly reported architectures.

One of the bottleneck problem hampering engineering applications of TiO₂ photocatalysis today is the constraints of recovering spent photocatalysts from treated effluent for reuse (Peng and Chen 2006). This holds true especially for powdered suspension in fluidized bed systems, where nanopowdered photocatalysts can potentially become a form of secondary contamination in environmental remediation processes. In addition, diffusion-model studies of micro- and mesoporous bulk particles have reported that solute-diffusivities and intraparticle mass transfer rates are substantially retarded, suggesting strong hindrance effects

caused by tortuosities and narrow pore constrictions (Papelis et al. 1995). In view of the practical limitations of nanopowdered photocatalysts, different strategies to immobilize nanoparticulate TiO_2 on solid substrates have thus been proposed (Ho et al. 2005, Yang and Zeng 2003). However, due to the tedious preparation process and weak particulate attachment on foreign substrates, such supported photocatalysts are largely restricted to laboratory or small scale applications. Scientists have thus proposed various synthetic methods to induce direct crystal growth of TiO_2 nanostructures over Ti substrates, for instance, anodization (Macak et al. 2007, Macak et al. 2005a), sol-gel (spin or dip coating) (Pierre and Pajonk 2002), hydrothermal (Mao et al. 2006, Wang et al. 2010, Wu et al. 2008, Wu et al. 2005a, Wu 2007, Wu et al. 2009a, Yang and Zeng 2004), chemical vapor deposition (Wu and Yu 2004), physical vapor thermal deposition (Wu et al. 2005c), and template-based assembly using structure-directing agents (Huang et al. 2008, Lechmann et al. 2009), etc.

The photocatalytic oxidation technology is based on the principle of hole and electron generation under light irradiation. The advantage of using the hole for oxidation treatment is to enable it to purify the water but the energy consumption used for such treatments has been ignored. To fully utilize both hole and electron, it is necessary to investigate the use of the same semiconductor TiO_2 for energy generation such as H_2 from water, which can be used to substitute energy consumption required for water decontamination processes. Therefore, it will be ideal to develop a novel nanostructured TiO_2 photocatalyst for not just purification of water for reuse, but also able to produce clean energy in the form of H_2 via photocatalytic reduction of hydroxide ions present in the water. If these can be achieved, we can address both clean water and energy supply problems at one time with the cross-disciplinary science and engineering behind the multifunctional, photocatalytic nanomaterials.

1.2 Research objectives

It is known that the performance of TiO_2 relies primarily on its crystalline phase, morphology and dimensionality. High crystallinity and specific surface area have been reported to contribute positively towards surface-based processes such as heterogeneous photocatalysis, in achieving high photocatalytic oxidation activity and adsorption efficiencies by virtue of their induced shape- and size-dependant properties. On the other hand, low quantum efficiency, which is a common predicament of intrinsic semiconductors such as TiO_2 , is also a main antecedent of poor photocatalytic activity. It is mainly caused by rapid recombination of photogenerated holes and electrons within the semiconductor particles that result in an abated generation of reactive oxygen species. It is noteworthy that quantum yields can be influenced by morphological factors of the nanostructured catalyst.

The overall research objective of this study is to design and synthesize a variety of hybrid nanocomposite photocatalysts with hierarchical nanostructures, on the basis and consideration of environmental engineering applications in photocatalytic disinfection and decontamination of water, as well as photocatalytic hydrogen generation via water splitting reactions. Henceforth, ease in separation and recovery of spent photocatalysts, controlled optimization of dimensionality and morphologies, as well as modification to the crystallographic structures and electronic band gap configurations to enhance photocatalytic efficiencies, are some of the essential elements during contemplation of the catalyst design.

The explicit objectives of this work include:

- I. Fine-tuning of synthesis parameters with optimization of photocatalytic efficiencies, during design and fabrication stage of the respective nanostructured photocatalysts.
- II. Illustration of time-progressive electron microscopic images to investigate the evolution of different hierarchical nanostructures across various reaction durations, and postulate formation mechanisms behind the final nanostructure morphology.

- III. Investigate the modification of different nanostructured morphologies and coupling of dissimilar semiconductors on suppressing recombination of photogenerated electron-hole pairs, and their influence towards photocatalytic performance and quantum yields.
- IV. Explore diverse environmental applications of water decontamination and renewable energy production via photocatalytic disinfection of *E. coli* cells, photocatalytic degradation of organic pollutants such as Acid Orange 7 and Bisphenol A, and photocatalytic hydrogen generation over water splitting reactions.
- V. Elucidate the photocatalytic reaction mechanisms involved behind the oxidation and reduction processes, and the respective contributory roles of photogenerated reactive oxygen species and radicals towards the enhancement of photocatalytic efficiencies.

1.3 Thesis overview

This thesis comprises of 8 chapters. **Chapter 1** covers the introduction, which outlines the background and scientific motivation of this study, as well as the overview of this thesis. **Chapter 2** presents a detailed literature review of heterogeneous photocatalysis and the different approaches and dimensions of TiO₂ photocatalysts. **Chapter 3** lists down the experimental details of the synthesis, characterization and application methodologies that were conducted for the research work documented in this thesis. **Chapter 8** is the collation of final conclusions drawn from the conducted research work and offers detailed recommendations for future works to augment this thesis.

Chapter 4 reports the development of a multifunctional TiO₂ nanotube-arrayed thin film using anodization techniques. The as-synthesized free-standing photocatalyst possess superior photocatalytic efficiency and characterizes high mechanical strength and are comprised of vertically-oriented and highly ordered nanotube arrays. Experimental results have shown that the photocatalyst exhibits effective

photocatalytic disinfection of drinking water and demonstrates photocatalytic stability in terms of photocatalytic inactivation efficacy of *E. coli* under the influence of different ionic species and organic compounds.

Chapter 5 describes in detail the synthesis of a hierarchically-structured anatase film that is comprised of radially-aligned, ultra-long nanowhiskers. The progressive morphological evolution of highly-ordered anodic nanotubes to the radial nanowhiskers is elucidated via a time-dependant, step-by-step illustration FESEM images taken at various reaction times; while crystallographic transformations are illustrated by the corresponding HRTEM and SAED figures. Photocatalytic activity of the as-synthesized TiO₂ nanowhiskers was evaluated over the photocatalytic degradation of an organic model compound, Acid Orange 7. For the purpose of comparing photocatalytic activities, photocatalytic experiments with other immobilized TiO₂ films of 1D nanostructure of nanowires, nanotubes, as well as a nanoparticulate Degussa P25 TiO₂ coated film were conducted under identical experimental conditions.

Chapter 6 presents a facile one-pot hydrothermal method to prepare a hierarchical and mesoporous nanofungus-like anatase thin film. The possible reaction pathways en-route to obtaining the final morphology of the photocatalyst is presented via a series of FESEM images depicting the time-progressive morphological evolution. Detailed material characterization of synthesized photocatalysts prepared under different hydrothermal durations hypothesize the growth mechanisms involved behind the synthesis process; while their respective photocatalytic activities are compared to optimize synthesis parameters based on degradation of Bisphenol A. By means of probe species and hole/radical scavengers, the working mechanism and respective contributions of free radical species behind photocatalytic oxidation of BPA were investigated. Photocatalytic stability of the as-synthesized photocatalyst was also evaluated after 10 consecutive cycles of usage.

Chapter 7 illustrates a 2-step hydrothermal method in preparing a highly stable and well-coupled TiO₂/SrTiO₃ thin film with a novel hybrid nanostructure of nanowires

and nanocubes, immobilized on a Ti substrate for photocatalytic hydrogen generation. The coupling of TiO_2 and SrTiO_3 formed unique heterojunctions at boundary interfaces of the 2 crystalline semiconductors of unequal bandgaps which enhanced spatial delocalization of interfacial charge carriers, and served as potential traps for photogenerated electrons, prolonging their reaction lifetimes. The negative shift in Fermi level also reinforced reduction of hydroxide ions, thus photocatalytic generation of hydrogen gas was substantially increased.

CHAPTER 2 LITERATURE REVIEW

2.1 Semiconductor heterogeneous photocatalysis

2.1.1 Introduction

Since the discovery of photocatalytic water splitting at TiO₂ electrodes in 1972 (Fujishima and Honda 1972), intense studies have been conducted towards understanding the fundamentals of photocatalysis and enhancing its process efficiency. The major advantages of this technology include the following (Kabra et al. 2004):

- I. Photocatalysis offers a good substitute for the energy-intensive conventional treatment techniques by using renewable and pollution-free solar energy.
- II. Unlike conventional treatment methods which may transfer pollutants from one medium to another, photocatalysis leads to the formation of innocuous final products such as CO₂, H₂O etc, and resulting minimal secondary waste.
- III. The photocatalytic process can be applied to degrade a variety of hazardous contaminants in water and wastewater streams.
- IV. This process can be used for water and air purification, as well as solid-(soil-) phase treatments to some extent.
- V. The photocatalytic reaction occurs at mild conditions within modest reaction time.

Semiconductor photocatalysis with a primary focus on TiO₂ as a durable photocatalyst has been applied to a variety of problems of environmental interest in addition to water and air purification. This technology has been widely investigated for color removal and destruction of dyes (Pelaez et al. 2012, Tanaka et al. 2000), degradation and mineralization of organic pollutants (Gaya and Abdullah 2008, Kabra et al. 2004), destruction of hazardous inorganic such as cyanides and

treatment of heavy metals (D. C. Cid et al. 2012, Shirzad Siboni et al. 2011), purification and disinfection of water (Byrne et al. 2011, Malato et al. 2009, McCullagh et al. 2007), and decontamination of indoor air (Zhao and Yang 2003).

2.1.2 Basic principles of heterogeneous photocatalysis

Heterogeneous photocatalysis is a multidisciplinary field of study that encompasses multidisciplinary theories and reactions. Heterogeneous photocatalysis can be carried out in either aqueous or nonaqueous solutions or in gaseous mixtures. The process involves a number of steps similar to conventional heterogeneous catalysis as follows (Herrmann 1999):

- I. Transfer of reactants in the fluid phase to the surface
- II. Adsorption of some of the reactants
- III. Reaction in the adsorbed surface
- IV. Desorption of formed product(s)
- V. Removal of the products from the interface region

For the photocatalysis, the only difference with classical catalysis is that the mode of activation of the catalyst is replaced by a photonic activation. Heterogeneously dispersed semiconductor surfaces provide both a fixed environment to influence the chemical reactivity of a wide range of adsorbates and a means to initiate light-induced redox reactivity in these weakly associated molecules.

It is widely accepted that three components must be present in order for the heterogeneous photocatalytic reaction to take place: an emitted photon with appropriate wavelength, a semiconductor surface and a strong oxidizing agent (in most cases oxygen). The photocatalytic process is initiated when a photon with energy equal to or greater than the band gap energy (E_g) of the semiconductor photocatalyst reaches the photocatalyst surface, resulting in molecular excitation. E_g is defined as the difference between the filled valence band and the empty

conduction band of the photocatalyst, in the order of a few electron volts. This molecular excitation results in the generation of mobile electrons in the higher energy conduction band (E_{cb}) and positive holes in the lower energy valence band (E_{vb}) of the catalyst. The valence band holes are powerful oxidants (+1.0 to +3.5 V vs normal hydrogen electrode depending on the semiconductor and pH), while the conduction-band electrons are good reductants (+0.5 to -1.5 V vs NHE) (Fujishima et al. 2000, Gratzel 2001). The photocatalytic reaction proceeds via a series of chemical events, following the initiation step of pair electron-hole formation. Excited state conduction-band electrons and valence-band holes can recombine and dissipate the input energy as heat, get trapped in metastable surface states or react with electron donors and electron acceptors adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles. With reference to Figure 2.1, Red (i.e. reductant) is an electron donor and Ox (i.e. oxidant) is an electron acceptor. If a pair of suitable Red or Ox is available to trap the hole or electron, recombination is prevented and subsequent redox reactions may occur at the surface of the photoexcited semiconductor photocatalyst. Oxygen is the most common electron acceptor served in the photocatalytic processes, which could lead to the formation of superoxides, its protonated form the hydroperoxyl radical and subsequently H_2O_2 (Gaya and Abdullah 2008). Eventually these formed reactive oxidative species can be used for the oxidation processes. While in the absence of suitable electron and hole scavengers, the stored energy is dissipated within a few nanoseconds by recombination (Hoffmann et al. 1995). Recombination of electron and hole results in process inefficiencies and the waste of the energy supplied by the photon. Therefore the electron-hole recombination is usually considered as one of the major factors limiting the efficiency of the photocatalytic process (Herrmann 1999).

Figure 2.1. Schematic photophysical and photochemical processes over photon activated semiconductor (p) photogeneration of electron-hole pair, (q) surface recombination, (r) recombination in the bulk, (s) diffusion of acceptor and reduction on the surface of semiconductor, and (t) oxidation of donor on the surface of semiconductor (Gaya and Abdullah 2008).

2.1.3 Semiconductors

Solids that can promote reactions in the presence of light and are not consumed in the overall reaction are considered as photocatalysts. These are invariably semiconductors. A good photocatalyst should be photoactive, biologically and chemically inert, photostable, nontoxic and inexpensive. In order for a semiconductor to be photoactive under visible and/or UV light, the photogenerated valence band hole must be sufficiently positive to generate $\bullet OH$ radicals, which can subsequently oxidize the organic pollutant, or the redox potential of the photoinduced electron must be sufficiently negative to be able to reduce the adsorbed O_2 to superoxide (Bhatkhande et al. 2002). Various chalcogenides (oxides and sulfides) semiconductors such as TiO_2 , ZnO , Fe_2O_3 , CdS , and WO_3 etc. have been examined and used as photocatalysts due to their electronic structure, which is characterized by a filled valence band and an empty conduction band. The valence and conduction band positions for various semiconductors in contact with aqueous electrolyte at pH 1 are provided in the Figure 2.2. The lower edge of the conduction

band (red color) and upper edge of the valence band (green color) are presented along with the band gap in electron volts. The energy scale is presented in electron volts using either the normal hydrogen electrode or the vacuum level as a reference. It is known that in order to photoreduce a chemical species, potential of conduction band of the semiconductor must be more negative than its reduction potential. Similarly, to photooxidize a chemical species, potential of valence band of the semiconductor must be more positive than its oxidation potential. Generally speaking, the photo-induced electron transfer occur with the adsorbed species on the semiconductor photocatalysts depends on the band-edge position of the semiconductor and the redox potentials of the adsorbates (Fujishima et al. 2000).

Figure 2.2. Valence and conduction band positions of various semiconductors in contact with aqueous electrolyte at pH 0 (Jiang et al. 2003).

2.1.4 Mechanism of TiO₂ photocatalysis

Among the various semiconductor photocatalysts, TiO₂ appears the most active, exhibiting high photocatalytic performance with maximum quantum yields. In addition, although TiO₂ is only photo responsive under UV light, it is cheap, insoluble under most conditions, photostable, and non-toxic (Chen and Mao 2007b). Other advantageous characteristics of titanium dioxide include its high refractive index, large surface-to-volume ratios, high surface activity, high sensitivity and controllable pore size. The photogenerated holes in the valence band of TiO₂, hole-trapping radical species and activated oxygen species are strong oxidation agents and possess sufficient oxidizing power to perform non-selective oxidation of any organic compounds to CO₂, water and other mineral acids. Moreover, anatase TiO₂ is the most active allotropic form among the various ones available, natural (rutile and brookite) or artificial (TiO₂-B, TiO₂-H). It has been reported that anatase TiO₂ shows the best combination of photoactivity and photostability (Herrmann 1999, Zeltner and Tompkin 2005).

TiO₂-assisted heterogeneous photocatalytic reaction can be represented as a number of mechanistic steps. The primary step involved in the photocatalysis and characteristic time for corresponding elementary reaction has been proposed in the literature as shown in Table 2.1 (Hoffmann et al. 1995). The >TiOH represents the primary hydrated surface functionality of TiO₂. e⁻ is a conduction-band electron, e_{tr}⁻ is a trapped conduction-band electron, h⁺ is a valence-band hole, Red is an electron donor (i.e. reductant), O_x is an electron acceptor (i.e. oxidant), (Ti^{iv}OH^{•+}) is the surface-trapped valence band hole (or surface-bound •OH), and (>TiⁱⁱⁱOH) is the surface-trapped conduction band electron. Although surface-bound •OH and surface-trapped hole use the same term of (Ti^{iv}OH^{•+}), it has been accepted that the trapped hole and a surface-bond •OH are indistinguishable species. The dynamic equilibrium of equation 2.3 represents a reversible trapping of a conduction-band electron in a shallow trap below the conduction-band edge such that there is a finite possibility that e_{tr}⁻ can be transferred back into the conduction band at room temperature. According to the mechanism, the overall quantum efficiency for

interfacial charge transfer is determined by two critical processes. They are the completion between charge-carrier recombination and trapping, as well as the competition between trapped carrier recombination and interfacial charge transfer. On the basis of flash radiolysis, Bahnemann et al. pointed that the interaction of trapped e_{tr}^- and h^+ (presumably $\bullet OH$) pairs near TiO_2 surface induce the fission of bond in organic molecules, indicating the existence of trapped charge carrier (Bahnemann et al. 1984).

Table 2.1. Primary process in TiO_2 -assisted photocatalysis and characteristic time of corresponding step.

Major processes	Characteristic time	Eqn
Charge carrier generation		
$TiO_2 + h\nu \rightarrow h^+ + e^-$	fs (very fast)	(2.1)
Charge carrier trapping		
$h^+ + >Ti^{IV}OH \rightarrow (>Ti^{IV}OH^{\bullet+})$	10 ns (fast)	(2.2)
$e^- + >Ti^{IV}OH \leftrightarrow (>Ti^{III}OH)$	100 ps (shallow trap, dynamic equilibrium)	(2.3)
$e^- + >Ti^{IV} \rightarrow >Ti^{III}$	10 ns (deep trap)	(2.4)
Charge-carrier recombination		
$e^- + (>Ti^{IV}OH^{\bullet+}) \rightarrow >Ti^{IV}OH$	100 ns (slow)	(2.5)
$h^+ + >Ti^{III}OH \rightarrow >Ti^{IV}OH$	10 ns (fast)	(2.6)
Interfacial charge transfer		
$(>Ti^{IV}OH^{\bullet+}) + Red \rightarrow >Ti^{IV}OH + Red^{\bullet+}$	100 ns (slow)	(2.7)
$e_{tr}^- + O_x \rightarrow >Ti^{IV}OH + O_x^{\bullet-}$	ms (very slow)	(2.8)

Figure 2.3. Schematic diagram showing the potentials for various redox processes occurring on the TiO_2 surface at pH 7 (Fujishima et al. 2000).

In this general mechanism, it is assumed that the photocatalytic reaction is caused by indirect oxidation via surface-bound $\bullet\text{OH}$. However, there is another group argue in favor of a direct oxidation via the valence-band h^+ (Hoffmann et al. 1995). In support of the argument for surface-bound $\bullet\text{OH}$ mechanism, there is an intermediate presence of hydroxylated structures during the photocatalytic degradation of halogenated aromatics. These hydroxylated intermediates are also found when similar aromatics react with a known source of $\bullet\text{OH}$. Furthermore, the studies using electron paramagnetic resonance spectra confirm the existence of hydroxyl and hydroperoxyl radicals in aqueous solution of illuminated TiO_2 (Hoffmann et al. 1995, Linsebigler et al. 1995).

However, the important roles of surface trapped hole (or surface-bound $\bullet\text{OH}$) and electron in the photooxidation of organic compounds have been agreed in the literature (Lawless et al. 1991, Serpone et al. 1995a). In most case, photocatalytic reactions are carried out in presence of water, air and the photocatalyst. It has been considered that the presence of water is indispensable in TiO_2 photocatalysis for degradation of organic contaminants. As shown in Figure 2.3, the redox potential for h^+ is + 2.53 V versus the standard hydrogen electrode in solution of pH 7. After reaction with water, these h^+ can produce $\bullet\text{OH}$, whose redox potential is slightly decreased. Both are more than positive than that of ozone. The redox potential for conduction band electrons is - 0.52 V, which is negative enough to reduce

dissolved oxygen to superoxide O_2^- , or to hydrogen peroxide (H_2O_2). Depending upon the exact conditions, the h^+ , $\bullet\text{OH}$, O_2^- , H_2O_2 and O_2 itself can all play important roles in the photocatalytic reaction mechanisms (Fujishima and Zhang 2006).

2.2 Properties of TiO_2 nanomaterials

2.2.1 Lattice structure of TiO_2

Three different crystalline forms of TiO_2 , namely the rutile, anatase, and brookite polymorphs, occur naturally in mineral form, and at low temperatures, only rutile and anatase crystals can be synthesized in pure form. Therefore, these 2 polymorphs have been widely studied on their synthesis, characterization and photocatalytic properties. Until now, anatase TiO_2 is known to show higher photocatalytic efficiency as compared to the rutile phase. Since it is difficult to prepare pure brookite without mixture of rutile or anatase phases, there has been limited investigation on the synthesis, characterization and properties of the brookite phase, which belongs to the orthorhombic crystal system. The structures of rutile and anatase can be described in terms of chains of TiO_6 octahedra, where each Ti^{4+} ion is surrounded by an octahedron of six O^{2-} ions. Figure 2.4 shows the unit cell structures of the rutile and anatase TiO_2 crystals (Chen and Mao 2007a, Linsebigler et al. 1995). The two crystal structures differ in the distortion of each octahedron and the assembly pattern of the octahedral chains. The octahedron in rutile is irregular and displaying a slight distortion. The octahedron in anatase is significantly distorted so that its symmetry is lower than orthorhombic. The Ti-Ti distances in anatase are larger (3.79 and 3.04 Å vs 3.57 and 2.96 Å in rutile), whereas the Ti-O distances are shorter than those in rutile (1.934 and 1.980 Å in anatase vs 1.949 and 1.980 Å in rutile). In rutile structure, each octahedron is in contact with 10 neighbor octahedrons (two sharing edge oxygen pairs and eight sharing corner oxygen atoms), while, in the anatase structure, each octahedron is in contact with eight neighbors (four sharing an edge and four sharing a corner). These

differentiated in lattice structures cause different mass densities and electronic band structures between the two forms of TiO_2 , as shown in Figure 2.4.

Figure 2.4. Lattice structure of rutile and anatase TiO_2 (Linsebigler et al. 1995).

2.2.2 TiO_2 Thermodynamic properties

Rutile is the stable phase at high temperatures, but anatase and brookite are common in fine grained natural and synthetic samples. On heating concomitant with coarsening, the following transformations are all seen; anatase-brookite-rutile, brookite-anatase-rutile, anatase-rutile, and brookite-rutile. These transformation sequences reveals very closely balanced energetic as a function of particle size (Chen and Mao 2007a). It has been found that the crystal structure of TiO_2 nanoparticles highly depended on the preparation method (Ma et al. 1998). For small TiO_2 nanoparticles ($< 50 \text{ nm}$), anatase seemed more stable and transformed to rutile at $> 973 \text{ K}$ (Ma et al. 1998).

2.2.3 Electronic properties of TiO_2 nanomaterials

The DOS of TiO_2 is composed of Ti e_g , Ti t_{2g} (d_{yz} , d_{zx} , and d_{xy}), O p_σ (in the Ti_3O cluster plane), and O p_π (out of the Ti_3O cluster plane), as shown in Figure 2.5 (Chen and Mao 2007a). The upper valence bands can be decomposed into three

main regions as follows: the σ bonding in the lower energy region mainly attributed to O p_σ bonding; the π bonding in the middle energy region; and O p_π states in the higher energy region due to O p_π nonbonding states at the top of the valence bands where the hybridization with d states is almost negligible. The contribution of the π bonding is significantly weaker than that of the σ bonding. The conduction bands are decomposed into Ti e_g and t_{2g} bands. The d_{xy} states are dominantly positioned at the bottom of the conduction bands. The rest of the t_{2g} bands are antibonding with p states. The main peak of the t_{2g} bands is recognized to be mostly d_{yz} and d_{zx} states (Linsebigler et al. 1995). As shown in Figure 2.5, it can be seen the nonbonding O p_p orbital located at the top of the valence bands and the nonbonding d_{xy} states at the bottom of the conduction bands. It is well known that for nanoparticles the band gap energy increases and the energy band becomes more discrete with decreasing size. As the size of semiconductor nanoparticle falls below the Bohr radius of the first excitation state or become comparable to the de Broglie wavelength of the charge carriers, the charge carriers begin to behave quantum mechanically and charge confinement leads to a series of discrete electronic states (Chen and Mao 2007a).

It has been accepted in literature that the valence band of wide-gap rutile and anatase consist of O 2p states, whereas the conduction band is formed by Ti 3d states (Henrich and Cox 1994). TiO_2 crystals show a high resistivity due to its wide band-gap, and the bulk oxygen vacancies, titanium interstitials, and reduced crystal surfaces tend to generate shallow electron donor levels that contribute to the electric conductivity of TiO_2 (Paxton and Thin-Nga 1998). Point defects in terms of doubly charged oxygen vacancies and interstitial Ti^{3+} or Ti^{4+} affect the conductivity and ionization energy of the rutile crystal (Banerjee 2011). In addition, the dominant crystal defects in anatase TiO_2 have not been fully understood, some studies suggested Ti interstitials caused the dominant defects, while others agreed oxygen vacancies for the same, and several reports suggested the existence of both phenomena, with an activation energy of carrier generation around 4 meV. For both anatase and rutile, high concentrations of donors lead to the formation of impurity

bands, and a transition from nonmetallic to metallic behavior is observed when the donor concentration exceeds a critical value (Banerjee 2011) .

2.2.4 Optical properties of TiO₂

Figure 2.5. (A) Total and projected densities of states (DOS) of the anatase TiO₂ structure. (B) Molecular-orbital bonding structure for anatase TiO₂: a) atomic levels; b) crystal-field split levels; c) final interaction states. The thin-solid and dashed lines represent large and small contributions, respectively (Asahi et al. 2000).

The main mechanism of light absorption in pure semiconductors is direct interband electron transitions. This absorption is especially low in indirect semiconductors, e.g., TiO_2 , where the direct electron transitions between the band centers are prohibited by the crystal symmetry. It has been reported that small TiO_2 crystallites showed enhancement of light absorption due to indirect electron transitions with momentum nonconversion at interface. The indirect transitions are considered due to a large dipole matrix element and a large density of states for the electron in the valance band. Remarkable enhancement of light absorption is expected in small TiO_2 nanocrystals, as well as in porous and micro-crystalline semiconductors, when the share of the interface atoms is large enough. As reported by Enyashin and Seifert (Enyashin and Seifert 2005) by theoretical study, the band structures for anatase nanotubes, nanostrips, and nanorolls were similar to the DOS of the corresponding bulk anatase. The valence band of both bulk TiO_2 and their nanostructures was composed of Ti 3d-O 2p states, and the lower part of the conduction band was formed by Ti 3d states. The difference between these nanostructures was insignificant. All anatase systems showed a wide direct band gap of ca. 4.2 eV, while the nanotubes were semiconductors with an indirect band gap of ca. 4.5 eV. Independent from the specific topology of the TiO_2 nanostructures, the band gap approached the band gap of the corresponding nanocrystals with radii of about 25 Å (Enyashin and Seifert 2005).

2.3 Fabrication of nanostructured TiO_2

Quantum size effects (QSE) occur for semiconductor particles (Q-particles) on the order of 10-100 Å in size. The anomalies arise from the size of the semiconductor particles become comparable to the de Broglie wavelength of the charge carriers in the semiconductor. The range of size for particles experiencing QSE is therefore dependent on the effective mass for the particles. The electron and hole produced in the Q-particles are confined in a potential well of small geometrical dimensions. The electron and hole do not experience the electronic delocalization present in a bulk semiconductor possessing a conduction band and a valence band. Instead, the

confinement produces a quantization of discrete electronic states and increases the effective band gap of the semiconductor. Such effects can change the physical and chemical properties of the material and consequently the photocatalytic activities. As continued breakthroughs have been made in the development of nanotechnology, TiO_2 nanostructures in various forms are finding increased applications because of their specific size-related properties. The energy band structure becomes discrete for nanometer-scale TiO_2 , and its photophysical, photochemical, and surface properties are quite different from those of the bulk TiO_2 due to the QSE, and hence, many studies have focused on the synthesis of nanocrystal-line TiO_2 with a large specific surface area. Fabrication of 0-, 1-, and 2-dimensional nanostructures of TiO_2 has been widely reported recently.

2.3.1 TiO_2 nanoparticles

TiO_2 nanoparticles have specific advantages in the enhancement of light absorption due to the large fraction of surface atoms. Light absorption in pure semiconductor is primarily due to the interband electron transition. This absorption is relatively small in the direct-forbidden gap semiconductor of TiO_2 . It has been reported that considerable enhancement of light absorption can be achieved in small nanocrystals in which the indirect electron transitions can take place, because of the high ratio of surface to volume and sufficient fraction of surface atoms. The particle size around 20 nm shows the significant enhanced light absorption at the interface. An additional advantage for the nanoparticles with few nanometer size is that the large surface-to-volume ratio could result in the timely utilization of photogenerated carriers in interfacial processes (Banerjee 2011).

2.3.1.1 *Solution-based techniques*

The most convenient and widely used method for TiO_2 synthesis is the wet-chemical process. Advantages of this liquid phase process are as follows: possibility of stoichiometry controlling, preparation of composite materials, and formation of

homogenous materials (Tomovska et al. 2007). The most commonly used methods are as follows:

Sol-gel method is one of the most exploited, used mainly for producing films and powders. Many researchers have applied different variants and modifications of this process to produce pure thin film or powders in large homogeneous concentration, and stoichiometry-controlled, with large surface area. The sol-gel method usually uses titanium alkoxide or titanium chloride as precursor (Bu et al. 2006, Campostrini et al. 2003, Li et al. 2004, Sivakumar et al. 2002). By the sol-gel method, surfactants have been introduced in the preparation of a number of nanoparticles with good size distribution. Adding surfactants serving as capping agents, such as acetic acid and acetylacetone, into the reaction matrix could lead to the mono-dispersed TiO_2 nanoparticles (Chen and Mao 2007a). Some studies have reported the sol-gel method in combination with other methods, such as hydrothermal (or solvothermal) for preparation of new and efficient photocatalysts (Li et al. 2005).

Aqueous (hydrothermal methods) or organic media (solvothermal methods) solutions of precursor are used at high temperature (usually less than $250\text{ }^{\circ}\text{C}$) to produce powders or thin films of the photocatalyst (Yin et al. 2003). For solvothermal method, the organic media that are widely used include methanol, butanol, toluene, etc. The most often used precursors for hydrothermal synthesis of TiO_2 are TiCl_3 and TiOSO_4 (Tomovska et al. 2007).

Liquid-phase deposition method is a novel wet technique for fabrication of functional TiO_2 thin film or coupled oxides thin film, deposited directly on the substrate.

Among many advantages of the above-mentioned methods, there are some weaknesses: 1) precursors are expensive, 2) the procedures are relatively long, 3) obtained film might not be in the high purity.

2.3.1.2 Direct oxidation

In addition, TiO₂ nanomaterials can be prepared by oxidation of Ti metal using oxidants or under anodization. It has been reported that TiO₂ nanorods on a Ti plate are obtained when the clear Ti substrate is put in a 30 wt% H₂O₂ solution at 353 K for 72 h. The crystalline TiO₂ is formed by a dissolution precipitation mechanism. Additionally, acetone can be used as a oxidant for preparation of TiO₂ nanorods by oxidizing the Ti plate (Chen and Mao 2007a). Extensive studies have reported TiO₂ nanotubes can be obtained by anodic oxidation of titanium foil (Macak et al. 2005b, Macák et al. 2005).

2.3.1.3 Gas phase techniques

Photocatalysts syntheses via the gas phase are based upon chemical or physical techniques. One of the early reported non-solution techniques is metal organic chemical vapor deposition. Instead of using costly metalorganic precursors, some researchers used inorganic materials in conventional chemical vapor deposition systems to fabricate silica supported TiO₂ nanoparticles with the size of 10-20 nm (Chen and Mao 2007a).

2.3.2 One-dimensional TiO₂ nanostructures

Several different types of TiO₂ nanostructures have been tailored and developed over the last few decades of nanomaterial synthesis research. 1D nanostructures in the form of nanowires, nanofibres, nanorods, hollow nanotubes, nanopillars, nanocylinders, nanoneedles, and nanowhiskers have received considerable attention because of their potential applications in catalysts as carrier materials, in pharmacy as drug-delivery agents, in nanoelectronics for the isolation of ultrasmall wires, etc. Substantial magnitude of research was carried out on 1D TiO₂ nanomorphologies due to their unique structural and physical properties, as well as superior performance as compared to bulk TiO₂ nanoparticles. TiO₂ nanotubes have attracted intense attention due to their applications in highly efficient photocatalysis, lithium

ion batteries, photovoltaic cells, as well as environmental applications (Tomovska et al. 2007). Huang et al. (2001) remarked that 1D nanostructures represent the smallest dimension for efficient transport of electrons and excitons and thus are ideal building blocks for hierarchical assembly of functional nanoscale electronic and photonic structures.

Two important processes govern the overall quantum efficiency for transfer of interfacial charges: 1) competition between charge carrier recombination and trapping, 2) subsequent competition between trapped carrier recombination and interfacial charge transfer. Increase in the lifetime of charge carriers or interfacial electron-transfer rate constant would result in greater quantum efficiency during state-state photolysis (Martin et al. 1994). Henceforth, effective and efficient electron transport within TiO_2 nanocrystallites is critical in achieving high photocatalytic performance. It is worthy to note that structural disorders at the interface between two crystalline nanoparticles lead to enhanced scattering of free electrons which would reduce electron mobility (Peng et al. 2003). This paves way for extensive research to develop highly-ordered and strongly interconnected nanoscale architecture for improved electron transport and greater photocatalytic efficiencies.

2.3.2.1 Solution-based techniques

Kasuga et al. (1998, 1999) synthesized TiO_2 nanoneedles (anatase) using sol-gel-derived fine TiO_2 -based powders under hydrothermal treatment with NaOH. Following their pioneer studies, several research groups have also synthesized 1-dimensional TiO_2 nanostructures using similar chemical processes with some variations in experimental parameters and/or precursors (Chang et al. 2009a, Liu and Aydil 2009, Tang et al. 2012, Wang et al. 2009a, Wu et al. 2009b, Ye et al. 2009, Zhang et al. 2009b). TiO_2 nanowires are obtained by treating TiO_2 white powders in a 10-15 M NaOH aqueous solution at 150-200 °C for 24-72 h under hydrothermal condition. Figure 2.6 shows the SEM images of TiO_2 nanowires and a TEM image of a single nanowire (Zhang et al. 2002). Chang et al. (2009a) have

prepared the TiO_2 nanotube using a microwave-assisted hydrothermal method similar to the Kasuga's group. Zhu and colleagues used a sonication-assisted hydrothermal method to fabricate TiO_2 nanotubes and nanowhiskers (Zhu et al. 2001). With respect to the formation mechanism of TiO_2 nanotubes, Kasuga et al. (1998, 1999) proposed that TiO_2 nanotubes were grown by the connection between the two ends of Ti-OH forming sheets during the process of washing the alkali-treated TiO_2 raw materials. Later, Yao et al. (2003) explained the nanotube formation mechanism using TEM studies. They observed that the TiO_2 nanotube walls were not seamless, unlike multiwall carbon nanotubes. They argued that crystalline TiO_2 raw material underwent delamination in the alkali solution to produce single-layer TiO_2 sheets during alkali treatment. These single-layer TiO_2 sheets were later rolled to form TiO_2 nanotubes.

Various groups have reported syntheses of 1-dimensional TiO_2 nanostructures via porous membrane-based sol-gel and electrochemical routes. TiO_2 nanorods have been synthesized by dipping porous anodic alumina membrane template into a boiled TiO_2 sol followed by drying and heating processes (Miao et al. 2004, Yoon et al. 2006). TiO_2 nanotubes can be also obtained by the sol-gel method by templating with AAM and other organic compounds (Hoyer 1996). Miao and colleagues reported an electrochemically induced sol-gel method to synthesize TiO_2 single-crystalline nanowire arrays. Firstly, the hydroxyl ion was generated due to the cathodic reduction, and then the generation of OH^- ions increases the local pH at the electrode surface, resulting in the titanium oxyhydroxide gel formation in the pores of the template. Subsequent heat treatment and the removal of the template leads to the formation of TiO_2 single-crystalline nanowire arrays (Miao et al. 2002).

Figure 2.6. SEM images of TiO₂ nanowires with the inset showing a TEM image of a single TiO₂ nanowire. (Zhang et al. 2002)

Figure 2.7. TEM image of anatase nanorods and a single nanorod composed of small TiO₂ nanoparticles or nanograins (inset) (Miao et al. 2004).

2.3.2.2 Anodization techniques

Anodization of Ti foils and films is one of the most extensively used methods for template-free electrochemical deposition of TiO₂ nanowire/nanotube (Gong et al. 2001, Varghese et al. 2003). In a typical experiment, a clean Ti plate is anodized in a HF solution under 10-20 V for 10-30 min. Platinum is used as counterelectrode. Crystallized anatase TiO₂ nanotubes are obtained after the anodized Ti plate is annealed at 500 °C for 6 h in oxygen. The length and diameter of the TiO₂ nanotubes could be controlled by a wide range with the applied potential between 1-25 V in optimized phosphate/HF electrodes. Figure 2.8 shows SEM images of TiO₂ nanotubes prepared by this method.

Figure 2.8. SEM images of TiO₂ nanotubes prepared with anodic oxidation (Varghese et al. 2003).

Vertically oriented, highly ordered TiO₂ nanotube arrays made by potentiostatic anodization of titanium are becoming increasingly prominent today due to their properties and applicability in a variety of fields. One of the important applications of TiO₂ nanotube arrays includes dye-sensitized solar cells (DSSCs) (Mor et al. 2006b), where in comparison to nanoparticulate systems; the use of highly ordered nanotube arrays improves photogenerated charge carrier lifetimes by more than an order of magnitude. This is due to the individual TiO₂ nanotube perpendicular to the membrane surface, thus providing two separate channels for efficient electron and hole transport from interface to the electrodes (Mor et al. 2006a). The vertically oriented and closely-packed morphology of nanotubes provides a direct pathway for electron transport at the nanotube walls as compared to the “electron-hopping” in TiO₂ nanoparticles that are commonly utilized in DSSCs (Macak et al. 2007). The vertically aligned nanotubes with an ultrahigh aspect ratio improves the incident light absorption efficiency, offers a large interfacial area for excited ions to effectively dissociate and also facilitate efficient electron transports from the tube walls to the electrodes, thereby enhancing photoconversion efficiency.

Properties and applications of TiO₂ are closely related to its geometric surface areas; hence, keen attention has been devoted in the precise control and synthesis of ultra high aspect ratio of TiO₂ nanotube arrays, as well as controlling its pore size, surface area porosity and wall thickness. In the anodization technique, the basic

criteria for growth of nanotube array hinges on the dynamic equilibrium between the growth and dissolution processes of the oxide layer within the electrolyte phase.

In its virgin state, the titanium surface is covered by a thin layer of natural oxide (TiO_2). When a voltage is applied, due to the high electric field, positive ions such as Ti^{4+} move outwards from the anode while negative ions (O^{2-} , OH^- and F^-) are driven inwards into the thin oxide layer to reach the Ti anode, as shown in Figure 2.9(a). Hence, the growth of the anodic layer can take place at both the metal/oxide and oxide/electrolyte interfaces. The anodized layer, when formed, has a certain degree of hydration. The presence of fluorine ions in the anodic layer can cause etching and generation of cavities, as depicted in Figure 2.9(b). The anodic layer can evolve and become thicker, as shown from Figure 2.9(c), because of the high electric field which causes ionic motion. The cavities, which contain liquid and ionic species, would concentrate in the larger arrays due to lower localized resistance and act as a channel for ionic flow. Under the action of the electric field, cavities would tend to orient vertically to the surface of the metal, that is, in the direction of the electric field. The cavities would link together, breaching cavity walls to optimize the passage of the current, as seen in Figure 2.9(d). As a result, the anodic oxide will develop as a series of nanotubes normal to the Ti metal substrate. The thickness of the tubular layer ceases to increase and reaches an equilibrium thickness, once the chemical dissolution rate of the oxide layer at the oxide/electrolyte interface becomes equal to the rate of inward movement of the metal/oxide interface, as schematically shown in Figures 2.9(e) and (f). The 3-D perspective of the formed tubular structure is presented in Figure 2.9(g).

Figure 2.9. Growth mechanistic model of anodizing a Ti foil (Jaroenworarluck et al. 2007)

2.3.2.3 Gas phase techniques

Recently, the process of vapor deposition has been widely explored to fabricate various nanomaterials. If no chemical reaction occurs, this process is called physical vapor deposition (PVD); otherwise, it is called chemical vapor deposition (CVD). In CVD process, thermal energy heats the gases in the coating chamber and drives the deposition reaction. TiO₂ nanorod arrays with a diameter of ca. 50-100 nm and a length of 0.5-2 μ m can be prepared by metal organic CVD on a WC-Co substrate using TTIP as precursor (Wu et al. 2005b). In addition, TiO₂ nanowire arrays have been synthesized by a simple PVD method or thermal deposition (Wu et al. 2005c). The typical SEM image of TiO₂ nanowires obtained by the PVD method is presented in Figure 2.10.

2.3.3 Other TiO₂ nanostructures

Formation of various other nanostructures of TiO₂ includes nanoplatelet via hydrothermal/anodization route, porous nanofoam via direct decomposition and reaction of hydrogen peroxide inside a TiO₂/hexadecylamine slurry dispersion, nanosheet by delaminating layered protonic titanate into colloidal single layers, and

nanocrystalline thin film using spray deposition of TiO_2 nanoparticles (Banerjee 2011, Chen and Mao 2007a), etc.

Figure 2.10. SEM images of TiO_2 nanowire arrays prepared by the PVD method (Wu et al. 2005c).

2.4 Modifications of TiO_2 nanomaterials

One of the hottest areas of heterogeneous photocatalysis research is the development of a photocatalytic system capable of tapping natural sunlight to degrade organic and inorganic pollutants in the air and water medium. Factors determining overall photocatalytic activity of a semiconductor photocatalyst include the efficiency of the photocatalytic process, stability of the photocatalyst under irradiation, selectivity of the pollutant degraded and the response of various wavelength ranges. Large band gap semiconductors like TiO_2 , possess strong oxidative potential but are limited by their optical photoresponsive region in the UV range, therefore significantly increasing plant operating costs. Henceforth, extensive research on surface and bulk chemical modifications of TiO_2 have been conducted, attempting to shift the photoresponsive wavelength to the visible light spectrum, so that these semiconductors are capable of receiving excitation in the visible region of the solar spectrum and continue to provide optimum degradation of contaminants under the presence of limited ($< 10\%$) UV light in natural sunlight and at low operational costs.

Currently, practical engineering applications of the photocatalytic technique are greatly restricted due to narrow light-response range and poor anti-recombination of the photogenerated electron-hole pairs in semiconductor photocatalysts, which are widely identified as bottleneck issues of photocatalysis, greatly reducing process efficiencies. These limitations of photocatalyst for a particular use can be surmounted by modifying the surface of the semiconductor.

2.4.1 Metal semiconductor modification

The semiconductor surface properties could be changed by loading metal on its surface. The metal can enhance the yield of a particular product or the efficiency of the photocatalytic reaction. Figure 2.11 illustrates the electron capture properties at the Schottky barrier of the metal in contact with a semiconductor surface. In this system, the metal has a higher work function than the semiconductor. When the two materials are connected electrically, electron migration from the semiconductor to the metal occurs until the two Fermi levels equal. The electrical contact has formed a space charge layer. The surface of the metal acquires an excess negative charge while the semiconductor exhibits an excess positive charge due to the electron transfer. The bands of the semiconductor bend upward toward the surface, and the layer is said to be depleted. The formed Schottky barrier at the metal-semiconductor interface can serve as an efficient electron trap preventing the recombination of electron-hole pairs in the photocatalysis. The electronic modification of TiO_2 surface via metal deposition has been observed in the Ag/TiO_2 , Pt/TiO_2 , Au/TiO_2 , etc (Chan and Barteau 2005, Epifani et al. 2000).

Figure 2.11. Metal-modified semiconductor photocatalyst particle (Linsebigler et al. 1995).

2.4.2 Doping

Only this small fraction of solar spectrum can be utilized for the TiO_2 photocatalysis due to its wide intrinsic band gap. Therefore, it is of great interest to develop the visible-light responsive photocatalyst. Doping plays an indispensable role in modifying the properties of functional materials. Impurity doping is one of the typical approaches to extend the spectral response of a semiconductor with wide band-gap to visible light. Various metal doping and non-metal doping have been extensively studied (Liu et al. 2010a, Zaleska 2008).

2.4.2.1 Transition metal doping

It has been reported that metal doping could introduce a new energy level within the band gap of TiO_2 , responsible for its absorption of visible-light. Another benefit of transition metal doping is the improved trapping of electrons to inhibit electron-hole recombination, resulting in the enhanced photocatalytic activity (Zaleska 2008). Anpo (2000) reported the second generation TiO_2 photocatalysts obtained by an advanced high-voltage metal ion-implantation method. The metal ions (Cr and V ions) were injected into the deep bulk of TiO_2 when high acceleration energy was applied, then calcined in oxygen at high temperature. The derived metal doped TiO_2

exhibited good visible-light photocatalytic activity for decomposition of NO. TiO_2 doped with a series of transition metals, such as V, Cr, Ni, Mn and Fe, can be obtained by the similar method (Yamashita et al. 2002). The other methods, such as hydrothermal, sol-gel, etc., also can be employed for preparation of metal doped TiO_2 photocatalysts (Zaleska 2008). Only certain transition metals such as Fe^{3+} and Cu^{2+} actually inhibit electron-hole recombination (Yalçin et al. 2010). Other metal dopants such as Cr^{3+} create sites which increase recombination of electron-hole. It is believed these metals could create acceptor and donor center, leading to direct recombination (Wang and Lewis 2006).

2.4.2.2 Non-metal doping

Alternatively, TiO_2 doping with non-metals such as N, C, S, P, is another promising approach to induce visible-light activity (Wang and Lewis 2006, Zaleska 2008). Some of the studies have proposed that this red-shift is caused by a narrowing of band gap of pristine TiO_2 , while others have agreed that the appearance of intragap localized states of the dopants. In addition, it has been proposed that the formation of oxygen vacancies and the advent of color centers in the doped TiO_2 are responsible for the visible light absorption. Various schemes illustrating the possible modification mechanisms of TiO_2 doped with non-metals, as shown in Figure 2.12. Among all non-metal doping in TiO_2 , Asahi et al. (2001) hypothesized on the basis of spin-restricted local density approximation (LDA) calculations that N doping of TiO_2 crystals is the most effective because its N 2p states contribute to band-gap narrowing by mixing with O 2p states in the valence band. Sulfur (S^{2-}) is too large and thus more difficult to be incorporated into TiO_2 compared to N. The states introduced by C^{4+} and P^{3+} are too deep in the gap to overlap sufficiently with the band states of TiO_2 . Thus, nitrogen-doped TiO_2 (N- TiO_2) is proposed to be the most preferable candidate for the TiO_2 -based photocatalysts with efficient visible-light activities.

Figure 2.12. Various schemes illustrating the possible changes that might occur to the band gap electronic structure of anatase TiO₂ on doping with various nonmetals: (a) band gap of pristine TiO₂; (b) doped TiO₂ with localized dopant levels near the VB and the CB; (c) band gap narrowing resulting from broadening of the VB; (d) localized dopant levels and electronic transitions to the CB; and (e) electronic transitions from localized levels near the VB to their corresponding excited states for Ti³⁺ and F⁺ centers (Serpone 2006).

2.4.3 Surface sensitization

Surface sensitization of a wide band-gap semiconductor photocatalyst TiO₂ via chemisorbed or physisorbed dyes can increase the efficiency of the excitation process. The photosensitization process can also improve properties. Organic dyes are usually transition metal complexes with low lying excited states. The metal centers for the dyes include Ru²⁺, Zn²⁺, Mg²⁺, Fe²⁺ and Al³⁺, while the ligands include nitrogen heterocyclics with delocalized π or aromatic ring systems. These organic dyes are normally linked to TiO₂ nanoparticle surfaces via functional groups by various interactions between the dyes and the TiO₂ nanoparticle substrate: 1) covalent attachment by directly linking groups of interest or via linking agents, 2) electrostatic interactions, 3) hydrogen bonding, 4) van der Waals forces.

The charge separation between the adsorbed dyes and TiO_2 nanomaterials involves one of three mechanisms, which differ by the nature of the donor that transfers the electron to the semiconductor: 1) excited state, 2) reduced state, or 3) molecule-to-particle charge-transfer complex (Chen and Mao 2007a). There are several requirements for the dye as an efficient photosensitizer. First, the dye should exhibit high absorption ability in a wide spectral range. Second, the excited states of the dye should have a long lifetime and high quantum efficiency. Third, the energy level of the excited states of the dye should be well matched to the lower hand of the conduction band of TiO_2 to minimize the energetic losses during the electron transfer.

2.4.4 Heterostructuring

Compared to single photocatalysts system, hybrid or integrated multi-semiconductor systems show significant advantages in promoting the electron-hole separation and extending the energy range of photoexcitation for the system. Depending on the charge carrier-transfer mechanisms, six heterostructure modes can be classified, as summarized in Table 2.2.

Table 2.2. Various heterostructures models with different charge carrier-transfer mechanisms.

Mechanisms	Representative systems
Traditional charge-carrier transfer	CdS/TiO_2 (Sun et al. 2008), PbS/TiO_2 (Brahimi et al. 2008), $\text{Bi}_2\text{S}_3/\text{TiO}_2$ (Bessekhouad et al. 2004)
Sensitization	$\text{Cu}_2\text{O/TiO}_2$ (Senevirathna et al. 2005), CdSe/TiO_2 (Kongkanand et al. 2008)

Indirect Z-Scheme

RuO_2/WO_3 (Sayama et al. 1997), $\text{Pt-WO}_3/\text{Pt-SrTiO}_3$ (Cr-Ta-doped) (Sayama et al. 2002)

Direct Z-Scheme

WO_3 -dye-sensitized TiO_2 (Hagfeldt and Gratzel 1995), ZnO/CdS (Wang et al. 2009b)

Vectorial electron transfer

$\text{TiO}_2\text{-Au-CdS}$ (Tada et al. 2006)

Co-catalyst coupling

Co catalyst: Pt, RuO_2 , NiO, Rh- Cr_2O_3 , MoS_2 (Osterloh 2008)

2.5 Environmental Applications of TiO₂ nanomaterials

As reported in literature, the applications of TiO₂ nanoparticles include paint, toothpaste, UV protection, photocatalysis, photovoltaics, sensing, and electrochromics as well as photochromics (Chen and Mao 2007a). The non-selective and exceptional photooxidation ability of the TiO₂ system has been widely applied in environmental applications, particularly in air and water treatment processes for the mineralization of organic contaminants. TiO₂ photocatalysis has been applied to a variety of problems of environmental interest besides water and air purification. It has shown to be useful for production of electricity and/or hydrogen, destruction of microorganisms such as bacteria and viruses, etc (Abe 2010, Byrne et al. 2011, Chong et al. 2010, Pelaez et al. 2012).

2.5.1 Photocatalytic applications for water and air purification

TiO₂ has been considered as the most efficient and environmentally friendly photocatalyst, and it has been widely used for photocatalytic decomposition of various pollutants (Akpan and Hameed 2009, Gaya and Abdullah 2008, Hoffmann et al. 1995). TiO₂ photocatalysts can also be applied for destruction of *E. coli* in water (Hu et al. 2006) (Malato et al. 2009). The strong oxidizing power of the illuminated TiO₂ can be used to kill tumor cells in cancer treatment (Abdulla-Al-Mamun et al. 2011, Liu et al. 2010b, Rozhkova et al. 2009).

2.5.1.1 Degradation and mineralization of organic compounds

Figure 2.13. Conceptual diagram for the primary process involved in the photocatalytic mineralization of organic compounds (Gaya and Abdullah 2008).

Photocatalytic degradation of persistent organic contaminants is of considerable interest for environmental applications and in particular for the control and eventual destruction of hazardous wastes in both air and water. Most of the pollutants disappear following an apparent first order kinetics (Herrmann 1999). For aromatics, the dearomatization is rapid even in the case of deactivating substituents on the aromatic ring. Although the oxidation of carbon atoms into CO₂ is relatively slower than the dearomatization of the molecule, the complete mineralization (i.e. oxidation of organic compounds to CO₂, H₂O, and associated inorganic products such as HCl, HBr, SO₄²⁻, NO₃⁻, etc.) of a variety of aliphatic and aromatic hydrocarbons via heterogeneous photooxidation on TiO₂ has been reported (Gaya and Abdullah 2008, Herrmann 1999, Hoffmann et al. 1995). The mechanism of photocatalytic degradation of organic compounds has been widely studied (Chen and Mao 2007a, Gaya and Abdullah 2008). The photo-generated holes have great potential to oxidize organic species directly or indirectly via the combination with hydroxyl radicals predominant in aqueous solution. The photo-induced processes of the photomineralization of organic contaminant in the presence of TiO₂ are shown in Figure 2.13.

It is accepted that the charge carriers (electron-hole pair) play the critical roles in photocatalytic degradation. These charge carriers migrate to the surface and react with the adsorbed species to decompose these species. Essentially, hydroxyl radicals, holes, superoxide ions (or radicals), and hydroperoxyl radicals are highly reactive intermediate species that will act concomitantly to oxidize large number of organic pollutants including volatile organic compounds (VOCs) and bioaerosols (Jacoby et al. 1996, Sleiman et al. 2007). It has been reviewed in the literature that the pollutants successfully photodecomposed over TiO_2 include alkanes, haloalkanes, aliphatic alcohols, carboxylic acids, alkenes, aromatics, haloaromatics, polymers, surfactants, herbicides, pesticides, and dyes, etc (Bhatkhande et al. 2002, Vinod and Anirudhan 2002).

2.5.1.2 Detoxification or removal of inorganic pollutants

In addition to organic pollutants, various toxic anions can be oxidized into harmless or less toxic compounds by TiO_2 photocatalysis. For example, nitrite is oxidized into nitrate, sulfide, sulfite and thiosulfate can be converted into sulfate, whereas cyanide is transferred into isocyanide or nitrogen or nitrate (Herrmann 1999, Shirzad Siboni et al. 2011).

Heavy metals are generally toxic and can be removed from industrial waste effluents as small crystallites deposited on the photocatalyst through the redox process, when the redox potential of the metal cation couple is higher than the band potential of the semiconductor (TiO_2).

2.5.1.3 Water disinfection

TiO_2 -assisted water disinfection for a wide range of microorganisms has also been studied (Byrne et al. 2011, Dalrymple et al. 2010, Mills and Le Hunte 1997). In the most cases, the bacterium under study was *E. coli*, which can generally be considered as an easy target bacterium to destruct. Up to date, there seems to be a consensus in the mechanism of destruction of bacteria by TiO_2 photocatalysis. The

first target of the oxidative radicals is the surface of the external membrane of the cell wall. Initially damage occurs on the lipopolysaccharides layer of the external cell wall and on the peptidoglycan layer. Then the peroxidation of the lipid membrane (the radicals oxidize to fatty acids), the oxidation of the proteins' membrane (amino acids) and of polysaccharides happen (Malato et al. 2009).

2.5.1.4 Photocatalytic water splitting

Figure 2.14. Reaction scheme of semiconductor photocatalysis for water splitting (Chen and Mao 2007a).

Enormous researches have been carried out to study the photocatalytic splitting of water into H_2 and O_2 using TiO_2 nanomaterials since 1972. The principle of water splitting using a TiO_2 photocatalyst is shown in Figure 2.14. Conduction band electrons and valence band holes are generated when TiO_2 absorbs light with energy larger than its band gap. The photoproduced electrons and holes can initiate redox reactions. Water molecules are reduced by the electrons to form H_2 and oxidized by the holes to produce O_2 , leading to overall water splitting. The potentials of conduction and valence band and the band gap are very important. The bottom level of the conduction band has to be more negative than the reduction potential of H^+/H_2 (0 V vs NHE), while the top level of the valence band has to be more positive than the oxidation potential of O_2/H_2O (1.23 V). The potential of the band structure of TiO_2 is just the thermodynamical requirement. Other factors such as charge separation, mobility also influence the photocatalytic properties of TiO_2 .

These factors are dependent upon the bulk properties such as crystallinity, surface properties such as surface states, surface chemical species, surface area, active reaction sites. It has been reported that pure TiO_2 could not split water in the simple aqueous suspension system. Therefore, water splitting using modified TiO_2 has been studied (Chen et al. 2011a, Kim et al. 2012, Matsumoto et al. 2004, Yu and Ran 2011). In addition, the photoefficiency of the process can be highly improved by the addition of sacrificial reagents, which helps to inhibit the electron-hole recombination and prolong the lifetime of charge carriers. Various compounds such as methanol, ethanol, EDTA (an ethylenediaminetetracetic derivative), Na_2S , and Na_2SO_4 or ions such as I^- , IO_3^- , CN^- , and Fe^{3+} have been used as the scavengers (Chen and Mao 2007a) .

2.6 Photocatalytic reactors

2.6.1 Introduction

Over the last two decades, various reactor designs have been proposed to optimize performance of photocatalytic reactors used in water treatment processes. Most of the photoreactors installed in industrial wastewater treatment plants, are designed to operate at continuous flow modes, with high volumetric flow rates and short residence time. In contrast, batch reactors are generally limited in scale and constructed for analysis in pilot plants or kinetic studies.

Harada et al. (1999) commented that the design of efficient photocatalytic systems is of vital interest and one of the most challenging aspect in the research of environmentally-friendly catalysts. Several fundamental parameters must be optimized during the reactor design stage, including photoreactor geometry, type of photocatalyst, and utilization of radiated energy. The transmission of light irradiation within a highly homogeneous, scattered and "milk-like" aqueous suspension composed of fine TiO_2 particles and water is a critical engineering consideration. Apart from reactor design strategies, operating variables that control

the rate and extent of chemical species transformation should be precisely executed. Augugliaro et al. (1995) investigated the operational parameters and reported that the critical variables include concentration of semiconductor photocatalyst, reactive surface area, particle aggregate size, concentration of electron donors and acceptors, incident light intensity, pH, presence of competitive sorbates and temperature.

One of the key factors behind the high efficiency of TiO_2 photocatalytic oxidative systems in degrading organic contaminants dissolved or dispersed in the water/air medium, is attributable to the maximum utilization of the large surface areas of photocatalyst in achieving efficient mass transfers. To efficiently utilize the high surface areas of powdered photocatalyst, they should be suspended within the fluid matrix; but since size of the nanoparticulate catalyst is in the nanometer range, eventual separation and reclamation of solid photocatalyst particles from the reaction medium may create subsequent energy and environmental problems on an industrial scale. Post-treatment catalyst recovery would be unfavourable since it would significantly increase capital and operating costs of the treatment process.

From this perspective, the processes revolving TiO_2 heterogeneous photocatalysis can be mainly classified into two main categories, mainly the aqueous slurry dispersions (fluidized bed slurry photoreactor) or the immobilized thin films on a supporting substrate (fixed bed photoreactor).

2.6.2 Light sources

Photocatalytic reactors are able to be powered by solar energy as 4-5% of the solar spectrum wavelengths are able to achieve activation of TiO_2 . In visible-light photocatalysis, it is common to observe that a first-order photoreaction rate constant is often established for low levels of irradiation, and there is a directly proportional relation between photoconversion rates and irradiation intensities. At greater irradiation intensities, the relation between photoconversion rate and irradiation intensity reduces significantly to a fractional order. Henceforth, the increasing inefficiency in photoreactor performance with greater intensity of irradiation

remains a significantly limiting factor in applications of solar photoreactors. Overall, there has been limited success thus far in terms of utilizing direct natural sunlight to drive photocatalytic reactions, hence a solar collector is usually employed to harvest sunlight and improve light efficiency.

On the other hand, artificial light sources like UV lamps are widely used in photocatalytic reactors. Lamps can be submerged in the solution and are usually placed in quartz jackets to protect them from mechanical damage and also convenience during periodical replacements. The choice and arrangement configuration of light sources are critical to the design of photocatalytic reactors. The arrangement configuration of UV lamps will affect fluid dynamics within the reactor and thus photocatalytic efficiencies (Pan et al. 2010). Alternatively, UV lamps may be installed at the exterior of the photoreactor, irradiating the catalysts from the outside, or with the assistance of light transmission media which is placed inside the reactor. The light incidence angle has to be tuned and adjusted precisely to achieve maximize light transmission distance and to avoid total internal reflections.

The photocatalyst can be coated in the form of thin films on the walls of UV lamps or light transmission medium such as glass rods, to ensure minimal light is reflected away across the interface distance between the lamp and catalyst, therefore maximizing photoefficiency. The wall surfaces of the UV lamps are usually roughened to improve adhesion of photocatalyst and reduce total internal light reflection. However, there is limited contact area of exposure on the walls of the UV lamps for substantially large masses of photocatalyst.

2.6.3 Suspended nanoparticulate TiO₂ in slurry photoreactor

The majority of photocatalytic reactors currently in use for water treatment applications are of the well-mixed slurry systems as they have exhibited the highest photocatalytic activity as compared to reactors employing immobilized photocatalyst. Wyness et al. (1994) reported a 2-5 times larger reaction rate

constant for suspended photocatalyst operation than that of an immobilized catalyst in a solar photocatalytic reactor. In the photodegradation of aqueous phenol in a simulated shallow pond reactor under natural sunlight, suspended photocatalysts registered degradation rates of approximately 3 times larger than observed in immobilized catalytic system (Matthews and McEvoy 1992).

In an aqueous TiO_2 suspension, photocatalytic activity is generally considered to be highly efficient since slurry reactors offers good contact and mixing by utilizing the exposed 3D (all-rounded) surface area of suspended catalyst, as opposed to an immobilized catalyst system where the active catalyst surface area is limited to a 2D (length and width) space. Henceforth, from the perspectives of higher mass transfer efficiencies and greater exposed catalyst surface area, slurry type photoreactors of powdered TiO_2 in aqueous suspensions yield better photocatalytic performance than immobilized TiO_2 (Dijkstra et al. 2001a).

After dosage of nanopowdered TiO_2 photocatalyst into solution, the slurry suspension is irradiated by a UV light source during the photocatalytic treatment process. Due to the minuscule size and structure of TiO_2 nanoparticles, a low dosage of photocatalyst being churned and mixed rigorously would result in the solution becoming highly turbid, restricting UV penetration. Thus, a "shadowing effect" occurs where only limited TiO_2 particulates within close proximity to the UV source can be irradiated, while the distant bulk of TiO_2 will not be activated (Wei and Wan 1991). Henceforth, it is difficult to achieve uniform light intensity distribution for all catalyst particles due to light absorption and scattering by the solid particles in the fluid phase. The aforementioned problems are the main hindrance to engineering applications of slurry photoreactors.

Due to the extremely fine sub-micron particulate size of TiO_2 nanopowder, separation of the suspended catalyst from the treated water of "milk-like" slurry is a major difficulty as they are too light and minuscule to be removed by gravity settling. The catalyst separation process may severely complicate the overall treatment process and substantially decrease economical viability of slurry

photoreactors. Over the years, many researchers have attempted to tackle the post-separation of spent powdered photocatalysts via a variety of recovery methods, ranging from high-cost ultra centrifugation to inexpensive overnight particle settling. Catalyst recovery techniques of intermediate costs include coagulation with ferrous sulphate or basic aluminum chloride (Baran et al. 2005, Kagaya et al. 1999), hollow-fiber ultrafiltration membrane (Erdei et al. 2008, Molinari et al. 2000) and magnetic separation (Chung et al. 2004, Kurinobu et al. 2007).

Coagulation processes require the addition of coagulants, for e.g. aluminium chloride, to flocculate the suspended TiO_2 particles, causing them to settle rapidly. Other coagulating agents such as iron (II) sulphate and calcium chloride have been experimented, but the clarity and transmittance of supernatant solution was not as ideal as that of basic aluminium chloride. The TiO_2 particles recovered from the precipitates require further treatment steps prior to recycling and reuse. Moreover, the coagulation method produces large amounts of chemical sludge that has to be disposed of.

The integration of membrane technology and photocatalysis in the field of water decontamination has been widely reported in the past decade. A new type of photocatalytic membrane reactors have been designed to tackle the problem of photocatalyst separation from the slurry suspension of the reaction mixture. In such reactors, TiO_2 can be physically immobilized on the membrane itself or suspended in the slurry and subsequently recovered and retained by the membrane. The membranes employed are mostly pressure-driven types such as microfiltration, ultrafiltration or nanofiltration. Choo et al. (2008) designed and investigated the performance of a laboratory-scale submerged hollow-fiber membrane photocatalytic reactor on its removal of natural organic matter, as well as its membrane fouling characteristics and control. Figure 2.15 shows such a typical TiO_2 slurry-membrane photoreactor.

Figure 2.15. Schematic diagram of a laboratory submerged photocatalytic membrane reactor (Choo et al. 2008).

Although application of membrane processes offers the opportunity to separate and recover suspended catalyst from the treated water and at the same time, provide high quality effluent, two key parameters of membrane operation must be precisely engineered: 1) selected membrane pore size and 2) operating transmembrane pressure. However in cases of suspended nanosized photocatalyst, membrane fouling is frequently observed in microfiltration and ultrafiltration membranes, and quality of permeate is not exactly high since small molecules and nanosized particles of photocatalyst may permeate through the membrane and "leach" into the filtrate. In addition, the short membrane lifespan and high operating costs from membrane fouling trends would severely limit practical applications in wastewater treatment.

A flexible modular photocatalytic reactor has been designed to separate an aqueous suspension of relatively large titanium dioxide catalyst particles (c.a. 10 to 100 μm)

using a robust hydrocyclone for catalyst recovery (Gogate and Pandit 2004). Zhang et al. (2008) developed highly porous basketry-like microspheres that were primarily constructed with TiO_2 (β) nanowires for photocatalytic oxidation of methylene blue in suspension. The fabricated microspheres were in the micron-size range and denser than commercial TiO_2 nanopowder such as Degussa P25, thus offering greater ease of separation from the treated water. However, it should be noted that such microspheres generally have poorer catalyst reactivity as compared to nanosized particulates due to lower active surface area of exposure and would require post-treatment stage prior to reuse.

Titania-coated magnetic particles have been proposed to enhance separation of catalyst from treated effluent with application of an external magnetic field. Usually, the magnetic core materials mainly contain three strong magnetic elements, namely iron, nickel and cobalt. Ferrite is the most commonly employed due to its strong ferromagnetism and ease of preparation with colloidal particles. Chung et al. (2004) successfully prepared a photocatalyst of TiO_2 - SiO_2 layer coated on a magnetic core of NiFe_2O_4 via ultrasonic spray pyrolysis. Since magnetic core preparation and coating of TiO_2 - SiO_2 was undertaken via two steps, high crystallinity of TiO_2 was achieved and the core magnetic particles did not undergo any phase transformation. The as-prepared photocatalyst exhibited good photocatalytic performance and demonstrated strong magnetic properties to be separated from the slurry and recycled to the reactor with application of an external magnetic field. The adhesion of coated photocatalytic layer over magnetic core particles was also sufficiently durable to withstand vigorous homogenization in the slurry photoreactor. However, there are some major issues in the photocatalytic application of TiO_2 -coated magnetic core particles. Firstly, there may be some abatement and attenuation of photoactivity arising from the poor crystallinity of TiO_2 , depending on the nature of synthesis method undertaken. Secondly, photodissolution of the iron oxide may occur due to prolonged electronic interaction between the titania coating and ferrite core. Attachment of TiO_2 powder on the magnetic carrier supports may not be adequately stable over an extended or long

period of operation. In conclusion, there are apparent severe drawbacks and engineering issues behind the discussed techniques of performing catalyst separation and recovery in a slurry photoreactor, giving rise to the opportunity for developing immobilized TiO_2 films in fixed bed photoreactors.

2.6.4 Immobilized TiO_2 films in fixed bed photoreactor

Immobilized TiO_2 is an alternative solution to suspended TiO_2 systems mainly because of the convenience of not requiring additional post-treatment recovery of catalyst after the reaction process. Such photoreactors have photocatalysts immobilized or coated on porous and non-porous support substrates that are UV-transparent. The support materials vary largely depending on reactor design, requirements and applications. Some researchers have also designed immobilized photoreactors with catalyst coated on the reactor walls (Dijkstra et al. 2001b, Fathinia et al. 2010, Ray and Beenackers 1998, Seabra et al. 2011).

However when the photocatalyst is immobilized, one has to sacrifice a substantial reduction in active surface area available for reaction since the catalyst has to be adhered onto a support substrate. Inadequate mixing and interaction between the photocatalyst and aqueous matrix in the reaction solution may also impede and reduce photocatalytic efficiency. Moreover, undesirable introduction of foreign ionic species from the supporting substrate can compromise catalyst purity and contribute to recombination of charges within the photocatalyst, leading to its deactivation (Rachel et al. 2002). Immobilization of catalyst can result in severe limitations in mass transfer and light transmittance within the photoreactors, which would substantially reduce reactor efficiency, as well as cause difficulties in determining photocatalytic reaction kinetics (Krysa et al. 2000). In drastic cases, it has been reported that the photocatalytic efficiency of immobilized fixed bed reactors can be reduced to only 1/200th than that of slurry photoreactors (Rachel et al. 2002, Shephard et al. 2002). To ensure reaction rates of immobilized photocatalytic systems are optimized, one should adopt a configuration in which the supplied UV illumination is able to acquire adequate access to the supported

photocatalyst. Therefore, thickness of the supported catalyst should be limited to a certain depth to facilitate UV penetration and also to ensure that the underneath layers can be reached and irradiated by UV rays (Ray and Beenackers 1998). It is also imperative that the solid support substrate or constructed photoreactor material to be UV transparent, thus reactor design is limited by several optical absorption constrains (Alexiadis and Mazzarino 2005, Li and Chen 2011, Nikazar et al. 2008, Saïen et al. 2009). Based on the preceding discussions, to improve catalytic efficiency of the photoreactor, one has to look into design optimization of the photoreactor and maximize surface area-to-volume ratio of photocatalyst from their inherent nanostructures.

Xu et al. (2008) constructed a rotating disk photoelectrocatalytic (PEC) reactor using a TiO_2/Ti thin film, which simultaneously integrate thin film photoelectrocatalysis and conventional PEC processes on a single TiO_2/Ti electrode to degrade Rhodamine B and other textile dyes. As shown in Figure 2.16, the top part of the round TiO_2/Ti disk photoanode was coated with a thin layer of wastewater and UV-irradiated in air. The bottom part of the disc electrode was submerged in bulk wastewater and irradiated by the same light source. From conventional PEC reactor design, the photoanode is completely submerged in wastewater solution and radiation has to pass through walls of reactor and sample solution before reaching the photoanode surface (Li et al. 2000, Yang et al. 2005). Results have shown that thin-film PEC removed higher percentage of total colour and total organic carbon by 3-55% and 0-30% respectively, as compared to conventional PEC under same treatment conditions. It should also be noted that the non-porous film electrode contains aggregates of interconnected nanoparticles that cannot sustain development of a space charge layer (Hagfeldt and Gratzel 1995). The delocalization of photogenerated electrons and holes will be mitigated, thus reducing photocatalytic efficiency of TiO_2/Ti thin films, although a bias voltage can be applied to the electrode (Jiang et al. 2003).

Figure 2.16. (a) Schematic diagram of the side view of the TiO₂/Ti rotating disk PEC reactor. The figure is not drawn to scale. 1. speed controller, 2. motor, 3. electrolytic cell, 4. TiO₂/Ti rotating disk anode, 5. cathode, 6. UV lamp, 7. aluminum foil, 8. DC power supply. (b) The front view of the TiO₂/Ti rotating disk electrode. The cell is filled with sample solution (Xu et al. 2008).

Some relevant examples of immobilized photocatalytic reactors include the coated fiber optic cable reactor (Peill and Hoffmann 1995, 1996, 1997, 1998) and the multiple tube reactor (Ray and Beenackers 1998). Other alternative design configurations for fixed/packed-bed catalytic reactors are to entrap TiO₂ particles on glass beads, to immobilize photocatalyst on fiberglass and woven fibers, or to encapsulate catalytic particles within ceramic membranes by means of compression (Ray and Beenackers 1998).

2.6.4.1 Porous thin films

The physical dimension of thickness was used to differentiate thick and thin films historically but the critical thickness value depends on the application and

discipline. Scientifically, if a coating is used for surface properties such as electron emission or photocatalytic activity, it should be considered as a thin film. On the other hand, if it is employed for bulk properties (for e.g. corrosion resistance), then it can be viewed upon as a thick film. Henceforth, an identical coating material of exact thickness can be a thick film or thin film depending on its applications.

In the last decade, there have been many attempts to optimize photocatalytic performance of immobilized TiO₂-based thin films by enhancing porosity of the nanostructures to increase active surface areas significantly (Pan et al. 2010). Porous photocatalysts provide high density of active centers for photocatalytic reactions, as well as enhanced light harvesting due to light reflection and scattering within the porous network of the photocatalyst. The ease in recovery and possible reuse after each photocatalytic cycle is an added incentive of developing porous nanostructures.

Despite their low crystallinity, mesoporous TiO₂ films have demonstrated remarkably higher photocatalytic activity than nonporous films in several environmental applications such as, water splitting (Hartmann et al. 2010) and degradation of organic contaminants, for e.g. organic dyes (Carreon et al. 2007, Tschirch et al. 2008, Wark et al. 2005), lauric acid (Sakatani et al. 2006), stearic acid (Bosc et al. 2004), as well as gaseous pollutants such as acetone (Yu et al. 2004) and 2-propanol (Pan and Lee 2006). Oveisi et al. (2010) reported the excellent disinfection properties of mesoporous TiO₂ film through inactivation of *E. coli* cells that are prevalent in the aquatic environment. The superior photocatalytic performance of mesoporous TiO₂ films can be largely attributed to their large accessible surface area and well-defined mesopores with excellent connectivity and uniform pore size, which facilitate efficient mass transfer of reactants and products and promote effective charge carrier transfer.

Zhao et al. (2008) developed micro-/nano-composite hierarchical TiO₂ films on glass substrates by a electro-hydrodynamic method. As compared to nanostructured non-porous films, the catalytic activity of hierarchical porous films was increased

by 60-70% in the mineralization of liquid-phase phenol. It was suggested that hierarchical pore structures played critical roles in the photocatalytic performance of thin film photocatalysts as they offer continuous composite pore channels and provide direct and efficient transport pathways for products, reactants and oxygen transporting in and out of the catalytic framework.

In addition, photocatalytic TiO₂ coatings on various substrates may present other advantageous and interesting properties such as self-cleaning and superhydrophilicity. An oxide bilayer was developed to impart anti-reflectivity, water-repellence, anti-fogging (high water-wetting) and self-cleaning photocatalytic functionalities to the coated glass (Faustini et al. 2010). The bilayer was constructed with a transparent, water-resistant, hybrid methyl-functionalized nanoporous SiO₂ layer covered with an ultrathin mesoporous TiO₂ nanocrystalline film, acting as a protective barrier towards mechanical aggressions.

Practical application of mesoporous TiO₂ films in photocatalytic membrane filtration has been extensively investigated. Highly organized cubic mesoporous TiO₂ films deposited on ceramic membranes showed a comparable photocatalytic activity to that of Degussa P25, by virtue of its anti-fouling property on the membrane (Bosc et al. 2005, Julbe et al. 2008). Permeate flux did not substantially reduce since the upper 3D cubic mesoporous structure allowed water molecules to permeate through the mesoporous TiO₂ films without building up much resistance.

2.6.4.2 Strategies of immobilizing TiO₂ thin films on various substrates

Immobilized TiO₂ photocatalytic reactors have suitable configurations for both water and air treatment. The immobilization of catalyst can be in the form of a thin film coating or directly fixed/anchored onto a solid support via physical surface forces or chemical bonds. In a typical immobilized photoreactor, the catalyst can be coated or anchored onto the reactor walls, at or around the light source, or on an auxiliary solid matrix. Such photoreactors carry the intrinsic advantage of permitting continuous use of photocatalyst and eliminate requirement for post-

process filtration coupled with particle recovery and catalyst regeneration since TiO_2 is not present in the water or air stream at any time.

To preclude the complicated and uneconomical process of catalyst reclamation required in slurry photoreactors, several different techniques (as shown in Table 2.3) have been developed over the years to immobilize and deposit crystalline TiO_2 films on porous and non-porous support substrates (Byrne et al. 1998).

Generally, the process of immobilization involves usage of TiO_2 precursors in the form of sol-gel with thermal treatment of the film at temperatures of 400 and 500 °C. The synthesized sol-gel is first immobilized onto a Pyrex or quartz glass tube by dip coating, which is also known as the wet coating method. The dip coating procedure from an alkoxide solution is usually carried out on transparent substrates (glass and fused silica), and is a method of immersing the substrate in a liquid, which in this case is the sol-gel, and then withdrawn at specific preset speeds. The coated media is then thermally treated to achieve a crystallized film on its surface. The whole process is repeated until a desired thickness is acquired and the film thickness can be tuned by adjusting the viscosity of the sol-gel. The final thin-film coated substrates, which are generally soft but with good adherence, are arranged such that subsequent samples are placed consecutively behind one another and aligned along the light trajectory up to the total attenuation of the beam (Fernandez et al. 1995). Magnetron sputtering engage high energy electrons in the plasma to break/form chemical bonds, thus substrate temperatures can be low (Wang et al. 1998). Electrophoretic deposition of nanopowdered TiO_2 in thin film form, electrochemical/thermal oxidation and direct anodization of Ti foil, would require metallic substrates to be employed due to reactions with the underlying supports.

Table 2.3. Methods of immobilization of TiO_2 and support substrates coated.

Method of immobilization	Substrate coated	References
Dip coating from suspension	Glass beads	(Lee and Cho 2001)
	Glass tubings	(Ryu et al. 2003)
	Glass plates	(Negishi et al. 2007)
	Glass fibers	(Lu et al. 2006)

	Silica gel Sand	(Zhang et al. 1994) (Matthews 1991)
Sol gel related methods	Quartz Optical fibers Glass beads Glass plates Tin oxide coated glass	(Fernandez et al. 1995) (Lin et al. 2012) (Bideau et al. 1995) (Sonawane and Dongare 2006) (Kim and Anderson 1994)
Electrochemical oxidation	Titanium	(Kim and Anderson 1994)
Thermal oxidation	Titanium Titanium alloy	(Camara et al. 1995) (Kudo et al. 1990)
Anodization of TiCl_3	Tin oxide coated glass, Ti, Pt and Au	(Kavan et al. 1993)
Electrophoretic coating	Stainless steel	(Fernandez et al. 1995)
Aerosol powder coating	Hollow glass beads	(Nair et al. 1993)
Sputtering	Glass	(Kang et al. 2011)
Liquid phase disposition	Glass plates	(Deki et al. 1996)

Immobilized TiO_2 nanostructured thin films directly grown from Ti metal substrates exhibit good mechanical adhesion strength and electronic conductivity. Peng et al. (2006) demonstrated this with a template-free and seedless method to continuously grow large arrays of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ nanoplates and nanowires, directly from Ti substrates under alkaline hydrothermal conditions. Via an ion-exchange and annealing procedure, the titanate compounds preserve their nano-morphologies and completely convert into anatase and rutile TiO_2 phases. Corresponding photocatalytic performance of the final TiO_2 -based nanostructured materials for the degradation of an organic dye, Eosin Y, yielded superior results. The Ti substrate used has a dual role: to provide a Ti source for synthesis of TiO_2 -based nanostructured materials and to act as supporting substrate for the immobilized thin

film. Adherence between the nanostructures and Ti substrate was thus observed to be very strong and stable.

An immobilized form of photocatalyst is beneficial since reaction process is direct, straight-forward and doesn't require a separation and recovery stage for the photocatalysts, thus reducing possible losses of materials. The research focus on development of immobilized TiO₂ systems with maximum active exposed surface area per unit reactor volume, optimal light intensity and catalyst film thickness, would be highly appealing, considering the expensive downstream separation step required for slurry suspension systems.

2.6.5 Comparison of TiO₂ slurry photoreactors with TiO₂ immobilized photoreactors

Table 2.4 summarizes the advantages and disadvantage of slurry and immobilized photocatalytic reactors (Alfano et al. 2000, Parent et al. 1996). It should be noted that some of the listed characteristics may be specific to one type of reactor and can be totally or partially overcome in other designs.

Table 2.4. Suspended versus immobilized photocatalytic reactor systems

Slurry reactors	Immobilized reactors
Advantages	Advantages
✓ Fairly uniform catalyst distribution	✓ Continuous operation and use of photocatalyst
✓ High photocatalytic surface area to reactor volume ratio	✓ Improved removal of organic material from water phase while using a support with adsorption properties
✓ Minimum catalyst fouling effects due to possible continuous removal and catalyst replacement	✓ No need for additional post-process catalyst separation
✓ Well mixed particle suspension	

✓ Low pressure drop throughout the reactor	
Disadvantages	Disadvantages
✓ Requires post-process filtration	✓ Limited mass transfer due to low surface area to volume ratios
✓ Important light scattering and adsorption in the particle suspended medium	✓ Restricted processing capacities due to possible mass transfer limitations
	✓ Possible catalyst fouling deactivation and catalyst wash out
	✓ Low light utilization efficiencies due to light scattering by immobilized photocatalyst
	✓ Inherent inefficiencies introduced by light absorption and light scattering in the particle suspension medium
	✓ Difficult "in-situ" catalyst regeneration
	✓ Significant pressure drop across reactor

2.7 Summary

This chapter presents an exhaustive coverage of literature pertaining to the scope of TiO_2 heterogeneous semiconductor photocatalysis, including the various synthetic methods of preparation, morphologies, physicochemical properties and modifications. The different roles of TiO_2 photocatalysts and their photocatalytic applications in environmental remediation, particularly in water treatment/purification and water splitting for hydrogen production were also reviewed in detail. The hierarchical nanostructures constructed on a variety of hybrid nanocomposite photocatalysts were achieved via diversified modes of fabrication and the most common due to its ease of scale-up and low cost, is the

hydrothermal method. Different preparation methods can drastically influence nanostructure morphologies, crystal structures, surface functional groups and properties. Surface modification of photocatalysts is commonly performed in attempting to effectively utilize visible light and harness energy from solar irradiation. These modifications include dye/organic polymer sensitization, transition metal ion-doping and semiconductor coupling. The mechanisms of such modifications work by altering surface and bulk electronic structure and thus shifting the photoresponse wavelength range to the visible light spectrum, at the same time reducing the common photocatalysis predicament of electron-hole recombination, hence significantly improving photocatalytic efficiency. Henceforth, the enhancement and modification methodologies of semiconductor photocatalysts remain a potential testbed for fundamental scientific research and technological development.

The use of suspended TiO_2 nanoparticulate photocatalyst in an aqueous medium is highly efficient due to the large exposed surface area of catalyst available for reaction. In such a case that a TiO_2 slurry photoreactor is employed, it is imperative that following the treatment, a solid-liquid separation stage (for e.g. coagulation, membrane separation, magnetic separation, etc) must be implemented to remove the catalyst, but that would add to the overall capital and operation costs of the plant. An immobilized catalyst on a stable matrix support would eliminate the need for post-treatment catalyst recovery and offer several operational convenience and advantages. However, it should be kept in mind that when the catalyst is immobilized, whether it is a epitaxial thin film grown directly from a crystalline substrate support or coating of bulk TiO_2 nanoparticulate powder on a fixed bed reactor or rigid support (for e.g. glass, quartz or stainless steel), there is inherently a decrease in available surface area for reaction since the catalyst must adhere to the solid support and unless substrate is UV-transparent, the reactor design is limited by many optical absorption constrains. In addition, the use of immobilized TiO_2 films may result in mass transfer limitations in photocatalytic reactors which would significantly reduce reactor efficiencies, as well as lead to inaccuracies in the

measurement of catalyst efficiency and kinetics. Henceforth, an important research impetus involves optimizing photocatalytic performance of immobilized semiconductor films by tuning its inherent crystalline and microstructure to compensate for its lower efficiency as compared to a nanopowdered aqueous suspension system.

In conclusion, controlled optimization of dimensionality and morphologies, as well as modification to the crystallographic structures and electronic band gap configurations to enhance photocatalytic efficiencies and provide ease in separation and recovery of spent photocatalysts are essential considerations during the contemplation stage of photocatalyst design. Since TiO_2 nanostructures directly grown from titanium metal substrates have shown to exhibit good mechanical adhesion strength and electronic conductivity, this research work will revolve mainly on the epitaxial growth and characterization of immobilized TiO_2 -based crystalline thin films on Ti substrates for environmental applications involving photocatalysis. The various unique nanostructured morphologies developed and their respective influence on photocatalytic performance will be studied in detail. In summary, the following results and chapters presented in this thesis is a cross-disciplinary study and culmination of leveraging technologies of materials science and its integration in application fields of environmental engineering, specifically in decontamination of water and production of renewable green energy in hydrogen gas via photocatalytic water splitting reactions.

CHAPTER 3 EXPERIMENTAL DETAILS

3.1 Synthesis of Immobilized TiO₂-based Epitaxial Films

3.1.1 Free-standing TiO₂ nanotube arrays

The anodization electrolyte was composed of ethylene glycol, 0.3 wt% ammonium fluoride (Alfa-Aesar), and a small volume of DI water. The Ti foil was first degreased by ultrasonication for 30 mins in acetone, followed by repeated rinsing with deionized water and then finally dried in N₂ gas stream. The Ti foil was then ultrasonically cleaned using 1% hydrochloric acid, rinsed thoroughly with deionized water and finally blown dried again using nitrogen gas. All chemicals and materials in the experiment were used as received without further purification.

For the fabrication of highly organized TiO₂ anodic nanotubes, the Ti foils were anodized in a one compartment, two electrode electrochemical cell at a voltage of 60 V and 500 mA of current, with the Ti foil (99.7%, 0.25 mm thick, Goodfellow) serving as anode and the Pt foil (99.99%, 1 mm thick, Goodfellow) serving as the counter electrode. Electrochemical anodization of the high-purity Ti foil was conducted for 6 hrs at room temperature (25 °C) with magnetic stirring at 260 rpm to ensure that the electrolyte is maintained at a homogeneous state throughout the anodization process and ion mobility is optimized. A small content of water was added into the anodization bath to increase the rate of oxygen donation in the organic electrolyte. The films were detached from the Ti substrate by washing the as-anodized Ti foil with plenty of methanol and DI water. It was then subjected to mild ultrasonication in methanol for 1-2 mins. The tips of the TiO₂ nanotubes were etched and chemically dissolved by a slow “bamboo-splitting” process, due to long hours of contact with hydroxide and fluoride ions in the electrolyte (Lim and Choi 2007). Mild ultrasonication is repeated according to experimental procedures from Wang et al. (2008) to completely remove nanofibrous surface debris of the chemically dissolved TiO₂ nanotubes. During the course of methanol evaporation,

the cleaned TiO₂ film gradually delaminated from the Ti substrate after overnight immersion in methanol (Wang and Lin 2008). The free-standing TiO₂ nanotube arrayed films, were amorphous and were crystallized to the anatase phase by 450 °C calcination in air for 2 hrs, with a temperature ramp of 2 °C/min.

3.1.2 Anatase nanowhiskers and one-dimensional TiO₂ nanostructures

A Ti foil measuring 20 mm by 30 mm (99.7%, 0.25 mm thick, Goodfellow Cambridge Ltd, Cambridge, England) was first degreased by ultrasonication in acetone for 30 min to remove organic grime, followed by repeated rinsing with large amounts of DI water, and finally dried in a N₂ gas stream. To smoothen out surface corrugation and ensure uniform electric field distribution on its surface, the Ti foil was electropolished at 20 V for 5 min in an organic electrolyte of perchloric acid and ethanol. The foil was then immediately washed with DI water and acetone to remove residual Ti fragments.

A 6 h electrochemical anodization procedure was subsequently performed in a one compartment, two-electrode electrochemical cell at 30 V, supplied by a DC power source (Agilent E3612A, Agilent Technologies, California, USA). The as-polished Ti foil served as the working electrode and a Pt foil (99.99%, 1 mm thick, Goodfellow Cambridge Ltd, Cambridge, England) was employed as the counter electrode. The electrolyte used comprise of ethylene glycol solution containing 0.4 wt % NH₄F and 2 wt % H₂O. The anodized Ti samples were then rinsed with DI water and acetone, before being dried in an N₂ gas stream.

The resulting anodized TiO₂ film is amorphous and firmly attached to the Ti substrate. It was then subjected to a wet corrosion alkali treatment in a 45 mL Teflon-lined autoclave (Parr Instrument, Illinois, USA), 80% filled with 10 M NaOH at 180 °C for 15 h. Thereafter, a white-coloured, sodium titanate film was developed on the Ti surface and the foil was then immersed in 0.1 M HCl for 5 h, in an ion-exchange process to obtain protonated titanate. The sample was then calcined in ambient air at 500 °C for 2 h with a heating/cooling rate of 2 °C/min,

transforming the protonated titanate structure to the final anatase “Nanowhisker” photocatalyst.

For preparation of the reference “Nanotube” photocatalyst, the degreased, electropolished and anodized TiO₂ film was calcined under identical conditions to convert its amorphous phase to anatase; the overall synthesis method was identical in comparison to the “Nanowhisker” photocatalyst, except that hydrothermal and ion-exchange procedures were excluded. On the other hand, the reference “Nanowire” photocatalyst was prepared by subjecting the starting degreased Ti foil to the same alkaline hydrothermal reaction, ion-exchange treatment and calcination process. Contrary to the “Nanotube” photocatalyst, the overall synthesis method was identical to that of the “Nanowhisker” photocatalyst except that electropolishing and anodization procedures were omitted. Additionally, for comparison purposes, a Ti foil was repetitively dip-coated in a Degussa P25 suspension to deposit a layer of homogeneous P25 nanoparticulate film on its surface. The suspension was prepared by dispersing 1.0 g of Degussa P25 TiO₂ powder in 20 mL of DI water, and then centrifuged to remove coarse and aggregated particles from the supernatant prior to the dip-coating process. The dip-coated foil was then air-dried at 120 °C for 30 min and the cycle was repeated continuously until an identical film weight across the 4 photocatalysts was achieved. The resulting sample is termed as “P25 coating”.

3.1.3 Hierarchical nanofungus-like anatase TiO₂ epitaxial film

Ti foils, each measuring 25 mm by 15 mm (99.7%, 0.25 mm thick, Goodfellow Cambridge Ltd, Cambridge, England) were first sonicated in acetone for 30 min to remove organic grime and washed with DI water. They were then etched in 20% HCl at 80 °C for 10 min to remove surface oxide layer, before thoroughly rinsed with copious amounts of DI water and finally dried in a N₂ gas stream. Each pre-treated Ti foil was then transferred to a 45 mL Teflon-lined autoclave (Parr Instrument, Illinois, USA), 75% filled with 30 wt. % H₂O₂ solution and 5% filled with 48 wt. % HF acid (Sigma-Aldrich). Caution! Hydrofluoric acid (HF) is

extremely corrosive and toxic. HF must be stored in plastic vessels and carefully handled within a fume hood. The autoclave was then placed in an electronic oven that was maintained at 150 °C, for 3 h (labelled “NF3”); 5 h (“NF5”); and 10 h (“NF10”). After the hydrothermal treatment, the sample was left to cool under room conditions and subsequently washed carefully with DI water and dried in air. The sample was finally annealed in air at 450 °C for 1 h with a heating/cooling rate of 2 °C/min. All 3 of the resulting TiO₂ films are in the form of anatase and are firmly attached to the Ti substrate.

3.1.4 Heterojunctioned TiO₂/SrTiO₃ epitaxial film

A 20 mm by 30 mm Ti foil (99.7%, 0.25 mm thick, Goodfellow, England) was first degreased by ultrasonication in acetone for 30 min to remove organic grime, followed by repeated rinsing with large amounts of DI water, and finally dried in a N₂ gas stream. The cleaned Ti foil was surface-etched and oxidized in a 45 mL Teflon-lined autoclave (Parr Instrument), 80% filled with 50 mM HF for 15 h at 180 °C. The foil was then subjected to a wet corrosion alkali treatment using 10 M NaOH, in hydrothermal conditions identical to the previous etching reaction. A white-coloured thin film was developed on the Ti surface and it was then immersed in 0.1 M HCl for 5 h to induce an ion-exchange process. To prevent “curling” of the film that would cause it to detach from the foil during drying, the foil was immediately immersed in low surface tension methanol after the hydrothermal reaction. The film then underwent a heat treatment at 60 °C to improve adhesion to the foil. The hydrogen titanate film, as attached on the Ti foil, was next transferred to a new 45 mL Teflon-lined autoclave, 60% filled with distilled water and 20% with 25% v/v NH₄OH solution (Merck). 0.5 g of Sr(NO₃)₂ powder (Merck, 99%) was added into the autoclave for both the heterojunctioned sample and the SrTiO₃ sample. For the anatase sample, no Sr(NO₃)₂ was added. The autoclave was placed in an electronic oven at 140 °C for 3 different time periods; 2 h, 3 h and 5 h for heterojunctioned TiO₂/SrTiO₃ (herein denoted as “hetero”), TiO₂ (“anatase”) and SrTiO₃ (“tausonite”) respectively. The as-synthesized films, attached firmly on Ti

substrates, were rinsed repeatedly with distilled water to remove residual surface debris, and finally dried under a N₂ stream.

3.2 Materials Characterization

Materials synthesized are characterized based on their inherent physical and chemical properties. A series of sophisticated and advanced instrumentation techniques were carried out to characterize the as-prepared catalysts.

3.2.1 Scanning Electron Microscopy & Field Emission Scanning Electron Microscopy

SEM (Zeiss Evo-50) and FESEM (Jeol JSM 6340F) were used extensively to examine the nanostructure and surface morphologies of the synthesized materials including the dimension and shapes. The magnification is up to 100,000x. Surface morphologies were surveyed using scanning electron microscopy (SEM) and field-emission scanning electron microscopy (FESEM) coupled with energy-dispersive X-ray spectroscopy (EDX) for examining surface morphologies and elemental analysis of the surface.

3.2.2 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is capable of capturing images of the samples at significantly higher magnification (up to 1,500,000). For the nanostructured TiO₂ 1-D materials, TEM (JEOL TEM-2010) can be used to identify whether the material is in tube form or fiber/wire form. The atomic structure of the synthesized tubular material is imaged by high-resolution transmission electron microscopy (HRTEM). HRTEM images can also be used to measure the d-spacing of the crystal lattices, affirming the crystal orientation of the as-prepared catalysts. Selected Area Electron Diffraction (SAED) patterns of the sample are captured to identify whether the material is monocrystalline or polycrystalline/amorphous as the

diffraction image consists of a pattern of dots in the case of a monocrystalline sample and a series of rings in the case of a polycrystalline or amorphous sample.

Prior to TEM analysis, the samples were first prepared by dispersing as-prepared sample powder in methanol under ultrasonication to obtain a methanol suspension of the sample particles. A few drops of it were then spread onto a porous, amorphous carbon-coated film supported on a copper grid, and then dried in air. All TEM images and diffraction patterns were taken with an accelerating voltage of 200 keV and a field-emission gun (FEG) TEM. HRTEM and selected area electron diffraction (SAED) micrographs were taken using the JEOL 2010F FETEM (JEOL Ltd, Tokyo, Japan).

3.2.3 X-Ray Diffraction

The Bruker Axs D8 Advance Powder XRD was used to identify the chemical and mineral composition of the fabricated photocatalyst. The analysis was carried at a voltage of 40 kV with a current of 30 mA; and scanning angle from 10° to 80° in step size of 0.0040° and step time of 2.0 seconds. The wavelength of the monochromatic Cu K α radiation used was 0.15406 nm. X-ray diffractometer is used to analyze the crystal structure and the chemical composition of the powder samples by matching the XRD experimental data with the Powder Diffraction File (PDF) database maintained by International Centre for Diffraction Data (ICDD). The crystal size can be calculated based on the XRD data.

3.2.4 Nitrogen adsorption/desorption isotherm

The BET surface area and pore size distribution of the metal oxides samples were analyzed using a gas adsorption analyzer, Quantachrome (USA) Autosorb-1 at liquid nitrogen temperature (77K). The specific surface area (SSA) was calculated with the Brunauer-Emmett-Teller (BET) equation, while the pore volume and pore size distribution were obtained with the Bopp-Jancso-Heinzinger (BJH) method

from the adsorption isotherm. Before the measurement, the sample was outgassed under vacuum for 10 h at 150°C.

3.2.5 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) analyzes the different types of elemental and chemical compound bonds present on the surface of the samples. The measurements were performed to elucidate surface chemical compositions and the oxidation states of the nanostructured samples. XPS analysis was carried out in an ultrahigh vacuum (UHV) chamber with a base pressure below 2.66×10^{-7} Pa at room temperature. Photoemission spectra were recorded by a Kratos Axis Ultra spectrometer (Shimadzu Corporation, Kanagawa, Japan) equipped with a standard monochromatic Al K α excitation source ($h\nu = 1486.71$ eV). Curve fitting was performed using a non-linear least square Gaussian-Lorentzian function with background subtraction by Shirley's algorithm. The binding energy (BE) scale was referenced and calibrated to the C 1s core level of the residual adventitious carbon at 248.8 eV. Atomic % ratio was deduced and computed using a relative sensitive factor (RSF) of unity, established by CasaXPS Version 2.3.15 (Casa Software Ltd, Acolyte Science, Cheshire, United Kingdom).

3.2.6 Energy Dispersive X-ray Spectroscopy

Energy dispersive X-ray spectroscopy (EDX) analytical technique was carried out for the elemental analysis of the sample. The Oxford EDX detector used is a peripheral hardware equipped on the Jeol 6340F FESEM and the EDX software used in the interpretation of results is the Inca Energy EDS Software from Oxford Instruments.

3.2.7 UV-vis Spectroscopy

The UV-vis diffuse reflectance spectra of the samples in the range of 200-700 nm were obtained using a Thermo Scientific Evolution 300 UV-Vis Spectrophotometer

(Thermo Fisher Scientific, Massachusetts, USA) that was equipped with an integrating sphere assembly and a Xenon lamp source. BaSO₄ was used as the reference. UV/Vis spectroscopy is used to measure the absorbance of the light of the wavelength in the ultraviolet and visible range for the synthesized photocatalysts. The spectra were then converted from reflectance to absorbance and in doing so, estimate the electronic bandgap of the semiconductor photocatalyst by Kubelka-Munk transformation.

3.2.8 Photoluminescence

Photoluminescence analysis was conducted using Fluorolog-3 Spectrofluorometer, equipped with a Nd:YAG laser system of excitation wavelength at 325 nm (Horiba Scientific, New Jersey, USA).

3.2.9 Interfacial Strength

The interfacial strength and adhesion of the film to the Ti substrate was qualitatively evaluated by immersing the film in water and subjecting it to ultrasonic agitation for 5 min. The mechanical stability of the films did not compromise as no broken fragments from the films were observed in water after ultrasonic vibrations.

3.2.10 Zeta potential

The zeta potential value of the synthesized photocatalyst in the solution was measured using a Malvern nano-zs zetasizer. The pH was adjusted through addition of 0.05 M HCl or 0.05 M NaOH solution.

3.3 Photocatalytic Experiments

The as-synthesized photocatalysts characterized various nanostructures including nanotubes, nanowhiskers, nanowires, nanofungus and nanocubes. The different

morphologies have imparted various functionalities and also tailor surface- and shaped-induced properties of semiconductor nanocrystalline phase. The increased surface area and reactive sites also resulted in a consistently higher activity for surface-based processes such as heterogeneous photocatalysis. The developed photocatalysts were employed to degrade recalcitrant, emerging contaminants and pathogens that are commonly present in water bodies (AO7, *E. coli* cells and BPA) via production of photogenerated holes and oxidative radicals.

E. coli is a gram-negative, rod-shaped bacterium and is prevalent in municipal wastewater systems since it is commonly found in the lower human intestines and thus abundant in faecal wastes. *E. coli* cells are relatively resistant and are able to survive outside of the host for a period of time, thus are an important and established indicator organism of fecal contamination in environmental engineering.

Acid Orange 7 (AO7) is a type of widely used water-soluble dye employed mostly in the form of sodium salts of sulfonic or carboxylic acids. They are extensively used in textile industries since they are anionic, hence attach strongly to cationic fibers and synthetics. AO7 are also commonly used in paints, inks and other modes of colouring, by virtue of their robust resistance to discolouration or degradation by UV photolysis and irradiation. Due to their highly photostable characteristics, they are known to be pervasive and recalcitrant aqueous contaminants and potential co-contaminants for nitrates in wastewater engineering.

Bisphenol A (BPA) is a colourless organic compound that is soluble in organic solvents. Due to its two phenol functional groups, BPA is a common precursor in the production of polycarbonate polymers and epoxy resins, along with other materials to make plastics. BPA is a potentially toxic substance and prevalent endocrine disruptor which exhibits hormone-like properties, thus a potential health and safety hazard to humans, in particular fetuses, infants and young children. The degradation and removal of BPA represents a significant advance in environmental remediation.

Hydrogen is a source of clean energy due to its zero carbon emission, high conversion efficiencies and recyclability. It offers immense potential as a green and renewable energy source to alleviate the overdependence on fossil fuels. Given its chemical stability and high photoactivity, TiO_2 is widely regarded as an efficient photocatalyst in the cleavage of H_2O into H_2 and O_2 gases. The free electrons produced from photocatalytic reduction half-reactions are harvested and utilized for the reduction of hydroxide ions present in the treated water to generate hydrogen gas.

3.3.1 Disinfection of *E. coli* cells

E. coli (K12 ER2925, New England Biolab) was chosen as the model pathogen for antibacterial activity tests. *E. coli* was cultivated in Luria-Bertani nutrient solution at 37°C for 18 h to obtain the exponential growth phase. The cells were harvested by centrifugation and washed with saline solution (0.9% NaCl) to remove residual macromolecules. Disinfection reactions were carried out in a cylindrical 35 mL glass vial and homogenized by a magnetic stirrer. The photocatalyst was introduced at a fixed dosage of 2 g/L into a 20 mL aqueous suspension of 10^6 cpu/mL of *E. coli*. UV-A irradiation was supplied via an immersed low-pressure mercury UVP Pen-Ray lamp (UVP 11SC-1L) with primary output at 365 nm and typical light intensity of 1150 mW/cm². Samples were drawn at ten minutes interval and subsequently diluted by a sodium phosphate buffer solution at pH 7. Operating pH was maintained at 7 throughout all experimental runs. All equipment apparatus, agar cell plates, materials and chemicals were autoclaved and UV-disinfected in a clean bench, prior to the photocatalytic disinfection experiments, to rid of all residual bacteria that would affect the accuracy of the experimental results. Sampling was carried out in triplicates and results averaged to minimize experimental discrepancies involved in biological experiments. Samples were streaked onto an agar plate prepared with broth culture medium to support the growth of *E. coli*. Manual counting of colonies per unit surface area of the agar plate was conducted to determine the *E. coli* cell counts after photocatalytic

disinfection. The effects on disinfection efficiency under presence of different dominant ionic species and organic compounds in the system were elucidated. Organic and ionic loadings were introduced into the suspension at typical concentration levels of surface waters.

With reference to the predominant ions as reported in a chemical analysis of surface water (Alrousan et al. 2009), Ca^{2+} (24.85 mg/L), Na^+ (13.94 mg/L), Mg^{2+} (12.22 mg/L), SO_4^{2-} (24 mg/L), NO_3^- (0.7 mg/L) ions were selected in the investigation of their respective influence towards the disinfection efficiency. 10 mg/L of humic acid was introduced as surrogate for total organic compound present in surface water. The salts used in this study are: CaCl_2 as source of Ca^{2+} ions, NaCl as source of Na^+ ions, MgCl_2 as source of Mg^{2+} ions, Na_2SO_4 as source of SO_4^{2-} ions, and NaNO_3 as source of NO_3^- ions.

To evaluate the antibacterial ability of the TiO_2 nanotube arrays, a control experiment was first carried out via UV-A irradiation of the *E. coli* cells without the nanotube array catalyst. All of the above experiments were conducted in triplicates.

The kinetics of the reaction was based on a pseudo first order reaction kinetics as derived from the classical disinfection model of the Chick-Watson's equation (Marugán et al. 2008).

$$\log\left(\frac{C}{C_0}\right) = -K[c]^n t \quad (3.1)$$

where C/C_0 is the reduction in the concentration of bacteria, K is the disinfection kinetic constant, c is the concentration of the disinfecting agent at time t , and n is the reaction order. It is noted that under a constant supplied irradiation, the concentration of the disinfecting agent can be considered to be constant with time for a fixed catalyst concentration and photoreactor lamp setup. Henceforth, the disinfection kinetic constant, K , in equation 3.1 can be simplified into a first-order disinfection kinetic constant, k , as shown in equation 3.2:

$$\log\left(\frac{C}{C_0}\right) = -kt \quad (3.2)$$

3.3.2 Photocatalytic Oxidation of Acid Orange 7

Photocatalytic experiments were carried out in a quartz petri dish secured on an orbital shaker set at 120 rpm to induce homogenization throughout the experiments. Prior to UV irradiation under a low-pressure UVP Pen-Ray mercury lamp (model no. 11SC-1L, UVP, LLC, California, USA), the catalyst sample (20 mm by 30 mm) was immersed in 15 mL of 20 mg/L Acid Orange 7 ($C_{16}H_{11}N_2O_4SNa$, Acros Organics, Belgium) for 1 h in the dark to establish dye adsorption/desorption equilibrium. The initial concentration of AO7 was taken after 1 h of dark adsorption. The primary emission energy of the lamp was centred at 365 nm and typical light intensity of the lamp was 1150 mW/cm^2 . The UV lamp was placed at a fixed proximity from the petri dishes, with the nanostructures facing the UV lamp; to ensure all photocatalysts receive the equal amount of UV irradiation during the photocatalytic experiments. Photolysis experiments (without catalyst dosage) were carried out under exact identical conditions over a blank Ti foil, also measuring 20 mm by 30 mm, to normalize the effect of dye molecule adsorption on Ti substrates across the experiments. Decomposition rate of the dye was obtained by periodically measuring absorbance of the test solutions using a UV/Vis spectrophotometer (Thermo Fisher Scientific, Massachusetts, USA) at wavelength, $\lambda = 484 \text{ nm}$. TOC of the solution was measured using a Shimadzu ASI-V TOC analyzer (Shimadzu Corporation, Kanagawa, Japan).

All of the above experiments were conducted in triplicates.

The Langmuir-Hinshelwood kinetics was used to model the photocatalytic process (Wang and Lim 2010), in which the reaction rate (r) is a function of the degree of substrate coverage (θ):

$$r = k_i \theta = k_i \left(\frac{KC}{1 + KC} \right) \quad (3.3)$$

where C is the concentration of AO7, k_i is the intrinsic reaction rate constant, and K is the Langmuir adsorption equilibrium constant. In this study, the low AO7 concentration (initial concentration of 20 mg/L) and negligible adsorption of AO7 on the film sample (dark adsorption did not result in any appreciable decrease in AO7 concentration), suggest that $KC \ll 1$. Hence, the Langmuir-Hinshelwood kinetics can be simplified to:

$$r = -\frac{dC}{dt} = kKC = kC \quad (3.4)$$

where k refers to the corresponding reaction rate kinetic constant. Thus, the pseudo first-order reaction rate can be applied:

$$-\ln \frac{C}{C_0} = kt \quad (3.5)$$

where C is the AO7 concentration at the stated time t , C_0 is the initial AO7 concentration measured after 1 h of dark adsorption and t is the reaction time.

3.3.3 Photocatalytic Oxidation of Bisphenol A

Photocatalytic experiments were carried out separately in 5 identical glass bottles, each having a magnetic stirrer to induce homogenization and aeration during reaction. Prior to UV irradiation from a low-pressure UVP Pen-Ray mercury lamp (model no. 11SC-1L, UVP, LLC, California, USA), the catalyst sample (25 mm by 15 mm) was immersed in 15 mL of 20 mg/L Bisphenol A (BPA, $C_{15}H_{16}O_2$) and stirred in the dark for 1 h to establish adsorption-desorption equilibrium. The initial

concentration of BPA was then taken after 1 h of dark adsorption. The primary emission energy of the UV lamp was centred at 365 nm and typical light intensity was 1150 mW/cm². The lamp was placed inside each glass bottle at a fixed proximity to the catalyst to ensure that all samples receive an equal amount of UV irradiation. Photolysis experiment (without catalyst dosage) was performed under identical conditions over a blank Ti foil, also measuring 25 mm by 15 mm, to normalize the effect of BPA molecule adsorption on Ti substrates across the experiments. Removal rate of BPA was examined using a high-performance liquid chromatograph (HPLC, Perkin-Elmer Series 200). The HPLC analysis was carried out using an Inertsil ODS-3 column and a Series 200 UV-Vis detector at 225 nm, with acetonitrile and water (70/30, v/v) as effluent at a flow rate of 1 mL/min. All standard chemicals and scavenger solutions used in the experiments were prepared using reagent grade (99.9% purity) chemicals with DI water. All adsorption and photocatalytic oxidation experiments were carried out in triplicates (i.e. repeated three times).

3.3.4 Photocatalytic hydrogen generation from water splitting

Photocatalytic hydrogen generation was carried out in a 45 mL quartz impinger, externally irradiated using 4 units of low-pressure UVP Pen-Ray mercury lamps (3SC-9). The primary emission energy of the UV lamps is centred at 254 nm and typical light intensity per lamp is 5400 μ W/cm². To maintain a constant reactor temperature of 298 K, a cooling water jacket cooled by recycled tap water, was circulated around the reactor to prevent evaporation of the solution. 3 pieces of films, each measuring 20 mm by 30 mm and attached to a Ti substrate, were suspended in 45 mL of solution (40 mL distilled water and 5 mL methanol as sacrificial agent) to maximize UV exposure to the films. Prior to irradiation, the impinger was thoroughly de-aerated by 30 min of nitrogen purging. Gas produced via the photocatalytic reaction was first collected by a water-displacement gas trap, from which volume of the trapped gas can be determined. A small volume of gas was periodically extracted by a gas tight syringe, through a silicon septum on the

gas trap for gas chromatography (GC) analysis. Hydrogen concentration was then evaluated using an off-line GC (Agilent 7890A) with a TCD detector, and the GC column used was a HP-PLOT MoleSieve/5A. All of the above experiments were conducted in triplicates.

CHAPTER 4 ANODIZATION OF SELF-ORGANIZED FREE-STANDING TiO₂ NANOTUBE ARRAYS FOR *E. COLI* DISINFECTION

4.1 Introduction

It is widely recognized that one of the most pervasive problems afflicting people throughout the world is inadequate access to clean water as well as sanitation. The lack of clean, fresh water is well known with millions of people dying annually from diseases transmitted through unsafe water or human excreta (Montgomery and Elimelech 2007). Countless more are diseased and ill from water contamination issues. Intestinal parasitic infections and diarrhoea diseases caused by waterborne bacteria like *E. coli* and enteric viruses have become a leading cause of malnutrition owing to poor digestion of food eaten by the affected fraternity (Lima et al. 2000).

E. coli is a gram-negative bacterium that is prevalent in conditions of poor sanitation and fecal-contaminated wastewaters. It is a common indicator for faecal contamination in water and can cause serious food poisoning in humans. Disinfection is a critical water decontamination process of guaranteeing the microbiological quality of drinking water. Over the years, considerable public attention has been raised, relating to the use of traditional disinfection processes, such as ozonation and chlorination. This is mainly due to severe drawbacks such as toxicity concerns, high costs, poor efficiencies and formation of chloro-organic disinfection by-products (Malato et al. 2009).

In 1985, Matsunaga et al. (1985) demonstrated TiO₂ nanoparticles to be effective in deactivating bacteria such as *E. coli* and *Lactobacillus acidophilus*. Subsequently in 2000, Fujishima et al. (2000) proved that TiO₂ was most effective in antibacterial and detoxification applications among all other related antibacterial agents. In 2004, Cho et al. (2004) provided further evidence that the •OH radical generated from TiO₂, has an *E. coli* inactivation effectiveness of approximately one thousand to ten

thousand times higher than conventional chemical disinfectants. It is worthy to note that TiO_2 -assisted photocatalytic disinfection is an effective process and does not produce any harmful disinfection by-products. Moreover, TiO_2 has many added advantages over other semiconductor photocatalysts due to its abundance, non-toxicity, high dispersion and high refractive index (Fujishima et al. 2000).

There have been several reports (Hoet et al. 2004, Lecoanet et al. 2004, Maynard 2007, Oberdörster et al. 2005) highlighting potential health risks surrounding the applications of nano-engineered TiO_2 in large-scale industrial and manufacturing processes. Particles in the nanosize range have been proven scientifically to enter human body via inhalation or ingestion (Hoet et al. 2004). Chances of penetration depend on size and physical properties of the particles. The extent of damage to health upon penetration is critical to surface characteristics of the catalyst. High exposure potential, especially nanomaterials, agglomerated particles of nanostructured materials; is inevitable in air and liquid suspensions or slurries (Oberdörster et al. 2005).

Physicochemical properties of semiconductor photocatalysts are vital aspects in heterogeneous photocatalytic processes. Particulate photocatalysts pose several environmental and engineering challenges due to their difficulties in recovery, recycling, disposal or management of spent photocatalysts. Photocatalysts with tunable morphologies at a wide range of scales are especially attracting research emphasis. The as-prepared anodic free-standing photocatalyst is synthesized in the form of films; hence mobility in the environment is substantially kept in check, as compared to other TiO_2 nanopowders, such as TiO_2 -P25 or Hombikat UV 100.

Recently, much work has been carried out on the fabrication of highly ordered TiO_2 nanotube arrays via electrochemical anodization, mainly due to its unique 1D nanostructure. Each individual TiO_2 nanotube is grown perpendicularly to the Ti substrate, thereby providing large surface areas and two separate channels for efficient electron and hole transport from interfaces to electrodes (Mor et al. 2006a). To the author's knowledge, there have been relatively few studies on photocatalytic

disinfection using the highly ordered TiO_2 nanotube arrays via electrochemical anodization.

The objective of this study is to synthesize an able photocatalyst for effective photocatalytic drinking water disinfection and to investigate the photocatalytic inactivation efficacy of *E. coli* under the influence of different ionic species and organic compounds.

4.2 Results and discussion

4.2.1 Profile of photocatalyst

Figure 4.1. Cross-sectional FESEM image of TiO_2 film. Inset: Close-up view of the open top ends of titania nanotubes.

As shown from Figure 4.1, the vertically-aligned TiO_2 nanotube arrayed film was highly ordered and possessed excellent morphological uniformity. The nanotubes were free-standing and the bottom ends were closed with open top ends (Figure 4.2-4.4). The average inner diameter of a single tube is 100 nm and the outer diameter of the tubes is approximately 150 nm. The length of a nanotube is tunable according to specific anodization times, with a range of 1 to 50 μm (Figure 4.5). It is worthy to note that water content in the electrolyte increases chemical dissolution of oxide

in the fluorine-based electrolyte, thereby leading to shorter nanotube formation (Paulose et al. 2006).

Figure 4.2. FESEM images showing uniform open top ends of the TiO_2 nanotubes.

Figure 4.3. FESEM images of calcined film. Broken shards from walls of fractured nanotubes can be observed on top of the opened titania tubes after calcination.

Figure 4.4. SEM images of the freestanding TiO_2 nanotubes, exposing closed bottom ends of the tubes.

The tubular structure of the TiO_2 was entirely retained after calcination in air for 2 hrs, albeit more “defects” are created on the surfaces of the tubes and overall

morphology of the tubes seems to have become more porous as observed from the FESEM images.

One of the most critical factors for a good catalytic performance of TiO_2 at the liquid-solid interface, not withstanding nanoparticle size and surface area, pH of the solution, concentration of the photocatalyst, and reactants and diffusion rate, is the TiO_2 crystalline structure. With that in mind, the as-anodized amorphous TiO_2 nanotubes were fully converted to the photoactive anatase phase after calcination.

Figure 4.5. (A) Cross-sectional FESEM image of the free-standing film after calcination, revealing the entire length of nanotubes from the film thickness. (B) High magnification image of the cross-sectional view. (C) FESEM image of the closed bottom ends (barrier layer) of nanotubes after detachment from Ti substrate. (D) FESEM image of the open top ends of the nanotubes.

The XRD peaks were accordingly indexed with reference to JCPDS card number 21-1272 for anatase (prefixed “A”). The XRD spectra of the free-standing TiO_2 film (Figure 4.7) consist of only anatase peaks. The film was amorphous after anodization (Figure 4.6) and upon calcination in air at 450°C for 2 hrs, with a heating and cooling ramp of $2^\circ\text{C}/\text{min}$, the amorphous TiO_2 nanotubes were totally crystallized into the anatase phase.

The BET surface area of the macroporous photocatalysts recorded was $28.97 \text{ m}^2/\text{g}$. The macro-porosity of the resulting TiO_2 nanotubes prevents decline in surface area values in the event of aggregation while the suspension is being stirred vigorously. Figure 4.8 illustrates the nitrogen adsorption/desorption isotherm curve with the volume adsorbed plotted against the equilibrium relative pressure. The classification of this isotherm is a Type II physisorption isotherm and a H3 hysteresis loop.

Figure 4.6. XRD Pattern of as-anodized TiO_2 amorphous film prior to calcination

Figure 4.7. XRD spectrum of the calcined TiO_2 nanotube film in anatase polymorph.

Figure 4.8. Nitrogen adsorption/desorption isotherm of the calcined photocatalyst.

According to the IUPAC report (Sing et al. 1985), the Type II isotherm is obtained with a non-porous or macroporous adsorbent and represents unrestricted monolayer-multilayer adsorption. The initial, linear section of the isotherm indicates the stage at which the monolayer coverage is complete and multilayer adsorption begins subsequently at the exponentially convex section.

The Type H3 loop, as exhibited in Figure 4.8, does not exhibit any limited adsorption at high relative pressures and is characterized by its distinct narrow slit-like pores. Apparent from the FESEM images, these narrow slit pores are in excellent agreement with the long, hollow pores of the synthesized nanotubes.

4.2.2 Photocatalytic activity for AO7 degradation

As shown in Figure 4.9, AO7 was completely degraded within 180 min by the synthesized TiO_2 nanotube film. The photolysis resulted in insignificant removal of AO7. This result indicates that the TiO_2 nanotube film could be an effective photocatalyst under UV irradiation.

Figure 4.9. Photocatalytic degradation of AO7 upon the TiO₂ nanotube photocatalyst.

4.2.3 Antibacterial activity of TiO₂ nanotube photocatalyst

Low-dimensional TiO₂ nanostructures, such as the as-synthesized vertically-aligned nanotubes, provide large interfacial areas for excited electrons to effectively dissociate, hence preventing recombination with the holes generated up UV irradiation. This structure greatly facilitates effective transport of electrons to significantly enhance photoconversion efficiency. The charge carriers are free to move throughout the length of the crystal, leading to an increased delocalization of charge carriers in the nanotubes. The moderate bet surface area of the photocatalyst makes it accessible for efficient adsorption of bacterial cells and efficient charge separation further improves the photocatalytic efficiency (Tachikawa et al. 2007, Tsuchiya et al. 2005).

Upon ultraviolet irradiation, TiO₂ generate reactive oxygen species (ROS), such as hydroxyl radicals that can inactivate microorganism by advanced oxidation processes. The generation of these species with a high oxidative potential, presents a positive, linear correlation between bacterial inactivation efficiency and the production of ROS (Cho et al. 2004). According to the photocatalytic disinfection

mechanism as proposed by Sunada and colleagues (Sunada et al. 2003), the ROS generated upon illuminated semiconductor photocatalyst photo-kills the *E. coli* by a 2-step decay dynamic pattern. First, it disorders the outer membrane of *E. coli* cells by changing its permeability and destroying it. Then, ROS penetrate into the cytoplasmic inner membrane, leading to lysis of the cell. The bacterial cells are subsequently inactivated due to cumulative effects of ROS' barrage on the cell membrane-wall configuration.

The photocatalytic activity of the synthesized photocatalyst for *E. coli* inactivation was also evaluated. All first-order disinfection kinetic constants, k , presented in this chapter will be calculated in application of the classic Chick-Watson's disinfection model. As apparent from Table 4.1 and Figure 4.10, the disinfection rate constant, k , increased by 300% (from 0.01609 - 0.06394 min⁻¹) and the corresponding $t_{1/2}$ of *E. coli* cells decreased by 75% after the catalyst was introduced. Both experiments were carried out under identical irradiation conditions.

Table 4.1. Apparent first-order rate constants k and $t_{1/2}$ of the photolysis and photocatalytic disinfection of 10⁶ cpu/mL of *E. coli* cells after 50 mins of irradiation at different experimental conditions.

Experimental Condition	k (min ⁻¹)	$t_{1/2}$ (min)	% kill ratio
Photolysis	0.01609	43.08	57.03
Nanoarray TiO ₂ Photocatalysis	0.06394	10.84	95.37
Nanoarray + Humic Acid	0.05283	13.12	95.20
Nanoarray + Na ⁺	0.0902	7.68	99.34
Nanoarray + Ca ²⁺	0.10279	6.74	99.35
Nanoarray + Mg ²⁺	0.09158	7.57	99.52
Nanoarray + NO ₃ ⁻	0.06099	11.36	95.92
Nanoarray + SO ₄ ²⁻	0.05516	12.57	95.53

Figure 4.10. Comparison of the survival fraction of *E. coli* cells with time by photocatalysis using TiO_2 nanotube array films and photolysis via 365 nm UV irradiation. Inset depicts linearized plot of $\ln$ [survival fraction] versus time.

Figure 4.11 shows that the TiO_2 nanotube array films achieved complete *E. coli* inactivation of > 5 log after 100 min of irradiation. According to surface water treatment rules as regulated by US EPA, the removal/inactivation efficiencies of bacteria and viruses should reach up to 99.9% (3 log) and 99.99% (4 log) respectively. Hence, enough contact time could ensure the complete bacteria disinfection using the synthesized TiO_2 nanotube system.

Figure 4.11. Complete *E. coli* inactivation over TiO_2 nanotube array films.

4.2.3.1 Effect of aqueous matrix species on inactivation of *E. coli* cells

Surface waters contain a range of organic and inorganic species which might significantly affect the efficiency of photocatalytic disinfection (Byrne et al. 2011). From the application perspectives, it is imperative to investigate the influence of common matrix species present in the surface waters on the *E. coli*.

4.2.3.2 Influence from natural organic matter in water

Humic substances constitute the major fraction of natural organic matter in water supplies and may account for up to 90% of total dissolved organic carbon in surface waters (Caballero et al. 2009). They are prevalent in natural waters as they are derived from the decomposition of natural organic compounds. Humic substances are also precursors of harmful disinfection by-products (DBPs), such as trihalomethanes, via a reaction with chlorine during disinfection chlorination. DBPs are reported to be hazardous to human health and possibly carcinogenic (Woo et al. 2002). Humic substances affect the colour and taste of drinking water and are also a significant cause of membrane fouling. It has also been reported that they support bacterial regrowth in water distribution systems (Vanderkooij et al. 1982). To elucidate the influence of organic compounds, synthetic humic acid was added into the system at a concentration of 10 mg/L to model natural organic matter and to investigate its effect on the efficacy of *E. coli* inactivation. As seen from Figure 4.11, there is a marked inhibition of bacterial inactivation and the disinfection kinetic constant was noted to decrease by 17.4% under the influence of humic acid compounds. This could be attributed to various mechanisms, including direct absorption of UV light, ROS scavenging and competition for active sites on the surface of TiO₂ nanotube film by the humic acid (Rincón and Pulgarin 2004). Humic acid, being dark with large molecular masses, are assembled by small bio-organic molecules (Piccolo 2002). Given their large surface areas, they can considerably intercept and filter off UV irradiation within an aqueous suspension. It has also been reported that the polyaromatic nature of the humic substances is the main factor that competes for the adsorption of UV photons, hence reducing the

amount of radiation available in activating TiO₂ (Marugán et al. 2008). The point of zero charge (pzc) of the TiO₂ nanotube film was found to be at ca. pH 6.2. Therefore surface of this photocatalyst is negative charged under neutral pH. The humic acid also became negatively charged at pH 7, owing to the deprotonation of the carboxylic groups present at the periphery of the molecules (Bai and Zhang 2001, Palmer et al. 2002). Although there would be a electrostatic barrier between negatively charged humic acid and TiO₂ nanotube photocatalyst, it is suggested that the –TiOH species on the surface of this photocatalyst could interact with the deprotonated functional groups of humic acid through ligand exchange to form surface complexes (Vermeer et al. 1998). This could lead to the strong adsorption of humic acid on the surface of TiO₂ nanotube photocatalyst, which would severely reduce the amount of adsorption and reaction sites available on the photocatalyst and certain amounts of generated ROS would be channeled into degradation of humic acid. On the other hand, according to a detailed surface charge study of *E. coli* by Li and colleagues (Li and McLandsborough 1999), the cell surface charge of *E. coli* is negative at pH 7. The repulsion between the *E. coli* cells and the surface adsorbed humic acid would further inhibit the interaction of the *E. coli* cells with the TiO₂ photocatalyst, leading to the reduced rate of photocatalytic disinfection. Moreover, the presence of humic acid on the TiO₂ surface could result in a decreased concentration of hydroxide ions and water molecules on the photocatalyst surface, which could reduce the concentration of hydroxyl radicals or equivalent ROS available to participate in *E. coli* inactivation.

Figure 4.12. Effect on survival fraction of total *E. coli* cells with time under the influence of humic acid in the system. Inset depicts linearized plot of $\ln$ [survival fraction] versus time, according to Chick-Watson's model.

4.2.3.3 Cationic Influence

The different cations introduced into the system exhibited a similar trend of enhanced efficiency. Figure 4.12 exhibits the influence of cations and Figure 4.13 exhibits the influence of anions on the overall efficiency of *E. coli* inactivation. Based on Figure 4.13, the cations seemed to have a positive effect on photocatalytic disinfection, as shown from the exponential decline in concentration of *E. coli* over time. Ca^{2+} is a hard cation present in natural waters and it is capable of enhancing TiO_2 adsorption and inactivation of *E. coli* (Li et al. 2002, Yoon et al. 1998). As mentioned above, both the surface charges of TiO_2 photocatalyst and *E. coli* cells are negative under neutral pH condition. Therefore presence of cations adsorbed on the catalyst weakens its overall negative charge and reduces the repulsion of *E. coli*. Ca^{2+} ion bridging (Yoon et al. 1998) with TiO_2 enhances surface charge attraction of *E. coli* cells to the catalyst, which further promotes adsorption; thereby explaining the slight superiority in antibacterial activity than in the presence of Mg^{2+} ions. Relative to the influence of Ca^{2+} ($k=0.10279 \text{ min}^{-1}$) and Mg^{2+} ($k=0.090379 \text{ min}^{-1}$) ions, efficiency of *E. coli* inactivation with presence of Na^+ ions, is noted to be slightly inferior ($k=0.0902 \text{ min}^{-1}$), largely due to the less positive

charge of Na^+ ions, which leads to a lower extent of neutralizing repulsion between *E. coli* and TiO_2 . In conclusion, these results provide evidence that the repulsion force of *E. coli* and TiO_2 is weaker with the introduction of cations in the system; and that divalent cations (Ca^{2+} and Mg^{2+}) are more superior in weakening this repulsion force as compared to monovalent cation (Na^+). Generally, with the presence of cations in the system, photoinactivation rate of *E. coli* cells was improved. Under the effect of cations, the average half-life of 10^6 cpu/mL *E. coli* cells was significantly shortened by 3 ½ mins.

Figure 4.13. Effect on survival fraction of total *E. coli* cells with time under the influence of different cations in the system. Inset depicts linearized plot of $\ln$ [survival fraction] versus time, according to Chick-Watson's model.

4.2.3.4 Anionic Influence

Contrary to cations, the effect of monovalent anion (NO_3^-) and divalent anion (SO_4^{2-}) on efficiency of *E. coli* inactivation was inhibitory as shown in Figure 4.14. The anions are known to attach to the positive surface sites of TiO_2 , thereby increasing its negative surface charge. In doing so, the repulsion forces against *E. coli* cells are reinforced and adsorption of *E. coli* is significantly diminished, therefore explaining the decline in photocatalytic reactions.

It has been reported (Zhang et al. 2005) that SO₄²⁻ ions can act as scavengers of h⁺ and SO₄^{•-}, generated by TiO₂ upon UV irradiation, to produce SO₄^{•-} radicals based on the following reactions:

SO₄^{•-}, also a strong oxidative radical (E_o = 2.6 eV), is produced from the reaction pathways (4.1) and (4.2), and should in theory, assist in photooxidation of *E. coli*. However, it is less reactive as compared to the scavenged h⁺ and •OH radicals (Zhang et al. 2005), thus the net photocatalytic reaction kinetic is still observed to be inhibitory, as noted from a 13.7% decline in disinfection kinetic constant during the presence of SO₄²⁻ ions.

Figure 4.14. Effect on survival fraction of total *E. coli* cells with time under the influence of different anions in the system. Inset depicts linearized plot of ln [survival fraction] versus time, according to Chick-Watson's model.

The decline in photoinactivation rate of *E. coli* in presence of NO₃⁻ ions (k=0.06099 min⁻¹) is less pronounced than that of SO₄²⁻ ions (k=0.05516 min⁻¹). Adsorption of SO₄²⁻ ions on the catalyst surface is comparatively more intense than NO₃⁻ ions due

to protonation of TiO_2 surface and modification of the TiO_2 double layer structure. It was previously reported that the specific adsorption of sulphate species is so strong that electrostatic forces and changes in the double layer structure do not exert any effect on it (Horanyi 2003). Another report also elucidated that $\text{SO}_4^{\cdot-}$ ions form a complex functional covalent bonding with TiO_2 (Jung et al. 2001), therefore fewer active sites of the TiO_2 are available in the presence of SO_4^{2-} ions as compared to NO_3^- ions. Since NO_3^- ions are monovalent and less negatively-charged than SO_4^{2-} , repulsion with TiO_2 is comparatively weaker, thus efficiency of *E. coli* inactivation in the presence of NO_3^- ions will be stronger than in the presence of SO_4^{2-} ions; which is in good agreement with the experimental trend as observed in Figure 4.13. Upon subsequent introduction of anionic species into the aqueous suspension, the average $t_{1/2}$ was lengthened by over 1 min of reaction time.

It is worthy to note that after a considerably short irradiation time of 50 mins, recorded % kill ratio of *E. coli* cells exceeded 95% for every experimental conditions. This reiterates the disinfecting efficiency of the nanotube array photocatalyst.

Triplicate tests were carried out in Section 4.2.2 and 4.2.3, and variation of the results was calculated within $\pm 5\%$, which indicated good repeatability of the results.

4.2.4 Roles of nanostructures in the destruction of *E. coli* cells

The main objectives of the as-synthesized photocatalyst are engineered for industrial applications; thereby there are 2 main aspects which are emphasized on, namely, superior photocatalytic performance and its ease of separation from treated effluent. The main advantages of film catalysts over powdered or slurry forms is that due to its higher density, the films can be conveniently recovered and subsequently regenerated, via a subsequent membrane filtration step which further polishes the effluent. Henceforth, a disinfection performance comparison test was not carried out against powdered TiO_2 or slurries - which would possibly be more

superior mainly due to their much higher surface to weight ratio that would severely hamper recovery of catalyst in the later stage of the water treatment train.

The dimensions of the nanoarrays show nanotube diameters of close to 100 nm. As the dimension of an average *E. coli* cell rod is 2 µm – 500 nm in diameter (Cho et al. 2004, Li and McLandsborough 1999), the bacteria should theoretically reside on the surfaces of the nanotube rafts. It is thus pertinent that the free radicals produced within the centre of the nanotubes upon irradiation, will have sufficiently long lifetimes to reach the bacterial cell membrane of the cells that are resting on the raft surface. It is noteworthy that the lifetime of hydroxyl radicals is very short, i.e., the lifetime of the hydroxyl or hydroperoxyl radicals is on the order of nanoseconds (Ermacora et al. 1996, Tullius 1987) and might thus have insufficient lifetimes to reach bacterial cells residing on the rafts of the nanotubes. However, as reflected from our results, the short reaction time (50 mins) as required to attain > 95% kill rate of *E. coli* cells demonstrates a sufficient concentration of radicals in inactivation of *E. coli* cells. Moreover, the •OH concentration increases with illumination time due to the interaction between light and TiO₂. The radicals generated from the rafts and surfaces of the nanotubes upon UV irradiation could henceforth be deemed optimal, striking a balance between the •OH generated and deactivation of bacteria (Caballero et al. 2009). In fact, an excess in the production of hydroxyl radicals could lead to their self recombination via equations 4.3 and 4.4:

The above reactions lead to the formation of HO₂•, hydroperoxyl radicals, which are less reactive and apparently does not contribute to the oxidation process. The anodic titania nanotubes are expected to be more efficient at chemical remediation than bacterial disinfection as the smaller chemical molecules can diffuse throughout

the nanoarrays and come into immediate contact with the radicals as soon as they're being generated upon UV activation.

As highlighted in the experimental results, the TiO₂ films managed to achieve a kill rate of over 95% of total *E. coli* cells (10^6 cpu/mL) in 50 mins of irradiation time. The disinfection efficiency of the TiO₂ nanotube film has surpassed several recently reported TiO₂ photocatalytic disinfection of *E. coli* with similar experimental conditions (Alrousan et al. 2009, Caballero et al. 2009, Kim and Kwak 2009), - where a longer irradiation period of 80-200 mins was required to achieve near equivalent kill rates under a similar or stronger intensity of UV irradiation.

4.3 Conclusion

In conclusion, self organized and highly-ordered TiO₂ nanotube arrays were synthesized following titanium anodization in a fluoride based organic electrolyte. The length and diameter of the nanotubes were controllable via different anodization parameters. BET analysis reflected a moderate surface area of 28.97 m²/g due to its double-walled nanotubes structure. The highly-ordered 1D nanotubular structure promotes efficient anti-recombination of electron and holes, as well as delocalization of charge carriers during photocatalytic reactions. In addition, the as-fabricated photocatalyst offers promising potential in industrial scale water treatment applications, owing to its superior photocatalytic disinfection ability under the influence of different ionic species and organic compounds.

This study was the first to be reported to date in the application of anodic TiO₂ nanotubular films for *E. coli* disinfection. At the end of 50 mins UV-A irradiation time, it is noteworthy that more than 95% of the initial 10^6 cpu/mL of *E. coli* cells were inactivated across all photocatalytic experiments. A 6-log unit reduction in bacterial population, as recommended by the WHO disinfection guidelines, can therefore be conservatively projected by increasing the UV-A irradiation time.

This is of great significance for all self-cleaning and water treatment applications. Besides the high performance of the as-synthesized free-standing nanotube films, their use would be potentially much more suitable in applications where the particle separation from the cleaned media is technologically expensive and difficult.

CHAPTER 5 HIERARCHICAL ASSEMBLY OF ANATASE NANOWHISKERS AND ONE- DIMENSIONAL TiO₂ NANOSTRUCTURES FOR PHOTOCATALYTIC DEGRADATION OF ACID ORANGE 7

5.1 Introduction

Following the conclusion of Chapter 4 where highly-ordered and vertically-oriented TiO₂ nanotubes have been successfully synthesized for effective disinfection of *E. coli* cells over a variety of water conditions, this chapter will present a novel hybrid synthetic method using the formerly prepared nanotubes as precursors in obtaining the final nanowhisker architecture. Due to their substantially greater density in film structure as compared to fine powder form, the nanotube photocatalyst in Chapter 4 has proven to settle much more rapidly in an aqueous suspension as compared to nanosized TiO₂ powdered catalyst with particulate size of 15-25 nm, for e.g. Hombikat UV-100 and Degussa P25. However, since the nanotube catalyst is free-standing in nature, i.e., it is not anchored on any substrate support and would form a heterogeneous suspension when applied to an aqueous medium, it is pertinent that a post-separation process is to be performed to recover suspended spent catalysts from the treated effluent after the photocatalytic treatment process. The inconvenience and engineering difficulty of such a recovery process are well documented, thus a series of TiO₂ photocatalysts immobilized and epitaxially-grown from Ti substrates have been developed in subsequent chapters. The novel photocatalyst characterize various 1D nanostructures in terms of their inherent morphologies, and photocatalytic efficiencies were studied in detail using Acid Orange 7 (AO7) as an organic probe molecule.

Much research attention has been focused on 1D nanostructure such as wires, tubes, rods and belts, owing to their important roles in the fabrication of various electronic

devices in nanoscale dimensions (Huang et al. 2001, Tian et al. 2009, Xia et al. 2003, Yang et al. 2010). 1D structures provide large interfacial areas and channels for excited electrons to effectively separate, thus preventing recombination with the photogenerated holes under excitation. The effective transport and movement of charge carriers is facilitated throughout the crystal length, unique to a 1D crystal, leading to an improved delocalization and enhancing photocatalytic reaction efficiencies (Tachikawa et al. 2007). Contrary to top-down nanolithography techniques, bottom-up self-assembly of 1D nanowires have inherent advantages of being single-crystalline and possessing atomically smooth surfaces with nearly defect-free lattice characteristics. Henceforth, chemically-grown nanowires are increasingly becoming a viable option as they offer choice of tailored design customizations which complements construction of multifunctional peripherals assembled on a common substrate.

Herein for the first time, we report the synthesis of a hierarchically-structured anatase film made up of radially-aligned, ultra-long nanowhiskers. Photocatalytic activity of as-synthesized TiO₂ nanowhiskers was evaluated using AO7, a common dye compound used in textile industries, as the model compound. For comparison, photocatalytic experiments with other TiO₂ films of various 1D nanostructures and a Degussa P25 TiO₂ coated film were performed under the same conditions.

A time-dependant, step-by-step illustration on the morphological evolution of nanotubes to nanowhiskers will be covered in this chapter via a series of FESEM images taken at various reaction times; while the corresponding HRTEM and SAED figures will elucidate crystallographic transformations. This would shed light on the formation and reaction mechanism of the hierarchical anatase nanowhisker structure from ordered nanotubes obtained via a typical anodization process as described in Chapter 4.

AO7 is widely recognized as a reasonably photostable organic dye compound that does not undergo photodegradation when subjected to visible light. The degradation of AO7 under UV photolysis is also limited. However, as shown from the

experimental results of Chapter 4, bacterial cells such as *E. coli* cells were inactivated under UV irradiation. This was also demonstrated from conventional UV disinfection process in drinking water treatment, although it was reported that cell inactivation by UV usually occur without any measurable morphological changes to cell membrane or damage to intracellular enzyme or compromise to structural integrity of the inner cell components (Cho et al. 2010). Hence, by investigating the photocatalytic degradation of AO7, a clearer elucidation of the photocatalytic efficiency as well as the mechanistic degradation pathway based on the different evolution of nanostructures, can be deciphered and better understood.

5.2 Results and discussion

5.2.1 Morphological and crystallographic evolution of trititanate nanowhisker

Figure 5.1 provides a schematic illustration of the hydrothermal coarsening process in converting hollow nanotubes to solid nanowhiskers. Highly-ordered TiO₂ nanotubes are obtained after electropolishing and a 6-h anodization process. This procedure yields vertically-aligned and closely-packed TiO₂ nanotube arrays, as shown in Figure 5.1. It was observed that each anodic tube has an inner diameter of 50 nm, tubular wall width of 20 nm and height of *c.a.* 30 μ m. Owing to its ordered tubular morphology, titania nanotubes possess high surface-to-volume ratios, and thus high surface free energy. It is noteworthy that coarsening of hollow nanotubes to solid nanowhiskers greatly reduces surface-to-bulk ratios and achieves free enthalpy gain in the process (Horvath et al. 2007), hence they are thermodynamically favoured over hollow nanotubes once systems enter thermodynamic control regime (Xia et al. 2003).

Figure 5.1. Left: FESEM image of the starting anodized TiO_2 nanotubes. Middle (Top): Illustration of the hydrothermal coarsening process converting hollow nanotubes to solid nanowhiskers. Middle (Bottom): Gradual filling of the nanotubes hollow channels by smaller nanocrystallites deposition via Ostwald ripening. Right: Cross-sectional FESEM images of radial $\text{Na}_2\text{Ti}_3\text{O}_7$ nanowhiskers.

Figure 5.2 and 5.3 show the respective FESEM and TEM images of samples obtained by treating the amorphous TiO_2 nanotubes with concentrated NaOH at 180°C for a series of durations. At the beginning (2 h), there is a clear indication of warping and convergence at the top section of the nanotubes as evidenced in Figure 5.2A and 5.2B. The dissolution of TiO_2 in concentrated NaOH starts from the open tubular end, which is the most vulnerable part of a nanotube (Horvath et al. 2007). It is also observed that the nanotubes were broken up into random clusters of relatively similar sizes. During the hydrothermal reaction, localized cracks due to shear forces were observed at the foot of the nanotubes where intrinsic surface-induced stress act - a location of highest surface free energy. Bavykin et al. (2004) detected a gain in free surface energy against a reduction of elastic energy during the curving of multilayered conjoined TiO_2 nanosheets. Similarly, we believe that the mechanical tension arising from the warping and upward flexure of nanotubes is being compensated by an increase in surface energy. Based on density function theory of $\text{H}_2\text{Ti}_3\text{O}_7$ and TiO_2 nanostructures, Zhang et al. (2003) postulated that an

asymmetrical chemical environment could give rise to excess surface energy due to hydrogen deficiencies, thus resulting in a wrapping phenomenon.

Figure 5.2. Low and high magnifications of FESEM images depicting progressive morphological evolution of nanotube to nanowhisker under different hydrothermal durations: (A-B) 2 h, (C-D) 4 h, (E-F) 8 h, (G-H) 10 h, (I-J) 15 h.

Figure 5.3. TEM and their respective HRTEM and SAED (inset) micrographs depicting progressive crystallographic transformation of nanotube to nanowhisker under different hydrothermal durations: (A-B) 2 h, (C-D) 4 h, (E-F) 8 h, (G-H) 10 h, (I-J) 15 h.

The coalescence and bunching of the vertically-ordered anodic TiO_2 nanotubes is a clear testament of the oriented attachment mechanism. Figure 5.3A and 5.3B show solute phase transport with subsequent precipitation and recrystallization of Ti(IV) within inner hollow channels and interspace pore boundaries of the nanotube walls after 2 h to yield solid nanorods. This is consonant to the claim that hollow channels of nanotubes are fused together by precipitation of Ti(IV) , resulting from dissolution of TiO_2 in NaOH (Huang et al. 2009). Such an observation displays the particular characteristic of Ostwald ripening, a phenomenon in which small crystals

formed initially gradually dissolve and coalesce to form bigger crystals before re-depositing on the surfaces of other larger crystals; thereby reducing surface-to-volume ratio and surface free energy of the system (Kabalnov 2001). In contrast to the oriented attachment mechanism which results in rapid coarsening of crystals, the Ostwald ripening process is a gradual phenomenon contributing to the enlargement of crystallite size. In other words, the filling of inner hollow channels of the nanotubes is driven by the Ostwald ripening process while the tube bunching trend is advocated by the oriented attachment mechanism.

After 4 h of hydrothermal treatment, the warped up clusters of nanotubes clearly self-assembled into hierarchical bundles of secondary structures each culminating at pronounced vertices of ca. 200 nm (Figure 5.2C). The geometric height of each structure was elevated slightly to ca. 50 μm , partially motivated by compressive surface-induced stress, i.e. intrinsic to such a structure (Su and Du 2010). The high-magnification FESEM image from Figure 5.2D shows the bunching and attachment of adjacent parallel nanotubes to form larger bundles, suggesting the preponderant mechanism as oriented attachment. Penn and Banfield have reported that oriented attachment is an important growth mechanism during hydrothermal coarsening of titania particles. When the structurally-similar adjacent nanotubes approach one another, atoms of opposing surfaces may form chemical bonds between them to achieve full coordination of crystallographic orientations, resulting in the observed densification of bundled titanate nanowires that fuse along identical crystal faces (Penn and Banfield 1998). Henceforth, energy levels of the overall system are reduced as a result of eliminating solid-liquid interface. The tailing of diffraction spots shown in the inset of Figure 5.3D demonstrates a typical case of short-range disorder within long-range order in the crystal lattice, as a result of the large amount of defects generated from the tube bunching process.

After 8 h, it is apparent that the nanowhisker structure has been generally constructed, however with presence of large amounts of incorporated defects (Figure 5.2E), believed to be inherited from misorientations and dislocations at interfaces of adjacent crystal lattices during oriented attachment of crystal planes.

Close-up inspection of the surface defects reveal a spiral network matrix of densely-assembled nanofibres in between two regions of radially-ordered nanowhiskers - a tell-tale sign of crystal lattice dislocations, forming critical sites of nucleation and phase transformations (Penn and Banfield 1998). Growth of such nanofibres takes place spirally around crystal dislocation sites, prior to a surface nucleation process, which explains the precipitation of titanate nanoparticles on the exterior of nanofibres shown in Figure 5.3E.

By $t = 10$ h, we notice the disappearance of the intermittent nanofibres networks and the nanowhisker arrays become more prominent. Figure 5.2H shows a close up image of the surface of a nanowhisker which appears to be corrugated and having a layered appearance of several nanofibres stacking atop one another. A high concentration of surface defects imparted by twins and stacking faults is apparent on each of the nanowhisker strand. The large amounts of defects inherent from the coarsening process is further evidenced through SAED images (insets of Figure 5.3D, 5.3F and 5.3H), exhibiting tailing of diffraction spots.

With extension of hydrothermal duration to 15 h, we successfully remove these generated defects to achieve smooth-surfaced, solid nanowhiskers, as evidenced from the respective low and high magnifications of FESEM micrographs in Figure 5.2I and 5.2J, as well as TEM image in Figure 5.3I. It is also notable from SAED patterns that with elongation of hydrothermal treatment time, tailing of diffraction spots became shorter - consistent to TEM images showing smoother nanocrystals. The corresponding clear spot SAED pattern (inset of Figure 5.3J) of the final nanowhisker product further exemplifies its high purity and crystal defect-free characteristics. Cross-sectional and overview FESEM images of the final nanowhisker film presented in Figure 5.1 confirm that the ultra-long nanowhiskers are highly uniformed and densely packed with aspect ratios as high as 300. HRTEM image of Figure 5.3J denotes single-crystallinity of the final trititanate nanowhiskers with almost defect-free lattice characteristics - continuous, uniform lattice fringes with clear spot diffraction patterns.

Figure 5.4. XRD patterns of the various products obtained after hydrothermal treatment of amorphous TiO_2 nanotubes with concentrated NaOH at different durations. From labels of the respective XRD peaks, ST refers to Sodium Titanate and Ti is Titanium.

From the XRD spectra in Figure 5.4, diffraction peaks of products obtained after 8 h can be well indexed to monoclinic $\text{Na}_2\text{Ti}_3\text{O}_7$ (JCPDS no 72-0148). It is apparent that with longer hydrothermal durations, intensities of diffraction peaks at 2θ 10.5° , 15.8° , 25.7° and 28.4° , increase with narrowing of widths, suggesting enhancement of crystallinity by the removal of crystal defects. At 0 h, only Ti peaks, ascribed to the Ti substrate, were present since the highly-organized TiO_2 nanotubes prepared via anodization is amorphous in nature. It is obvious that with longer hydrothermal durations, the typical XRD patterns of titanate became more prominent, without any trace of TiO_2 peaks. Based on calculations using the Scherrer equation (Patterson 1939), crystallite size of sodium titanate increased by more than 2 folds over the progression of 15 h. Figure 5.4 exhibits evidence of sodium titanate formation as early as 2 h, with a calculated crystallite size of 3.95 nm and growing to a final crystallite size of 10.53 nm after 15 h. The growth of titanate crystals seemed to be linear across the reaction, which was consonant to FESEM and TEM images from Figure 5.2 and 5.3, exhibiting gradual coarsening of crystals. The XRD patterns of

the titanate peaks are similar to those of powdered titanate obtained under similar hydrothermal conditions, albeit using anatase TiO_2 nanopowder as starting materials (Bavykin et al. 2004, Huang et al. 2009). It is worthy to note that the consequent XRD patterns of titanate products obtained by prolonging hydrothermal treatment up to 24 h, did not exhibit any apparent discrepancies from that of 15 h. The same can be mentioned about the morphology of products obtained beyond 15 h; no further morphological evolution could be observed by extending the hydrothermal duration, indicating that the nanowhiskers have reached its critical equilibrium state and likewise, there was no further increment in subsequent crystallite size.

5.2.2 Development of different morphologies of anatase TiO_2

Figure 5.5. Various synthetic routes in obtaining different morphologies of anatase TiO_2

The trititanate nanowhiskers were recrystallized into pure anatase polymorph of TiO_2 via calcination in air at 500 °C, while retaining its 1D morphology. Omitting either the anodization or hydrothermal step would not yield the final nanowhisker

structure and instead lead to formation of nanowires and nanotubes respectively. Figure 5.5 shows the respective synthetic routes taken in obtaining different morphologies of anatase TiO_2 .

Figure 5.6. FESEM images of the as-prepared (A-B) Nanotube sample, (C-D) Nanowire sample, (E-F) P25 coating sample. The left column shows low magnification overviews while the right column shows high magnification upclose images of the respective 1D nanostructured samples.

Figure 5.7. FESEM images of calcined TiO_2 Nanowhisker sample taken at different magnifications.

The FESEM images of the nanotube, nanowire, P25 coating samples and the final calcined nanowhisker sample are shown in Figure 5.6 and 5.7 respectively. As observed from Figure 5.6B, some of the anodic tubes were noted to fracture after calcination, exposing hollow inner channels that suggest that the tube walls are thin, porous and relatively fragile. On the other hand, the nanowire sample was made up of a network of overlapping TiO_2 nanowires that enmesh and interweave into a layer of fibrous film (Figure 5.6C and 5.6D). No morphological change was noted upon calcination. The P25 dip-coated film on Ti foil resulted in the agglomeration of aggregated nanoparticles with varying dimensions and shapes, enveloping both faces of the Ti foil. The aggregation of P25 nanoparticulates after the dip-coating and heat treatment process is a testimony of van der Waals forces acting on the particles leading to formation of primary particle clusters as clearly evident in Figure 5.6F.

As explained in the preceding section, anodic nanotubes are a necessary starting material in obtaining the final nanowhisker structure. The “bottom-up” construction of the final nanowhiskers involves evolution of intrinsically anisotropic ordered nanotubes in initiating 1D growth of longer nanowhiskers. As shown from the high and low magnifications of top-surface FESEM micrographs in Figure 5.7, the ultra-long nanowhiskers are highly uniform and densely packed with a characteristic flat rhombohedral cross-sectional plane. Figure 5.7B reveals the longest lateral dimension of a nanowhisker to be *c.a.* 100 μm , measured from a particular point of radial nanowhisker growth, diverging outwards. It is noteworthy that the high temperature calcination process did not alter overall morphology of $\text{Na}_2\text{Ti}_3\text{O}_7$, obtained after alkaline hydrothermal of anodic nanotubes.

5.2.3 Crystallographic phases and states of 1D TiO_2

Figure 5.8 compares the typical XRD patterns of the synthesized TiO_2 nanowhiskers, nanotubes, nanowires and P25 film coated sample. Ti (JCPDS no. 89-5009) peaks can be indexed to every spectra since all the films are embedded on a Ti substrate. Barring the Ti peaks, the spectra of nanowhisker, nanowire and nanotube exhibit evident presence of only the tetragonal anatase phase (JCPDS no. 21-1272), indicating that protonated titanate after the ion-exchange process has been completely transformed via a calcination step. In addition to the anatase phase, the P25 coating on Ti substrate reveals presence of rutile polymorph with a pronounced peak at $2\theta = 27.4^\circ$, since commercial P25 consists of a mixed phase of anatase and rutile in the ratio of *c.a.* 4:1 (Komaguchi et al. 2006). XRD profiles of all the samples clearly exhibit an enhanced peak for the $\langle 101 \rangle$ reflection centred at $2\theta = 25.3^\circ$, thereby affirming a preferential crystal growth of the 1D nanostructures along the thermodynamically-stable $\langle 101 \rangle$ plane of the body-centred tetragonal phase. It has been widely reported that the $\langle 101 \rangle$ plane has the lowest surface energy and thus most energetically-stable (Yang et al. 2008). The strong diffraction peaks of the nanowhisker sample are substantially higher and sharper than the rest of the spectra, suggesting it to be highly crystallized, therefore also yielding the

highest photocatalytic activity as seen from Table 5.1. It is also observed that XRD spectra of the nanowhisker sample consist of weaker anatase diffraction peaks that are absent in the other photocatalysts (namely, $2\theta = 37.8^\circ$, 53.9° , 55.1°), exemplifying its single crystallinity, high purity and crystal defect-free characteristics. The crystallite sizes of each sample are estimated by measuring the full width at half maximum (FWHM) values from respective peaks and applying the Scherrer Equation (Patterson 1939). The calculated P25 crystallite size of *c.a.* 20 nm coincides with previously reported figures (Bakardjieva et al. 2005).

Figure 5.8. XRD spectra of the as-prepared photocatalysts

From Figure 5.9A, the ends of the TiO₂ nanowhiskers are generally shaped in a rhombus – as delineated in red, while the edges of some whiskers were chipped off. The lateral dimension of each rhombus side is *c.a.* 200 nm and length of the longer diagonal across its centre axis is up to 400 nm. The clear spot diffraction pattern from its SAED pattern (Figure 5.9E) suggest that the anatase nanowhiskers obtained after calcination is monocrystalline. Figures 5.9C and 5.9D are the corresponding HRTEM images which exhibit almost defect-free lattice characteristics – continuous, uniform crystal lattices that are unbroken to the edge of the sample and without presence of grain boundaries, thereby reaffirming its

single-crystalline structure after calcination. An interplanar spacing of 0.352 nm between the planes of the atomic lattices, parallel to the $\langle 101 \rangle$ planes, can be readily measured from the micrographs. This is further evidence that the single crystalline anatase nanowhiskers grow along the $\langle 101 \rangle$ crystal plane with a preferred orientation in the $\langle 010 \rangle$ direction, thus resulting in a pronounced XRD peak for the $\langle 101 \rangle$ reflection as centred at $2\theta = 25.3^\circ$ where $d = 0.352$ nm based on Bragg's Law (Ewald 1969).

Figure 5.9. (A) High magnification FESEM image of the nanowhiskers (B) Typical TEM micrograph of a single TiO_2 nanowhisker, (C-D) HRTEM showing crystal lattice orientation and interplanar distance, (E) Corresponding SAED pattern of the single crystalline nanowhisker.

5.2.4 Optical properties: UV-Vis and Photoluminescence study

Figure 5.10. UV-Vis diffuse reflectance spectra of the as-prepared photocatalysts

The UV-Vis diffuse reflectance spectra of the respective nanostructured photocatalysts are shown in Figure 5.10. The inset of Figure 5.10 is plotted by application of the transformed Kubelka-Munk theorem, of $(\alpha h\nu)^{1/2}$ against $h\nu$, and the vertical segment of the spectra is extended to intersect the $h\nu$ axis (x-axis) in obtaining the indirect optical band gap (E_g) value of the TiO₂ samples. As recorded in Table 5.1, the measured optical band gaps of synthesized anatase-TiO₂ samples (nanowhisker, nanotube and nanowire) were in the range of 3.03 – 3.14 eV, consonant to reported band gap values of bulk anatase TiO₂ (Michalow et al. 2009). It can be observed that the TiO₂ nanowhiskers exhibited higher adsorption of light from 250 to 400 nm, as compared to the other samples. This can be ascribed to the enhanced light harvesting abilities and optimized UV penetration due to presence of voids between the individual nanowhiskers; therefore nearly the entire length of each nanowhisker can be exposed to the UV light. It can be suggested that the nanowhisker sample is thus able to utilize more UV photons from the irradiation source in its excitation to initiate photocatalytic process; which explains a higher photo activity (Chen et al. 2011b). As motivated by its unique macrostructure, a

slight red-shift was observed in the action spectrum and the onset of optical absorption was lowered to *c.a.* 400 nm. Despite having the same anatase crystalline phase, it is evident that the morphology of samples had a certain extent of influence on its band gap values.

The PL emission analysis is commonly used to evaluate the extent of transfer and separation, as well as trapping of charge carriers within an activated semiconductor photocatalyst. The transfer behaviour of photoinduced electron and hole pairs can also be interpreted from the spectra since recombination of these free charges contribute significantly to emission signals. Figure 5.11 depicts the PL spectra of the as-prepared 4 photocatalysts and it is apparent that all 4 spectra comprise of broad and structureless luminescence bands. The observed emissions can be assigned to the radiative recombination of self-trapped excitation luminescence due to their characteristic bands. It has been reported that the surface states of the photocatalyst, such as defect sites (or recombination centres) and oxygen vacancies that promote combination of photogenerated electrons and holes, are responsible for the observed luminescence (Zhang et al. 2000). The longer and surface defect-free nanowhiskers facilitate migration of charge carriers more efficiently than the other nanostructures, therefore reducing the phenomenon of charge recombination as hypothesized from its weaker PL signal. Since defect sites and oxygen vacancies constitute to recombination centres for photogenerated electrons and holes, we postulate that the nanowhiskers possess a more defect-free crystal structure as compared to the other nanostructures. With a greater suppression of charge recombination, reaction lifetimes and quantities of these electron and hole pairs are prolonged and increased substantially, which directly correlates to a higher concentration of active oxidative species being produced (Chen et al. 2005, Hirakawa and Nosaka 2002, Ishibashi et al. 2000a), and resulting in greater photocatalytic efficiencies.

Figure 5.11. Photoluminescence spectra of the as-prepared photocatalysts. The adventitious peak centred around 375 nm is attributed to the double-sided tape adhered on the film sample during PL analysis.

5.2.5 Photocatalytic and Quantum efficiencies

Figure 5.12. Photocatalytic degradation of AO7 over the as-prepared photocatalysts.

Figure 5.13. Pseudo first-order photocatalytic degradation of AO7 over the as-prepared photocatalysts.

In order to establish a rational comparison of photocatalytic activity among the 4 prepared photocatalysts, each specific Ti foil was weighed prior and after synthesis to determine the respective mass of film developed on the Ti foil. A maximum film weight variance of 15% between the samples is allowed, before evaluating their photoactivities.

The photocatalytic activity of the synthesized nanostructured TiO₂ films was evaluated based on degradation of aqueous AO7 under UV-A irradiation (365 nm). Figure 5.12 presents degradation trend of AO7 as logarithms of normalized dye concentration against irradiation time, and the corresponding k constants represent a good measure of the overall photodegradation rates since it is apparent from the linear shape of the curves that the degradation kinetics follows the pseudo first-order kinetics. The nanowhisker sample clearly exhibited the highest photocatalytic efficiency and the highly-ordered nanotubes was second best – a trend which supports the better quantum efficiencies and anti-charge recombination properties of ordered 1D nanostructures. In comparison to nanowires and P25

nanoparticulates, the higher efficiency of the nanowhiskers and tubes can be attributed to a more optimized geometry; hence electron-hole pairs travel shorter carrier-diffusion paths as opposed to migrating between single nanoparticles (Chu et al. 2005, Krysa et al. 2006). The highly-organized 1D geometry within the nanowhisker architecture offers a straightforward, hence shorter diffusion path across the liquid-solid interface for AO7 molecules to reach active surface sites of the photocatalyst. This is in contrast to the convoluted structure of the nanowire and nanoparticulate structures which contain a highly varied spectrum of longer mass transfer paths. For the nanowhisker sample, 99% of the AO7 was removed after 2.5 h of irradiation and the corresponding removal of total organic carbon (TOC) was also highest at 41.9%. The photocatalytic activities follow the order of nanowhisker > nanotube > P25 coating > nanowire. The apparent photocatalytic degradation of AO7 by nanowhisker is 1.2 times higher than the nanotube, more than 1.5 times better than commercial P25 nanoparticles, and almost 2 times more superior over the nanowire sample. The photolysis results revealed negligible degradation of AO7 at 1.6%, largely due to the photostability of AO7 under UV-A exposure (Macak et al. 2007).

Table 5.1. Film weight, physicochemical properties and photoactivity of the synthesized TiO₂ thin film photocatalysts.

Photocatalyst	FWHM (deg)	Anatase size ^a (nm)	Indirect band gap (eV)	Film weight ± 0.05 (mg/cm ²)	k (h ⁻¹)	TOC removal at 2.5 h (%)	$\eta_{app,in}$ (x10 ⁻⁴)
Nanowhisker	0.76	10.6	3.03	1.311	1.595	41.9 $\pm$ 1.8	10.8
Nanotube	0.497	16.22	3.07	1.231	1.339	25.2 $\pm$ 1.1	9.05
Nanowire	1.03	7.85	3.14	1.118	0.862	14.3 $\pm$ 0.6	5.83
P25 coating	0.38	21.21	3.11	1.193	1.039	17.1 $\pm$ 0.7	7.03

^aCalculated based on the [101] peak for anatase, according to the Scherrer Equation.

The apparent quantum efficiencies of the respective photocatalysts was calculated and tabulated in Table 5.1. Proper evaluation of quantum efficiency requires careful

assessment of absorbed photons by the photocatalyst; those which successfully generate electron-hole pairs, where charges are separated and collected at a junction. Due to simultaneous existence of light absorption, reflection, scattering and transmission in heterogeneous photocatalytic systems, the exact rate of absorbed photons becomes very complex to determine. The apparent quantum efficiency, $\eta_{\text{app, in}}$, is therefore employed to evaluate light utilization in this photocatalytic reaction. $\eta_{\text{app, in}}$ is calculated from equation 5.3,

$$\eta_{\text{app, in}} = \frac{\left(\frac{dN}{dt} \right)_{\text{in}}}{P} \quad (5.3)$$

with P representing the rate of photons entering the reactor, and $(dN/dt)_{\text{in}}$ is the rate of photoconversion of reactant molecules under initial conditions. $(dN/dt)_{\text{in}}$ and P can be derived from equation 5.4 and 5.5 respectively.

$$\left(\frac{dN}{dt} \right)_{\text{in}} = k \times C_0 \times N_L \times V \quad (5.4)$$

where k is the respective reaction rate constant of AO7 degradation in min^{-1} , C_0 is the initial AO7 concentration in mol L^{-1} (20 mg/L), N_L is the Avogadro number ($6.02 \times 10^{23} \text{ mol}^{-1}$), and V is the volume of aqueous pollutant (15 mL).

$$P = \frac{I \times S}{hc/\lambda} \quad (5.5)$$

where I is the supplied light intensity in W/m^2 (1150 mW/cm^2), S is the irradiated catalyst area in m^2 (20 mm x 30 mm), h is the Plank's constant ($6.62 \times 10^{-34} \text{ J.s}$), c is the speed of light in vacuum ($3 \times 10^8 \text{ m/s}$), and λ is the wavelength of emitted light (365 nm). As noted from Table 5.1, apparent quantum efficiency of the nanowhisker sample was calculated to be 1.5 times greater than that of anodic nanotubes, establishing a correlation that weaker PL intensities engender higher quantum efficiencies and henceforth give rise to higher photocatalytic (Ng et al. 2010). Low quantum yields are possibly caused by accentuated recombination of

photogenerated positive holes and electrons within the semiconductor particles, likely to be induced by morphological effects. In general, it can be observed that the highly ordered, vertically-aligned nanowhisker and nanotube samples exhibit higher quantum efficiencies as compared to the random matrix of intertwined nanowires and agglomerated nanoparticles of the P25 coating. This further demonstrates the intrinsic properties of 1D ordered structures in suppressing charge carrier recombination under excitation, via effective delocalization of electrons across the channels. Consequently among others, it can be deciphered that the photoactive nanowhisker sample produces the highest quantity of separated electron-hole pairs when irradiated with UV photons, thereby attributing to its high photocatalytic activity.

As shown in Figure 5.12 and Table 5.1, the range of results from triplicate tests was within a variation range of $\leq 5\%$, suggesting the high confidence of experimental reproducibility.

5.3 Conclusion

In summary, a template-free technique was developed to grow 1D anatase nanowhisker arrays from a Ti substrate. By means of FESEM and TEM techniques, the hierarchical evolutions of highly-ordered nanotubes to radially-aligned nanowhisker arrays were studied and the results were presented in this chapter. An extended hydrothermal reaction successfully removed inherent crystal defects of the titanate nanowhiskers, and calcination in air at 500 °C recrystallized the hydrothermally-prepared titanate into an anatase polymorph, while retaining its 1D morphology. Comparing with the free standing TiO₂ nanotube presented in chapter 4, the nanowhisker architecture demonstrates high thermal stability, without experiencing morphological change under prolonged hydrothermal duration (24 h) and calcination (500 °C). The TiO₂ nanowhisker film exhibits a single crystalline structure with almost defect-free lattice characteristics as evidenced from HRTEM and SAED results, and possesses excellent photocatalytic properties in comparison

to other TiO₂ photocatalysts. The high quantum efficiency reiterates strong ability to suppress recombination of photogenerated electrons and holes, by virtue of its 1D morphology in promoting efficient migration of charge carriers. Removal of AO7 and TOC over the nanowhisker product yielded the highest photocatalytic efficiency amongst other 1D TiO₂ photocatalysts, including a Degussa P25 coated film of nanoparticulates.

This radially-aligned, ultra-long TiO₂ nanowhisker array film is the first of its kind to be reported hitherto, and an integral member to a rapidly-expanding family of 1D nanostructures which includes ZnO nanorods (Choi et al. 2009), V₂O₅ nanowires (Velazquez and Banerjee 2009), In₂O₃ nanocrystal chains (Lao et al. 2004) and carbon nanotubes (Li et al. 1996).

As presented in this chapter from characterization studies of the final evolved nanowhiskers architecture in comparison to its initial nanotubular morphology, photocatalytic degradation of a recalcitrant and photostable organic probe molecule (AO7) yielded superior results. As exhibited in Table 5.1, the apparent quantum efficiency, photocatalytic degradation rate constant, as well as TOC % removal, have clearly shown that the developed novel nanowhisker morphology in this later phase of study, is superior to the initially synthesized nanotubes from anodization.

CHAPTER 6 HYDROTHERMAL SYNTHESIS OF A HIERARCHICAL NANOFUNGUS-LIKE ANATASE TiO₂ THIN FILM FOR PHOTOCATALYTIC DEGRADATION OF BISPHENOL A

6.1 Introduction

The world population is rapidly expanding and the effects of globalization are manifesting on important resources such as potable water and food availability. Development of new, synthetic chemicals and microorganisms are in tandem to the accelerated manufacturing of advanced commercial products to meet the demands of consumers today. The waste and by-products created from usage of unorthodox synthetic materials can often impact well-being of the environment and cause biological imbalances to natural ecosystems. The generated waste make their way into waterways and water bodies through municipal, agricultural, commercial and industrial discharge sources and pathways. Much of this waste contains contaminants that are resilient to degradation and can hence accumulate in the environmental biospheres where they can potentially cause environmental and health issues. These emerging contaminants have not been historically considered as contaminants but the threats that they bring about are present in the environment on a global scale. Developments in technological advances of analytical instrumentation have enabled detection of emerging chemicals or microbial contaminants within the environment.

Emerging contaminants are naturally occurring or anthropogenic chemicals that are not commonly monitored in the environment but have the potential to enter the environment and cause adverse ecological or human health effects. Among new emerging contaminants are pharmaceuticals and personal care products, industrial chemicals present at low concentrations, and chemicals that may affect hormone status which are commonly referred to as endocrine disruptors. Bisphenol A (BPA),

for example, is an endocrine disruptor which can mimic estrogen and prenatal exposure may lead to later neurological difficulties. The formation, management and treatment of BPA are rapidly gaining widespread concerns due to its toxicity and potential threat to environmental and human health.

Henceforth, apart from developing a multifunctional photocatalyst used for water decontamination that is able to tackle the bacterial population and recalcitrant organic compounds, a holistic and robust photocatalyst should also be able to degrade and mineralize emerging organic contaminants that are prevalent in water sources.

From the research bibliography of inorganic hierarchical nanostructures, it is not difficult to observe that the hydrothermal method is one of the most common techniques employed. Contrary to other methods of crystal growth, hydrothermal synthesis provides a simple mode of operation and the ability to grow large, high-quality crystals while maintaining a good control of their chemical composition (Chen and Mao 2007a). Wu et al. (2008) successfully synthesized long range ordered uniform arrays of F-doped TiO₂ nanoflowers by a facile hydrothermal reaction of Ti foil with dilute HF acid. Wang et al. (2010) prepared three-dimensional hierarchical anatase nanostructures with self-supported radially distributed nanoflakes, by hydrothermally treating Ti powder in the presence of H₂O₂ and NaOH, prior to an ion-exchange and calcination process. The growth process of the porous nanostructures was prompted by a self-organization process evoked by the Kirkendall effect and Ostwald ripening phenomenon. Direct oxidation of metallic Ti foil using H₂O₂ solution under hydrothermal conditions was carried out by Wu's group and successfully yielded vertically-ordered titania nanorod thin film after annealing (Wu et al. 2005a, Wu 2007).

In view of the lengthy durations and more complex preparation processes of synthesizing the nanotube and nanowhisker photocatalysts through hydrothermal and anodization methodologies, synthesis work in this chapter was substantially improved and optimized and a novel, facile one-pot hydrothermal method was

presented to prepare a hierarchical and mesoporous nanofungus-like anatase thin film. This work also presents a comparison between photocatalysts prepared under different hydrothermal durations, and aims to delineate a possible growth mechanism in obtaining the final nanofungus-like structure. A time-dependant morphological evolution of the final nanofungus-like structure was presented to interpret the formation mechanisms and postulate the possible reaction pathways involved en-route to achieving the mesoporous anatase TiO₂ photocatalyst. The as-prepared photocatalyst exhibited highly efficient photocatalytic degradation of BPA, which is prevalently used as a precursor in manufacturing of polycarbonate plastic containers and epoxy resins, thus representing a significant advance in environmental remediation.

6.2 Results and discussion

6.2.1 Possible reaction pathways

The development of the hierarchical anatase nanofungus-like thin film structure is driven by the following reaction pathways based on the reactions of H₂O₂ and HF with Ti:

- When H₂O₂ reacts with Ti atoms on the foil surface, formation of titanium oxide layer (TiO_x) on the surface of the foil takes place due to the Kirkendall effect (DeRosa et al. 2006, Wang et al. 2010, Wu and Qi 2007). Under thermally-activated conditions and because of differences in atomic diffusivities, interior Ti atoms tend to diffuse or migrate to the surface and react with H₂O₂ on the TiO_x/Ti interface based on the reaction below:

The Kirkendall effect commonly results in a highly porous structure of the titanium oxide layers due to directional matter flow and consequential

vacancy accumulation (Liu and Zeng 2004a). Other reports have also shown that direct oxidation of metallic Ti foil using H₂O₂ would produce an amorphous hydrated titania porous film (Tengvall et al. 1989).

- HF serves not only to provide the F source, but also to etch the Ti substrate, providing a Ti source for further oxidation and formation of TiO₂ nanostructures. Therefore, the reaction of HF with Ti substrate is able to hydrothermally nucleate TiO₂ nanoparticles via a series of reactions as follows (Wu et al. 2008):

- During the process of hydrothermal reaction, newly-developed TiO₂ layer can gradually be dissolved by the HF solution to form TiF₄, resulting in thinning of the nanoflake walls (Hu et al. 2009). It is known that HF is a corrosive chemical, hence the developed TiO₂ film may in turn be etched by HF as shown from equation 6.5 and 6.6:

The produced H₂TiF₆ species then diffuse to the exterior of the existing TiO₂ nanostructures already formed and new TiO₂ is repeatedly developed and aggregated on them, via reactions (6.3) and (6.4) (Macak et al. 2005a). The repeating cycles of dissolution and re-deposition result in the final mesoporous nanofungus-like structure (Wu et al. 2008). It is noteworthy that calcination at 450

°C improves the crystallinity of the sample and converts the TiO₂ to an anatase polymorph, without causing noticeable morphological changes to the overall hydrothermally-formed nanostructures.

6.2.2 Morphology

Figure 6.1. FESEM images of Nanofungus-like sample NF10, taken at different magnifications. Inset of (B): Digital photograph of commercially-available snow fungus.

The structural features of the final product NF10 and the series of intermediate samples, NF5 and NF3, exhibited different topological morphology under different hydrothermal durations. From the overview FESEM image of NF10 sample in Figure 6.1, densely packed 3D hierarchical microspheres with uniformly distributed nanoflakes, closely resemble commercial snow fungus commonly used as an ingredient in Chinese cuisine and medicine – photographed in the inset of Figure

6.1B. Each spherical structure measured about 10 μm in width. The dense gelatinous-like appearance of the photocatalyst comprises of a flakey matrix façade that clump and overlap one another and each flake appear crisp at the edges. High magnification FESEM image from Figures 6.1E and 6.1F reveal that the surfaces of nanoflakes are corrugated and covered with densely packed uniform primary nanoparticles of 20 nm. These nanoparticulates are primary building units and constituent components of the final nanofungus-like macrostructure; the driving force for their aggregation is likely associated with interfacial tension and van der Waals attractive forces (Liu and Zeng 2004b, Park et al. 2004, Yuan et al. 2003). Moreover, it has been reported that conventional hydrothermal synthesis compels slow convection within the autoclave, resulting in localized pockets of high concentrations of developed nanocrystallites, therefore promoting agglomeration (Bavykin et al. 2004).

As shown from the cross-sectional FESEM images of Figure 6.1B, the nanofungus-like thin film has a depth of *c.a.* 5-6 μm . The porosity and surface-to-volume ratios of the sample were greatly enhanced by these primary nanoparticles, which could induce efficient diffusion and mass transfer of organic pollutant molecules within the nanofungus architecture. The EDX spectra of NF10 (inset of Figure 6.5A) showed that the spherical structures of TiO₂ were elementally composed of only pure Ti and O elements and no extraneous elements from intermediates were observed in the final anatase product.

NF5 displayed a nanostructure consisting of disuniformed self-supported stratified layers of radial nanoflakes. From the high resolution image, some of the nanoflakes were supported vertically and possessed a smooth surface, bearing resemblance to petals of a chrysanthemum flower. The emanated flakes are ultrathin, with thicknesses of only a few nanometers and are broad-spanned with widths of *c.a.* 100-200 nm. NF3, on the other hand, was noted with presence of random and disordered nanoflake-like structures over its continuous film. Occasional small cavities that seem gradually eroded within the underlying nanofibrous network were noticed from Figure 6.2C. High magnification FESEM image from Figure 6.2D,

illustrates that the observed nanoflake-like structures, each spanning up to a few micrometers, were constructed by bunching and clustering of nanowires (widths of 10-20 nm).

Figure 6.2. FESEM images of (A-B) NF5 sample, (C-D) NF3 sample, (E-F) P25 coating sample.

As shown from the morphology of NF3 and NF5, the nanoflake structure was constructed by coalescence of nanofibres formed after 5 h of hydrothermal reaction. Under a hydrothermal environment, the primary nanoparticles were crystallized on the solid-liquid interface via a dissolution-precipitation mechanism, leading to nucleation and growth of anatase nanoparticles on the nanoflake structure. This mechanism is analogous to a recently reported hydrothermal synthesis of SrTiO₃ crystallites on TiO₂ nanowires (Ng et al. 2010). Since no discernible discrepancy in size was observed with the primary anatase particles on the nanoflake structure, the hydrothermal reaction mechanism proceeded in good agreement with the classic

LaMer model (Lamer and Dinegar 1950). The results from Figures 6.1 and 6.2 demonstrate that a longer hydrothermal reaction (10 h) with HF precursor has resulted in a progressively hollowing effect in its interiors, as indicated from the rough external façade of nanoflakes and the presence of mesopores from intraparticulate voids. This is caused by dissolution of amorphous components as well as interiors of the structural framework via an etching effect of F⁻ in acidic conditions. Furthermore, Yu et al. (2007) pointed out that the hydrogen bonding and surface absorption of F⁻ reduces attenuation of electrostatic repulsion, thus mobility of protonated TiO₆ octahedra and mass transfer from within the nanofungus structure to the bulk solution are significantly enhanced. In general, construction of the overall nanofungus-like morphology was driven by a coupled process of fluoride-mediated self-transformation and localized Ostwald ripening, where interior nanoparticles are selectively dissolved and new nanocrystals are crystallized and precipitated on the surfaces of the nanoflake stratification. On the other hand, NF5 possessed a solid, clean and smooth surface of nanoflakes as seen from Figure 6.2B. The absence of mesoporous intraparticle voids explains its lower specific surface area and macroporous structure. In the case of NF3 where coalescence of neighbouring short, broken nanofibres was evidenced in Figure 6.2D, specific surface area was recorded to be smallest among the 4 samples. Wu et al. (2007) reported such a trend as a result of crystal grain growth during coalescence of neighbouring nanoparticles, therefore notably reducing specific surface area of condensed titania films.

It should be noted that after 10 h, there was no discernible change in terms of morphology of the nanofungus-like structure, suggesting that a critical equilibrium state has been reached. Moreover, a lengthier hydrothermal duration beyond 10 h would result in poor mechanical strength of the film and weak adhesion to the Ti substrate. Due to natural capillary action and surface tensional forces, the overlaying film tends to curl and fracture into shards upon drying in air, thereby posing a significant problem for constructive applications. This may be engendered by anisotropic growth of nanoparticles in different crystallographic directions over

a prolonged crystallization reaction, which resulted in a thick depth of film. Henceforth, mechanical stability and adhesion to the underlying Ti substrate were compromised as a result of surface tension acting on the liquid-air interface.

From Figure 6.2E, it is palpable that the P25 coating consist of solid primary nanospherical particles measuring *c.a.* 25 nm each and the film coating recorded a specific surface area of 52.2 m²/g. Both figures were consistent to manufacturer's product specifications of commercial Degussa P25. Some remote clusters of aggregated P25 nanoparticulates were also observed among the nanospheres, which was expected after the repeated dipcoating and heat treatment process. The overall coating was uniform and well dispersed on both sides of the Ti foil.

6.2.3 Surface elemental analysis

XPS survey spectra of NF10 in Figure 6.3 manifest that the surface of the sample contains Ti, O and C elements. No other impurity elements, except C, are present. The small C 1s feature at 284.8 eV is in accord to residual carbonates and adventitious hydrocarbon following contamination from air exposure and the XPS instrument itself (Esaka et al. 1997, Lv et al. 2010). However, due to the low concentrations of residual F in the thoroughly-washed sample after calcination, EDX and the wide scan XPS analysis were unable to distinguish the origin of F signal. In order to decipher the F signal, a high resolution XPS spectrum of the F 1s region of NF10 was measured and presented in Figure 6.3. The high resolution scan evidenced the extent of HF etching that was consonant with XRD results, since NF10 was recorded to possess the smallest crystallite size (10.2 nm) among the other samples (Pan et al. 2008). The main feature from the high-resolution XPS spectra of the F 1s region was centred at 684.6 eV, which corresponds to the surface fluoride ($\equiv\text{Ti-F}$) originating from ligand exchange between F⁻ anions and surface hydroxyl group on TiO₂ (Lv et al. 2010, Minero et al. 2000). This is attributable to F⁻ ions physically adsorbed on the surface of TiO₂ (Yu et al. 2002). Contrary to nucleophilic substitution of F⁻ ions and titanium alkoxide during hydrolysis, absence of feature around 688.5 eV indicates that no signal of substituted F⁻ ions in

the lattice of TiO₂ was detected (Park and Choi 2004, Yu et al. 2002, Yu et al. 2009). Although, the atomic radii of F⁻ and O²⁻ ions are similar, the low relative concentration of F⁻ ions and hydrothermal temperature (150 °C) applied was insufficient to trigger substitution of F⁻ for O²⁻ in the lattice. Moreover, Yu et al. (2009) has also reported that surface fluorination of TiO₂ is more inclined to take place in an acidic hydrothermal environment thus preventing interstitial substitution of F⁻ for O²⁻ in the lattice of TiO₂. The hydrothermal environment, via an in-situ dissolution-precipitation process, has been reported to expedite crystallization of TiO₂ with reduced defects and impurities, also shown from the TEM and EDX results in Figure 6.5 (Ng et al. 2010, Yu et al. 2006). Henceforth, although the

Figure 6.3. XPS survey spectrum of NF10 sample and its corresponding high-resolution XPS spectra of the Ti 2p, O 1s and F 1s regions.

hydrothermal temperature was relatively low, the acidic hydrothermal synthesis conducted herein was able to yield surface-fluorinated anatase TiO₂.

Observations from high resolution XPS spectra of Ti 2p reveal 2 clear features, Ti 2p_{1/2} and Ti 2p_{3/2}, centred respectively at 464.2 eV and 458.5 eV. Based on previous literature and XRD results, these peaks originate from the presence of TiO₂ (Chen et al. 2007, Esaka et al. 1997, Guillot et al. 2002). No other peaks from partially oxidized Ti²⁺ or Ti³⁺ were detected. The curves of O 1s region can be deconvoluted into 2 peaks at 529.6 eV and 530.8 eV, both of which can be assigned to TiO₂ as well (Esaka et al. 1997, Guillot et al. 2002). The first O 1s peak is inherent from O atoms bounded to metals such as Ti (Atuchin et al. 2006), while the latter peak reveals possible surface contamination by hydroxyl species (Ng et al. 2010). It is noteworthy that the high resolution XPS spectrum of F 1s region was absent in samples NF5 and NF3, possibly due to the much shorter hydrothermal reaction time with HF precursor. Additionally, the high resolution scans of Ti 2p and O 1s spectra of NF5 and NF3 were very similar to NF10, further confirming the presence of pristine TiO₂, in the absence of fluoride.

6.2.4 Crystallographic phase and orientation

Figure 6.4 compares the XRD spectra of the 4 samples. As the film samples are embedded on a Ti foil, Ti (JCPDS no. 89-5009) peaks can be indexed to every spectrum. Well resolved and sharp peaks of TiO₂ body-centred tetragonal anatase phase (space group: *I4₁/amd* (141); measured lattice constants of $a_0 = 3.785 \text{ \AA}$ and $c_0 = 9.514 \text{ \AA}$; JCPDS no. 21-1272) are evidently present in all 4 samples, with 2θ values of 25.3°, 48.1°, 53.9°, 55.1°, indexed to the (101), (200), (105) and (211) peaks respectively. The anatase phase of TiO₂ has been reported to possess a higher photocatalytic efficiency as compared to the rutile phase (Park et al. 2000), largely because the rutile phase has a close packing structure, hence leading to its lower surface area (Kalyanasundaram and Gratzel 1998). Electron transfer within the anatase phase is also relatively faster than in the rutile phase, since the anatase phase possesses higher conduction-band edge energy (Wold 1993).

Figure 6.4. XRD spectra of the as-prepared photocatalysts.

It is apparent that the XRD peaks of NF3 are relatively weaker possibly due to short hydrothermal duration (3 h) which resulted in an incomplete growth process of the crystal structure. No peaks of the rutile or brookite phase were detected in the XRD spectrum of the hydrothermally-prepared samples of NF10, NF5 and NF3, indicating the high purity of anatase polymorph after calcination. The respective anatase crystallite sizes were calculated based on Scherrer Equation (Patterson 1939) and the P25 coated sample reveals an anatase crystallite size of *c.a.* 20 nm, consistent with reported literature (Bakardjieva et al. 2005). Calculated anatase crystallite sizes of the photocatalysts are tabulated in Table 6.1. Apart from recorded anatase phase, the rutile polymorph (JCPDS no. 21-1276) with a pronounced peak at $2\theta = 27.4^\circ$ of the (110) reflection, can be indexed from the XRD patterns of P25 coating on Ti substrate. This was expected since commercial P25 consists of a mixed phase of anatase and rutile in the ratio of *c.a.* 4:1 (Komaguchi et al. 2006). The enhanced intensity of the predominant (101) reflection centred at $2\theta = 25.3^\circ$ across all 4 samples, indicates a thermodynamically-stable (101) plane of the body-centred tetragonal anatase polymorph. In addition, it has also been widely reported that the (101) plane possesses the lowest surface energy and thus most energetically-stable (Yang et al. 2008).

Therefore, judging from intensity of the respective (101) peaks, the magnitude of crystallinity follow the order of NF10 > NF5 > P25 coating > NF3 and incidentally, it is consonant to the order of photocatalytic activity, suggesting that crystallinity of a sample is an essential property to its photoactivity. From the substantially higher and sharper XRD diffraction peaks of NF10, it can be observed that the longest hydrothermal duration (10 h) yielded highest crystallinity. This result re-establishes the fact that anatase crystallite growth was enhanced and lesser critical nuclei were formed in the presence of F⁻ ions, thus sufficient nutrients were available to promote anatase crystallization in the hydrothermal environment (Yu et al. 2002, Yu et al. 2007).

Figure 6.5. (A-B) Typical TEM micrograph of the ultrasonic-dispersed NF10 sample, Inset of (A): EDX spectra of NF10, (C-D) HRTEM showing crystal lattice orientation and interplanar distance, Inset of (D): Corresponding SAED pattern of NF10.

The TEM results show dispersed primary nanoparticles from sample NF10, after subjecting the sample to intensive ultrasonication in methanol prior to TEM analysis. Intraparticle voids between these aggregated nanoparticles create accessible hollow channels for increased surface area of reaction and optimized UV light penetration from the exterior. From TEM micrographs of Figure 6.5, it is apparent that the constituent components of the NF10's nanofungus structure reveal certain aggregated masses of nanoparticles with occasional arch-shaped and undulating, protruding features (Figure 6.5D) that were inherent from both the nanoflake and nanofungus-like structures – consistent to FESEM images. Fringe lattices were readily distinct from corresponding high resolution TEM (HRTEM) images of NF10, implying that the sample was well crystallized after calcination. From Figures 6.5C and 6.5D, it is evident that lattice characteristics reflect broken crystal fringe lattices to the edge of the sample, with presence of grain boundaries at overlapped interfaces of aggregated nanocrystallites – an indication of polycrystallinity. The inset of Figure 6.5D yields a selected area electron diffraction (SAED) pattern of NF10 which shows a series of concentric rings, thereby affirming the polycrystalline complex of NF10. The diffraction rings are composed of discrete spots which indicates that the matrix material consists of a small number of rather large crystallites, possibly from agglomerated crystallites. Applying the Bragg's Law and assuming that Bragg's angles are very small (*c.a.* 1°) in diffraction of fast electrons, the interplanar spacings and corresponding lattice planes diffracting the beam can be calculated and identified respectively (Ewald 1969). The four most distinct concentric diffraction rings, starting from the inner ring nearest to the centre electron beam, can be sequentially assigned to (101), (200), (105) and (211) diffraction planes of the body-centred tetragonal structure of anatase TiO_2 (Mao et al. 2006); a result in agreement with the observed XRD spectrum of NF10 (Figure 6.4). A parallel linear marking that measures an interplanar d-spacing of 0.352 nm between the planes of atomic lattices parallel to the (101) planes was highlighted in Figure 6.5C. This demonstrates a preferential crystallographic growth of nanoparticles along the (101) crystal plane with a preferred orientation in the [010] direction.

6.2.5 Optical spectrum analysis

Figure 6.6. UV-vis diffuse reflectance spectra of the as-prepared photocatalysts. Inset: Corresponding Kubelka-Munk transformed reflectance spectra.

Figure 6.6 presents the UV-vis diffuse reflectance spectra of the synthesized photocatalysts. The inset of Figure 6.6 is plotted by application of the transformed Kubelka-Munk theorem, of $(\alpha h\nu)^{1/2}$ against $h\nu$, and a straight line tangential to the vertical segment of the slope is extended to intersect the $h\nu$ axis (x-axis) in obtaining the indirect band gap (E_g) value of the samples (Serpone et al. 1995b). The synthesized photocatalysts show marked absorption at wavelengths shorter than 400 nm that can be ascribed to intrinsic bandgap absorption of pure anatase TiO₂. (Michalow et al. 2009). In comparison to the other samples, absorption edge of NF10 red-shifted in the bandgap transition, implying that F⁻ doping (observed from XPS results of NF10) results in narrowing of bandgap – a phenomenon that is widely agreed upon from literature (Nikazar et al. 2008, Pan et al. 2008, Yu et al. 2002, Yu et al. 2009). It is also worthy to note that among the 4 photocatalysts, NF10 exhibited the strongest absorption response across a UV-visible range of 250-650 nm. The observed trend may be attributed to enhanced light harvesting properties: high specific surface area associated with corrugated nanoflake surfaces

and accessible mesoporous voids of the hierarchical nanostructured framework permit light penetration and scattering within the interior of the catalyst morphology. The increased UV photons are expected to produce additional photogenerated electron-hole pairs and oxidizing radicals to participate in photocatalytic reactions, therefore improving photocatalytic activity of NF10 (Chen et al. 2011b). In addition, the steepest absorption band of NF10 among the 4 samples, as well as the presence of minor exciton peaks at around 320 nm, serve to suggest that the TiO₂ nanocrystals of NF10 are highly uniform in size and shape (Li and Chen 2011).

From Table 6.1, the indirect bandgaps of anatase-TiO₂ samples (NF10, NF5 and NF3) were in the range of 3.07 – 3.22 eV; consistent to reported bandgap values of bulk anatase TiO₂ (Michalow et al. 2009). Absorption edge of NF10 was shifted towards longer wavelengths, thus resulting in the decrease of bandgap energy due to the combined effects of several factors, namely, enhanced light harvesting abilities, presence of accessible mesopore voids and surface fluorination. Despite having the same anatase crystalline phase, it has been reported that morphology of semiconductor materials exercise a certain extent of influence on characteristic light absorption properties and can hence, alter the intrinsic electronic band structure (Gogate and Pandit 2004).

It is worth noting that absorption onset of the hydrothermally-prepared photocatalysts was observed at around 400 nm, similar to the P25 coated sample which was prepared without F precursor. This exemplifies the fact that absorption edge region was unaffected from the extent of surface fluorination (Yu et al. 2002). The result is also consistent with high resolution XPS spectra of F 1s region and further confirms that F element did not enter the lattice of TiO₂ (Yu et al. 2009).

6.2.6 Porosity and textural properties

Figure 6.7. Nitrogen adsorption-desorption isotherms of the as-prepared photocatalysts. Inset: Corresponding pore size distribution of NF10.

Figure 6.7 shows the N₂ adsorption-desorption isotherms of the photocatalysts. The isotherms of the scratched off P25 coated film and NF3 can be classified as Type III, with the adsorption and desorption curves coinciding, i.e. no hysteresis loop was observed. This would illustrate that the samples are non-porous, and are in good agreement with reported isotherm of P25; Degussa P25 is a type of non-porous powder formed by a mixture of anatase and rutile polymorphs (Agarwala et al. 2010, Raj and Viswanathan 2009, Wang et al. 2006a). Taking into account the absence of nitrogen adsorption at low pressures, it can be concluded that micropore contribution to the total pore volume was negligible for both P25 and NF3 samples. As seen from their isotherms, adsorption curves gradually increased in the middle-pressure region and exhibited an abrupt hike across the high-pressure region ($P/P_0 > 0.8$), hence adsorption behaviour of the samples can instead be attributed to capillary condensation and multilayer adsorption of nitrogen in macropores (Wang et al. 2006a). On the other hand, the adsorption-desorption isotherm of NF5 is categorized under Type II, indicative of a macroporous sample with unrestricted

monolayer-multilayer adsorption. The almost linear middle part of the curve represents the completion of monolayer coverage where multilayer adsorption would commence subsequently (Sing et al. 1985).

According to IUPAC classification (Sing et al. 1985), NF10 exhibited Type IV nitrogen isotherm with a Type H1 hysteresis loop, which is associated with the secondary process of capillary condensation and resulting in the complete filling of mesopores at $P/P_0 < 1$ (Chang et al. 2009b). As with most mesoporous TiO₂ samples, the adsorption of NF10 would proceed as multilayer adsorption initially before capillary condensation takes over as the dominant adsorption mechanism (Agarwala et al. 2010). With reference to the 3 other isotherms from Figure 6.7, adsorption trend of NF10 at low-pressure region appears to be similar initially, but with increase of relative pressure, uptake of N₂ increases sharply due to capillary condensation within the mesopores of NF10. The observed hysteresis loop between adsorption and desorption isotherms of NF10 was developed due to discrepancies in the rates of capillary condensation and evaporation. The two branches from the hysteresis loop are almost vertical and nearly parallel over a considerable range of gas uptake across a pressure region of $0.8 < P/P_0 < 0.95$ – characteristic of the H1 hysteresis loop (Sing et al. 1985). It can be observed from Figure 6.7 that the monolayer adsorption of mesoporous NF10 was only completed at a relative pressure of 0.7, implying abundance of mesopores within the NF10 sample. From the FESEM images, the primary nanoparticles were in uniform sizes of *c.a.* 20-40 nm, henceforth, mesoporosity of NF10 may be imparted by intraparticulate voids within pores of these nanoparticles, rather than the gaps between these particles (interparticulate voids). TEM results portend that the nanoparticles act as conjugate building blocks of the overall nanofungus morphology, henceforth the pores may be connected to other pores in forming an interconnected porous network.

Since the IUPAC guidelines recommend that the computation and interpretation of mesopore size distribution is valid only for Type IV isotherms (Sing et al. 1985), pore size analysis of only sample NF10 was plotted in the inset of Figure 6.7. The sharp peak centred at the pore diameter of 10 nm is in good agreement with

assertion that the mesopores were inherent from internal pores (intraparticle pores) of the primary nanoparticles, and that NF10 is characteristic of solids crossed by channels of uniform sizes and shapes. The narrow pore size distribution curve provides evidence that the sample contains mesopores ($2\text{ nm} < \text{pore size} < 50\text{ nm}$) with a high degree of uniformity and geometry.

It is generally accepted that an increased surface active sites offers positive effects to surface-based processes such as heterogeneous photocatalysis, by improving adsorption efficiency (Wu et al. 2005a, Wu 2007). Mesopores of NF10 aid in facilitating rapid diffusion and transport of molecules via an interconnected porous network, and enhance harvesting of UV light from a large surface area by multiple scattering within the porous framework (Wang et al. 2006b, Yu et al. 2007, Yu et al. 2003). It is noteworthy that in general, internal pores will be much smaller in size and volume than voids between particulates, but they often provide dominant contribution to the total surface area of the solid (Rouquerol et al. 1994).

Table 6.1. Physicochemical properties of the synthesized anatase nanofungus-like thin film photocatalysts.

Sample	Anatase Size ^a (nm)	Surface Area (m ² /g)	Average Pore Diameter (nm)	Total Pore Volume (cm ³ /g)	Band Gap (eV)	Film Weight ± 0.05 (mg/cm ²)	<i>k</i> (min ⁻¹)
NF10	10.20	102.1	7.5	0.38	3.07	1.182	0.053
NF5	11.92	63.2	12.3	0.67	3.12	1.097	0.018
NF3	11.04	34.5	25.6	0.19	3.22	1.073	0.008
P25 layer	21.21	52.2	11.8	0.245	3.17	1.127	0.013

^a Calculated based on the [101] peak for anatase, according to the Scherrer Equation.

The specific surface area and pore volume of the samples are tabulated in Table 6.1. Obviously, NF10 possessed the largest surface area of 102.1 m²/g, in comparison to

P25 (52.2 m²/g), NF5 (63.2 m²/g) and NF3 (34.5 m²/g). The active surface sites, related to BET surface areas, were important for the adsorption of pollutants and desorption of product molecules.

6.2.7 Dark adsorption

The adsorption of BPA over the synthesized photocatalysts without light irradiation was examined in detail. Difference in adsorption capacity can be correlated to the specific surface area and porosity of the photocatalysts. It is apparent from Figure 6.8A that the extent of BPA adsorption in dark was insignificant; less than 2% of BPA was removed after 60 min of dark adsorption. This can be attributed to a relatively high concentration of BPA (20 mg/L) applied in this study while only a small dosage of photocatalyst (*c.a.* 4 mg in 15 mL of aqueous BPA) was employed. BPA molecules, with respective pK_{a1} and pK_{a2} values of 9.6 and 10.2, consist of two negative oxygen atoms at the hydroxyl groups and four negative carbon atoms ortho to the phenolic group (Wang and Lim 2010). In this study, pH of BPA solution was not adjusted and hence maintained at *c.a.* 6.7 – 7.0. On the other hand, TiO₂ is known to be amphoteric in aqueous solution, and the point of zero charge for all the samples NF10, NF5, NF3 and P25 coating was found at *ca.* pH 5.7 using the Malvern nano-zs zetasizer. Thus the photocatalysts were negatively charged in BPA solution. At higher pH values ≥ 7 , deprotonation of BPA molecules to form BPA⁻ and BPA²⁻ ions are expected to occur, leading to repulsion from the negatively charged TiO₂ surface. In addition, it is noteworthy that highly oxidative peroxo complexes coordinated to Ti(IV) are formed from the reaction of Ti and precursor H₂O₂ (Tengvall et al. 1989). The abundance of such superoxide groups in TiO₂ resulted in an even more negatively charged photocatalyst surface, which readily repelled BPA molecules at pH 7 and leading to a poor adsorption affinity. However, the strong oxidative power of these complexes would accelerate the photodecomposition of organic compounds via its direct oxidation of BPA, or by surface-trapping photogenerated holes to produce reactive oxygen radicals (to be

discussed in the later section), which are primarily responsible in the oxidation of BPA.

Figure 6.8. (A) Change in BPA concentration over dark adsorption for 60 min, (B) Photodegradation of BPA (20 mg/L) in the presence of NF10, NF5, NF3, P25

coating and Ti substrate (Photolysis), obtained from an average of three runs, the error bar reflects root-mean square deviations of the values from each run, (C) Irradiation-time dependence of the relative concentration C/C_0 of BPA in solution over NF10 during repeated photooxidation experiments, from cycle 1 to cycle 10, under UV irradiation.

The Langmuir-Hinshelwood model was applied to model the rate of BPA disappearance (Wang and Lim 2010):

$$r = -\frac{dC}{dt} = k \left(\frac{KC}{1 + KC} \right) \quad (6.7)$$

where r is the rate of BPA disappearance (mg/(L.min)) and C (mg/L) is the BPA concentration. K represents the equilibrium constant related to monolayer adsorption and k is the reaction rate constant which represents a good measure of the samples' photoactivity.

$$\frac{1}{r_0} = \frac{1 + KC_0}{kKC_0} = \frac{1}{kK} \cdot \frac{1}{C_0} + \frac{1}{k} \quad (6.8)$$

The constant k and K were determined from a plot of $1/r_0$ versus $1/C_0$, with the slope equal to $1/(kK)$ and the intercept is $1/k$. To establish a better understanding of BPA adsorption behaviour on NF10, experiments of BPA photodegradation were carried out at different initial concentrations from 5 to 40 mg/L. The empirical and calculated results are shown in Table 6.2. Applying the kinetics results above results in the highest KC value of 0.14 at the initial stage of reaction when $C = C_0$. In addition, BPA concentration, C , would decline sharply as reaction proceeds with time due to ongoing photodegradation. Therefore in general, the KC term can be deemed negligible ($KC \ll 1$) and the kinetics equation can be further simplified to follow a pseudo first order expression in equation 6.9, which is in good agreement with the observed exponential trend from Figure 6.8B.

$$-\ln \frac{C}{C_0} = kt \quad (6.9)$$

where C is the BPA concentration at stated time, t , C_0 is the initial BPA concentration measured after 1 h of dark adsorption and t is the reaction time.

Table 6.2. Empirical data derived from photocatalytic degradation of BPA at different initial concentrations.

BPA initial concentration C_0 (mg/L)	Initial reaction rate constant, k (min ⁻¹)	Initial reaction rate, r_0 (mg/L.min ⁻¹)	Adsorption constant K (L/mg)	R^2
5	0.055	0.275		
10	0.053	0.53		
20	0.053	1.06	0.007	0.988
30	0.047	1.41		
40	0.045	1.8		

6.2.8 Photocatalytic evaluation

As shown in Figure 6.8B, photocatalytic degradation trend of BPA is presented as BPA concentration against irradiation time. NF10 recorded the highest photocatalytic activity (0.053 min⁻¹), by a factor of almost 3 times than that of NF5, which exhibited 2nd highest activity (0.018 min⁻¹). The P25 coated sample, due to its highly-crystallized state and large specific surface area in nanoparticulate form, recorded the next highest activity at 0.013 min⁻¹. NF3 yielded the lowest photocatalytic activity (0.008 min⁻¹), almost 6 times poorer than NF10. Due to the photostable nature of BPA, photolysis experiments carried out under UV-A irradiation for 60 min, only led to a negligible concentration reduction. Each Ti foil was weighed before and after synthesis to determine the respective mass of film developed on the foil. There was less than 10% variance in film weight across the 4 samples, therefore rational comparison of photoactivities between the photocatalysts can be established.

Figure 6.8C plots the photocatalytic removal percentage of BPA by sample NF10 over 10 repeated cycles of usage. After each photocatalytic reaction cycle of 75 min, the same sample of NF10 was transferred into a fresh (20 mg/L) solution of BPA to undergo reaction at identical conditions. It is apparent that 100% of BPA degradation was attained after 75 min of reaction and after 10 cycles of continuous usage, photocatalytic efficiency only dipped slightly to 98% but was conveniently restored to 100% after an additional 5 min of UV exposure to the sample. In addition, there was no distinctive change in the surface morphology of NF10 after 10 cycles of reuse, exemplifying the highly stable nanofungus-like structure.

The strong electronegativity of fluorine present on the surface of NF10 has been proven to trap photogenerated electrons and prevent recombination with photogenerated holes (Nikazar et al. 2008), therefore increasing production of free •OH which could explain its accelerated photocatalytic degradation of BPA. Minero *et al.* reported that fluorinated surface promotes generation of free mobile •OH while majority of •OH produced from pristine TiO₂ tend to remain adsorbed on the surface (Minero et al. 2000). Increased concentration of •OH generated by F-TiO₂ under UV illumination has also been confirmed by direct spin-trapping electron paramagnetic resonance measurements (Xu et al. 2008). Additionally, desorption and transport of •OH induced by surface fluorination can also enhance remote photocatalysis at the air/catalyst interface.

Deki *et al.* (1996) proposed that a highly porous photocatalyst will retard transportation of photogenerated intermediates within its pores and impede diffusion of intermediates into the bulk solution, thus increasing their likelihood of being further oxidized and mineralized. Henceforth, it is not unreasonable to postulate that the unique mesoporous nanofungus-like morphology with large surface area have contributed positively to enhancing photocatalytic activity. Furthermore, the corrugated and highly porous nature of NF10 provides access for UV light to scatter and irradiate inner folds of the thick and porous framework, generating higher concentration of active radical species in the process.

Figure 6.9. Photocatalytic degradation of AO7 upon the synthesized photocatalysts.

Photocatalytic activities of the prepared photocatalysts were also evaluated for degradation of AO7. As shown in Figure 6.9, the sample NF 10 exhibited highest rate of AO7 removal among the synthesized photocatalysts. AO7 was completely removed after 75 min of UV irradiation.

6.2.9 Photocatalytic reaction mechanisms

Upon UV activation of the photocatalyst, photoinduced holes (h^+), could react with adsorbed water or OH^- to produce hydroxyl radical ($\bullet OH$), and photogenerated electrons are quenched by surface chemisorbed oxidants (usually in the form of dissolved dioxygen), leading to the possible formation of other reactive oxygen species (ROS) such as superoxide radical ($O_2^{\bullet -}$) (Raja et al. 2005), singlet oxygen (1O_2) (Daimon and Nosaka 2007) and hydrogen peroxide (H_2O_2) (Stylidi et al. 2004). It has been reported that the holes, $\bullet OH$, dioxygen itself and the derived ROS could participate in the photocatalytic reactions (Fujishima et al. 2000). The formation and role of various oxidative species during the photocatalytic degradation of BPA were investigated indirectly with the use of appropriate scavengers of these species.

Figure 6.10. UV-photocatalytic degradation of BPA over NF10 under the interference of (A) DMSO, (B) KI, (C) BQ, (D) NaN_3 .

Dimethyl sulfoxide (DMSO) as an effective $\bullet\text{OH}$ scavenging agent, which has been commonly used to determine the generation of $\bullet\text{OH}$ in the advanced oxidation process (Abellán et al. 2009, Tai et al. 2004). The direct oxidation of DMSO by the photogenerated holes could be neglected because of the very weak adsorption of DMSO on the photocatalyst surface. Figure 6.10A shows that parallel to the increment of DMSO concentration, an obvious decline in BPA degradation was observed and the inhibitory effects were accentuated with increasing DMSO concentration. When 0.15 mM DMSO was added to quench free $\bullet\text{OH}$ in the system, photocatalytic efficiency was drastically impaired by 85.6% as the consumed $\bullet\text{OH}$ can no longer perform oxidative radical attack on BPA molecules. This is a clear indication that a high yield of $\bullet\text{OH}$ was generated in the UV/ TiO_2 system and exemplifies the pivotal role of $\bullet\text{OH}$ as the predominant species behind UV-

photocatalytic removal of BPA. Moreover, since •OH generated on fluorinated surfaces of TiO₂ (NF10) are more mobile than those generated on pristine TiO₂, inhibition of BPA degradation was more pronounced with the addition of DMSO, in comparison to scavengers of other reactive oxygen species (Park and Choi 2004).

Potassium iodide (KI), benzoquinone (BQ) and sodium azide (NaN₃) have been used as effective quenchers of hole (Ishibashi et al. 2000b), O₂^{•-} (Stylidi et al. 2004) and ¹O₂ (Bandara and Kiwi 1999, Zhang et al. 2009a) respectively. However, they might also interact with •OH. As shown in Figure 6.10B and C, removal of BPA under UV photocatalytic conditions was moderately suppressed by the introduction of KI and BQ. The presence of 5 mM of KI and BQ resulted in 30.4% and 21.2 % reduction of BPA removal efficiency within 60 min respectively. These results imply that photogenerated h⁺ and O₂^{•-} might contribute to the photocatalytic oxidation of BPA to some extent. It is however also plausible that the introduced KI and BQ competed with BPA molecules in utilizing •OH, hence engendering an overall decreased BPA degradation rate (Dijkstra et al. 2001a). NaN₃ exhibited marginal and negligible effect on photocatalytic removal of BPA (98.6% to 91.6%), even when added into the system at a high concentration (5 mM) in ensuring complete consumption of ¹O₂. The trend from Figure 6.10D shows that BPA removal rate was independent of NaN₃ concentration. This indicates that the role of ¹O₂ in the BPA degradation was insignificant. The decline of 7% could be due to presence of excess NaN₃ molecules in the system, subsequently inhibiting BPA adsorption and UV light exposure on the catalyst.

The experiments as mentioned in Section 6.2.7, 6.2.8 and 6.2.9 were conducted in triplicates. The range of results from the repeated tests was within a variation range of ≤ 5%, indicating the high confidence of experimental reproducibility.

6.3 Conclusion

In summary, a novel, hierarchical nanofungus-like anatase thin film photocatalyst was successfully synthesized via a facile one-pot hydrothermal method. The

superior photocatalytic performance over commercial P25-coated layers presents a significant advance as Degussa P25 has been widely regarded as a benchmark photocatalyst in heterogeneous photocatalysis. The well-established mesoporous system of NF10 with high surface area is favourable for the diffusion and adsorption of BPA molecules in achieving its high photocatalytic efficiency.

From the collective crystallographic data of XRD and TEM, we can conclude that the highly crystallized NF10 product can be categorized as the body-centred tetragonal anatase phase and is polycrystalline in nature. The typical HRTEM lattice images signify that the nanocrystallites of NF10 characterized a predominant crystallographic growth along the (101) crystal plane.

The porosity and textural properties of the sample play important roles in the interaction of photocatalyst with external fluid and solid media. Based on the preceding discussions, it can be concluded that the excellent photocatalytic performance of NF10 is derived from the synergistic effects of a unique hierarchical morphology, large BET surface area, mesoporosity, high crystallinity, extended optical absorbance and increased active surface sites available.

From BPA degradation trend in the presence of interfering scavenging species, it is manifest that $\bullet\text{OH}$ was the preponderant ROS in UV-photocatalytic oxidation processes of NF10. The photogenerated h^+ and $\text{O}_2^{\bullet-}$ might also involve in BPA degradation under UV irradiation, while the role of $^1\text{O}_2$ was trivial during photocatalytic degradation of BPA.

This one-pot hydrothermal synthesis method offers an easy method to prepare highly crystallized, mesoporous anatase TiO₂ photocatalyst which possessed excellent photocatalytic properties over commercial P25 titania film. The simple preparation strategy offers convenient scale-up for mass production. The nanostructures fabricated in this study were directly grown on the Ti substrate thus rendering ease of catalyst separation, recycle and reuse. Despite being used for 10 continuous cycles, photocatalytic efficiency of BPA did not deteriorate more than

2%. The experimental results obtained from this study indicated that the photocatalyst is effective in treating BPA contamination of wastewater. The conclusion of this chapter marked the successful development of a previously unreported fabrication of a novel nanofungus-like structure in the form of an immobilized anatase TiO₂ thin film grown from a Ti substrate. The photocatalyst was employed for degradation of a recalcitrant emerging organic contaminant, aligning to the research objectives of fabricating TiO₂ nanostructured photocatalyst and translating them for diverse environmental engineering applications in photocatalytic water treatment.

In view of the lengthier and substantially more complex methodology of synthesizing the nanotube and nanowhisker photocatalysts, in this chapter, a direct synthetic route of a one-pot hydrothermal method was developed to augment an able photocatalyst that is equally competent in photocatalytic oxidation of BPA, as demonstrated in the previous 2 chapters, with *E. coli* cells and AO7. Therefore in conclusion, a robust, immobilized TiO₂ photocatalyst that is capable of breaking down emerging organic contaminants like BPA was developed and optimized over the R&D work from the last 2 chapters.

CHAPTER 7 HYDROTHERMAL SYNTHESIS OF A HETEROJUNCTIONED $\text{TiO}_2/\text{SrTiO}_3$ EPITAXIAL FILM FOR PHOTOCATALYTIC HYDROGEN GENERATION

7.1 Introduction

The clean water technology of photocatalytic oxidation is based on the principal of photogenerated hole and electron pairs under light irradiation and activation of the photocatalyst. Over the last 3 chapters, recalcitrant, emerging contaminants and pathogens present in water bodies (AO7, *E. coli* cells and BPA) are treated and degraded via the photocatalytic generation of holes and the production of oxidative radicals over activation of the novel TiO_2 photocatalysts synthesized herein. However, free electrons that are produced from the photocatalytic reduction half-reaction are left unutilized by the existing system. To fully utilize both holes and electrons, it is necessary to investigate the use of the same semiconductor TiO_2 for energy generation such as H_2 from water which can be used to address energy demands of the water treatment processes.

Therefore, it is pertinent to develop a novel nanostructured TiO_2 photocatalyst that is not only capable of treating contaminants commonly present in today's waters for reuse, but is also able to generate sufficiently copious amount of H_2 gas through the photocatalytic reduction of hydroxide ions present in water. If these can be achieved, we are able to solve both clean water and energy supply problems concurrently by leveraging on the science behind photocatalytic nanotechnology.

Global climate change has prompted researchers from across the world to work together to search for new technologies espousing clean and renewable energy (Chornet and Czernik 2002, Overpeck et al. 1997, Thomas et al. 2004). Hydrogen is a very attractive fuel due to its zero carbon emission, high conversion efficiencies and recyclability. It offers immense potential as a clean and renewable energy source that is extremely important in alleviating the overdependence on fossil fuels.

Since the first report on water splitting using a TiO₂ photoelectrode by Fujishima and Honda (Fujishima and Honda 1972), photocatalytic generation of hydrogen has gained substantial research attention. Given its chemical stability and high photoactivity, TiO₂ is widely regarded as an efficient photocatalyst in the cleavage of H₂O into H₂ and O₂ gases (Kudo and Miseki 2009).

The issue of low quantum efficiency leading to poor photocatalytic activity is a common predicament with intrinsic semiconductors like TiO₂. It is caused by rapid recombination of photogenerated electron-hole pairs which greatly inhibits the generation of reactive radical species. It is well documented that charge separation of photogenerated electrons and holes is strongly required for a water splitting reaction than for photocatalytic reactions in presence of sacrificial reagents to inhibit recombination of charges (Kudo and Miseki 2009). Several attempts have been made to enhance photocatalytic performance by suppressing recombination of photogenerated electron-hole pairs via coupling of semiconductors such as CdS (Gao et al. 2009), Nb₂O₅ (Cui et al. 1995), SnO₂ (Liu et al. 2007), WO₃ (Kwon et al. 2000), CdSe (Harris and Kamat 2009) with TiO₂.

SrTiO₃ has a unique perovskite structure which is found to be favourable and catalytically active in water splitting reactions (Qin et al. 2007, Yang et al. 2006). It has been reported that SrTiO₃ is easily prepared by hydrothermal synthesis (Wrighton et al. 1976). Coupled with TiO₂ it would be effective at suppressing recombination of electron-hole pairs. To date, studies of TiO₂/SrTiO₃ coupled photocatalyst for hydrogen generation have not been reported.

Henceforth in this final chapter of research findings, a highly stable and well-coupled TiO₂/SrTiO₃ thin film with a novel nanostructure was prepared by a simple hydrothermal method. The synthesis process is facile, low cost and environmental-friendly. It simplifies the control of chemical homogeneity and purity, as well as tunable morphology and composition of the material. In addition, the as-synthesized TiO₂/SrTiO₃ photocatalyst in the form of thin film provides ease of separation and reuse from the bulk aqueous phase following the heterogeneous reaction. As

elucidated from the results, synergies leveraged from heterojunctions of TiO_2 and SrTiO_3 resulted in high efficiencies of water splitting, therefore photocatalytic generation of hydrogen gas was substantially increased.

7.2 Results and discussion

7.2.1 Characterization studies

7.2.1.1 Reaction Pathways

Using Ti foil and $\text{Sr}(\text{NO}_3)_2$ as precursors for titanium and strontium respectively, $\text{TiO}_2/\text{SrTiO}_3$ heterojunctions were created in the form of a thin film sample. The FESEM images shown in Figure 7.1 depict the structural evolution from the titanate nanowires to the respective TiO_2 , heterojunctioned $\text{TiO}_2/\text{SrTiO}_3$, and SrTiO_3 forms. Figure 7.2 shows the XRD patterns of the starting materials and the hydrothermal products of the thin films prepared under different conditions. The surface of Ti foil was first acid-etched and oxidized in the presence of F^- ions from HF in a hydrothermal reaction, forming a thin film of TiO_2 over the foil (Pan et al. 2008). The TiO_2 film then underwent a wet corrosion, alkali treatment process in 10 M NaOH at 180 °C. The strong alkali broke some of the Ti-O-Ti bonds from the starting materials to form $[\text{Ti}(\text{OH})_6]^{2-}$ monomers which are unstable in a saturation state at hydrothermal conditions. The monomers then combine to form nuclei which grow in size to achieve stability. As the growth of these nuclei continues beyond the critical nuclei size, thin nanosheets composed of layered unit cells are formed and difference in growth rate of the nanosheets along various crystallographic directions lead to formation of the one-dimensional (1D) $\text{Na}_2\text{Ti}_3\text{O}_7$ nanowires (equation 7.1) (Wang et al. 2008). As evidenced from Figure 7.1A, the diameter of a single nanowire is about 30 nm but 2 or more nanowires tend to merge to form larger nanowires with diameters of about 50-100 nm.

Figure 7.1. FESEM images of the respective thin films grown on Ti substrates. Appended insets: Corresponding high magnification FESEM image of the respective samples. (A) $\text{Na}_2\text{Ti}_3\text{O}_7$ nanowires. (B) Anatase TiO_2 nanowires. (C) Heterojunctioned $\text{TiO}_2/\text{SrTiO}_3$ nanowires and nanocubes. (D) Tausonite SrTiO_3 nanocubes.

Figure 7.2. X-ray diffraction patterns of the respective thin film photocatalysts and their precursors on a Ti substrate.

The Na^+ ions of the $\text{Na}_2\text{Ti}_3\text{O}_7$ nanowires then underwent an ion exchange process with H^+ by washing the samples in 0.1 M HCl, where residual Na^+ ions are replaced by H^+ ions to form protonated trititanate, $\text{H}_2\text{Ti}_3\text{O}_7$ (equation 7.2); as verified from the XRD peaks in Figure 7.2C. The dilute acid washing procedure is repeated until the Na peak from the corresponding EDX spectrum of the protonated titanate has subdued and disappeared. The basic framework of $\text{H}_2\text{Ti}_3\text{O}_7$ is built from a structural unit of three edge-sharing TiO_6 octahedrons that are arranged in a line per layer and the diffraction peak of $\text{H}_2\text{Ti}_3\text{O}_7$, observed around 10.0° , corresponds to the interlayer separation of 0.98 nm between the TiO_2 nanosheets. These layered titanate nanowires are composed of scrolled ultrathin titania sheets, henceforth cations such as H^+ ions, can easily diffuse into the interlayers of the TiO_2 sheets. The low concentration of HCl is pertinent in preserving the fibrous morphology of $\text{Na}_2\text{Ti}_3\text{O}_7$. It is to be noted that there were no apparent morphological discrepancy between the sodium and protonated titanate nanowires. Surface protonation of $\text{Na}_2\text{Ti}_3\text{O}_7$ to derive $\text{H}_2\text{Ti}_3\text{O}_7$ is imperative prior to the subsequent hydrothermal reaction, as the remnant Na^+ ions present at the interlayers of the titanate nanowires would suppress growth of TiO_2 and SrTiO_3 crystals.

The protonated titanate nanowires are thermodynamically metastable, thus only a small amount of energy (in this case, a short duration of low temperature hydrothermal reaction) is required to convert into TiO_2 . Contrary to the hetero and tausonite samples, the anatase sample was prepared by identical hydrothermal conditions but without addition of Sr precursor. The EDX spectra from the inset of Figure 7.4D revealed that the anatase sample composed of solely Ti and O elements. The scrolled nanowires separated by H^+ ions are formed by wrapping the [100] plane of titanate (Chen et al. 2002). The titanate nanowires are transformed into the anatase polymorph by rearrangement of its crystal layers in a controlled

manner, forming the resultant overlapping titania nanowires (Gateshki et al. 2007). The XRD peaks of TiO_2 as observed from Figure 7.2D and 7.2F, show good agreement with the anatase (JCPDS Card No: 21-1272), since the anatase phase is more easily obtainable from the titanate at mild conditions as compared to the rutile phase (Yin et al. 2005).

To form the hetero sample's unique morphology, protonated titanate then underwent a hydrothermal treatment with introduction of a Sr precursor. Sr^{2+} ions, having an ionic radii of 0.11 nm, diffused easily into the large interlayer space (0.98 nm) of the scrolled titanate nanowires and reacted with the TiO_6 octahedral layers (Miyauchi 2007, Wang et al. 2007). The process is advocated by negatively-charged surfaces of the titanate nanowires thus developing positive affinities to cations like Sr^{2+} and H^+ (Tokudome and Miyauchi 2004). As evidenced from Figure 7.1C, protons at interlayers of the titanate nanowires are exchanged with Sr^{2+} , forming in-situ SrTiO_3 while retaining the fibrous structure of the protonated nanowires. The XRD peaks of SrTiO_3 from Figure 7.2E and 7.2F show excellent agreement with the tausonite phase (JCPDS Card No: 73-0661). As shown from the FESEM image of Figure 7.1D, the SrTiO_3 compound was made up of nanocubic structures that tend to coagulate and a typical nanocube has an average width of 50 nm on each side. By cross-sectional SEM imaging (Figure 7.3), the typical thickness of a catalyst film on the Ti foil is c.a. 8 to 10 μm . It is noteworthy that the perovskite nanocubes were endowed with clean surfaces which are deemed to be desirable for building functional components and conducting ferroelectricity in nanoscale levels (Liu et al. 2006).

Figure 7.3. Cross-sectional FESEM image of the detached heterojunctioned $\text{TiO}_2/\text{SrTiO}_3$ film without Ti substrate.

Figure 7.4. Typical TEM micrographs of the TiO_2 anatase sample. (A) TEM of the TiO_2 nanowires. (B) HRTEM as enlarged from (A). (C) TEM image of the peripheral nanowires. Inset: Corresponding SAED image of the polycrystalline TiO_2 . (D) HRTEM of the peripheral polycrystalline nanowires enlarged from (C), showing uncrystallized edge boundaries and amorphous crystallites at the

interphase of broken lattices. Inset: Corresponding EDX spectra exhibiting elemental presence of solely Ti and O.

Figure 7.5. Typical TEM micrographs of the SrTiO_3 tausonite sample. (A) and (E) TEM overviews of the aggregations of SrTiO_3 nanocubes. (B) HRTEM enlarged from (A). (C) and (F) HRTEM of areas magnified from (E). (D) Enlarged HRTEM of an area from (A). Inset: Corresponding SAED image of the monocrystalline SrTiO_3 . (G) Corresponding EDX spectra with peak signals of Sr, Ti and O.

To further elucidate on the crystal structures of the as-prepared samples, TEM analysis was carried out for the hetero, anatase and tausonite samples. The TEM images from Figure 7.5 clearly reflect the microstructures of cubic strontium titanate and the uniform fringe lattice spacings of 0.276 nm can well be indexed to the predominant [110] direction. From the respective HRTEM images provided, interplanar fringe spacings normal to the axis of crystal grains were distinctly observed and measured to be 0.352 nm for the anatase sample and 0.276 nm for the tausonite sample, suggesting that the various nanocomposites are well crystallized under low temperature hydrothermal synthesis albeit annealing not carried out. This observation is consistent to the XRD spectra obtained; the main [101] peak of the

anatase sample is centered at a d-spacing of 0.352 nm, while the predominant [110] peak of the tausonite sample is centered at 0.276 nm. Apart from the peaks attributed to the Ti substrate, both peaks were noted to characterize the highest intensity among other peaks on the XRD spectra. Based on Figure 7.5, continuous lattice fringes were observed in the HRTEM images and grain boundaries were not present, denoting single crystallinity of the tausonite nanocubes. In the case of anatase nanowires from Figure 7.4, HRTEM images reflect broken crystal lattice fringes to the edges of the sample with presence of grain boundaries at its interfaces, thereby suggesting polycrystallinity.

Figure 7.6. Typical TEM micrographs of the heterojunctioned $\text{TiO}_2/\text{SrTiO}_3$ sample. (A) TEM image showing aggregated nanocubes with adjacent and embedded nanowires. Inset: Corresponding EDX spectra illustrating the presence of Sr, Ti and O elements. (B) HRTEM of the nanowires, as enlarged from (A) and identified as anatase TiO_2 . Inset displays the corresponding SAED pattern of the polycrystalline nanowires. (C) HRTEM of the nanocubes, as enlarged from (A) and identified as tausonite SrTiO_3 . Inset shows the corresponding SAED image of the

monocrystalline nanocubes. (D) High magnification of HRTEM from delineated area of (C).

The HRTEM image of Figure 7.6 indicates that the crux of $\text{TiO}_2/\text{SrTiO}_3$ composites present in the hetero sample was overlapped with several sets of mixed fringe lattices, suggesting presence of mixed phases of TiO_2 and SrTiO_3 . Likewise, the respective interlayer distances are consonant to the energetically stable crystal facets of TiO_2 (101) and SrTiO_3 (110). The SrTiO_3 nanocubes were grown in conjunction with the TiO_2 nanowire matrix, thus forming a tight and compact heterojunction structure between the 2 nanocrystals. By comparing intensities of the tausonite and anatase XRD peaks from Figure 7.2F, it was noted that composition ratio of SrTiO_3 and TiO_2 present in the hetero sample was relatively similar.

As observed from Figure 7.7, the extension of hydrothermal reaction time from 2 h (hetero) to 5 h (tausonite) witnessed a palpable increase in the amount of tausonite nanocubes on the surface of the embedded titania nanowires. At $t = 4$ h, the anatase nanowires were almost entirely coated with agglomerations of tausonite nanocubes, and at $t = 5$ h, the titania nanowires were dissolved and only SrTiO_3 nanocubes were existent in the tausonite sample. The corresponding EDX spectrum is very similar to that of the tausonite sample, except that the Sr elemental composition was relatively lesser due to the presence of remnant TiO_2 , yet to be converted to the tausonite phase. Apart from SrTiO_3 (tausonite) and TiO_2 (anatase), no other phases were found in the hetero sample, indicating no perceivable chemical reaction between SrTiO_3 and TiO_2 . The unique morphology obtained was postulated to be a result of a dissolution-precipitation mechanism (Tsumura et al. 2009). After a H^+ ion-exchange process, the protonated titanate nanowires were partly dissolved in the alkaline solution (induced by the introduction of NH_4OH) to react with Sr^{2+} ions (from $\text{Sr}(\text{NO}_3)_2$) present in the aqueous phase. Via a direct hydrothermal treatment, the protonated nanowires were converted to TiO_2 under autoclaving conditions (Bavykin et al. 2006). As each TiO_2 particle is a potential nucleation site of SrTiO_3 , the reaction took place at the solid-liquid interphase of the titania nanowires, leading to nucleation and growth of nanocubic SrTiO_3 crystals at close proximity to

Figure 7.7. FESEM images illustrating the morphological transition over a hydrothermal reaction of $\text{H}_2\text{Ti}_3\text{O}_7$ film in NH_4OH and $\text{Sr}(\text{NO}_3)_2$ at 140°C . Reaction time ranged from 1 h to 8 h. (A) 1 h, (B) 2 h, (C) High magnification image of (B), (D) 4 h, (E) 5 h, (F) 8 h.

and on the surface of the fibrous TiO_2 (Qi et al. 2004, Walton et al. 2003). The classical LaMer model can be applied to elucidate the growth of SrTiO_3 nanocubes by the dissolution-precipitation mechanism: The nucleation and growth of SrTiO_3 crystallites from an existing nucleus will proceed until its concentration is reduced to the equilibrium solubility, so that the amount of product will be the same as the amount of nucleus present (Lamer and Dinegar 1950). As observed from Figure 7.7,

no discernible discrepancy was noted in terms of the size of SrTiO_3 nanocubes obtained throughout the hydrothermal reactions from 1 h to 8 h; thus the reaction mechanism proceeded in good agreement with the LaMer model. It is deciphered that the equilibrium nanostructure of the hydrothermal-synthesized SrTiO_3 is of the nanocubic form, i.e. an extended hydrothermal reaction of SrTiO_3 beyond 5 h will not exhibit further structural changes.

Figure 7.8. Photoluminescence spectra of the as-prepared photocatalysts. The adventitious peak centred around 375 nm is attributed to the double-sided tape adhered on the film sample during PL analysis.

The photoluminescence (PL) emission spectrum is commonly used in evaluating the extent of transfer and separation, as well as trapping of charge carriers within an activated semiconductor photocatalyst. The transfer behaviour of the photoinduced electron and hole pairs can also be investigated as the recombination of the free charges contribute significantly to emission signals of the PL spectra. Figure 7.8 depicts the PL spectra of the as-prepared photocatalysts and all 3 spectra comprise broad and structureless luminescence bands. The observed emissions can be assigned to the radiative recombination of self-trapped exciton luminescence due to its characteristic bands. It has been reported that the surface states of the

photocatalyst, such as defect sites (or recombination centres) and oxygen vacancies that promote photogenerated electrons and holes, are responsible for the observed luminescence (Zhang et al. 2000). On the basis of the PL results, one can conclude the successful hybridization of the tausonite nanocube and anatase nanowire, resulting in the formation of a synergistic heterojunction between the 2 semiconductor interphases. The potential difference between the 2 hybridized compounds facilitated migration of charge carriers from SrTiO_3 to TiO_2 and reduced the phenomenon of charge recombination, which was evidenced by the weakest PL signal from the hetero sample.

From the respective insets of Figures 7.6B and 7.6C, the selected area electron diffraction (SAED) patterns portray a concentric spherical ring pattern for the anatase nanowires, indicating polycrystallinity; while the tausonite nanocubes yielded a regular spotted pattern which implies that the precipitated nanocubes are single crystals. In an equilibrium state, SrTiO_3 tausonite crystallites bear the structure of nanocubes, which are formed via aqueous diffusion of ionic species at hydrothermal conditions (Mao et al. 2003). The aggregation of tausonite nanocubes is a testimony of van der Waals forces acting on the particles leading to formation of primary particle clusters.

7.2.1.2 XPS and Band Gap configurations

The X-ray photoelectron spectroscopy technique was employed to investigate the surface chemical compositions and electronic structure of the as-prepared samples. The XPS survey spectra as presented in Figure 7.9 confirm the existence of Sr, Ti and O in the samples of hetero and tausonite, while only Ti and O in the anatase sample. No other impurity elements, except C, are present. The small C peak, corresponding to carbonates and adventitious carbon, is attributed to contamination caused by air exposure. Through XPS surface elemental analysis, the relative Sr/Ti atomic ratio of the hetero sample was detected to be 1.47. It suggests that the near-surface region of heterojunctioned thin film is Sr-rich; largely due to the in-situ

Figure 7.9. XPS surface scan spectra of the respective photocatalysts

Figure 7.10. 3-D crystal structure simulation using “ball-and-stick model”. Green spheres represent Sr atoms, red – O atoms, pink – Ti atoms. (A) 3-D perspective illustration of the cubic perovskite SrTiO_3 model. (B) The same SrTiO_3 molecular structure model when viewed from the [001] direction. (C) Cubic SrTiO_3 viewed

from the [111] direction. (D) Cubic SrTiO_3 viewed from the [101] direction. (E) 3-D perspective illustration of the tetragonal TiO_2 anatase model.

surface nucleation of SrTiO_3 nanocubes on the underlying TiO_2 nanowires. The higher Sr atomic concentration is explicable when the molecular structure of the perfect cubic perovskite structure of SrTiO_3 is scrutinized in various crystallographic directions as from Figure 7.10A-D. From the “ball-and-stick model” of the cubic SrTiO_3 , it is interesting to note that regardless of which crystallographic direction the model is being viewed from, or which symmetrical (001) facet of the cubic crystals is being exposed, a greater detection of Sr as compared to Ti, is always manifest. Contrary to the TiO_2 anatase model where Ti atoms are situated at the 8 corners of a tetragonal model, Sr atoms are bounded at each of the 8 corners of a cubic SrTiO_3 model, while its Ti atom is embedded within the external framework of the cube, hence attributing to the larger Sr/Ti atomic ratio by XPS analysis, which detects only the top 3-5 nm of the material analyzed. Another possible reason for surface Sr/Ti ratio to vary significantly from stoichiometric ratios could be due to the presence of carbon and hydroxyl groups on the surface (Yang 1999).

Figure 7.11. Comparison of high-resolution XPS spectra of Sr 3d peaks, Ti 2p peaks and O 1s peaks of the respective photocatalysts.

As shown in Figure 7.11, high-resolution XPS spectra of Sr 3d and Ti 2p for both hetero and tausonite samples were found to match very well, inferring that the

chemical states of Sr and Ti on the surface of these 2 samples are the same. Therefore, one can conclude that the existence of anatase nanowires did not change the chemical state of Sr in the hetero sample. This is consonant to the inference made above that the observed nanocubes in the hetero sample are SrTiO_3 crystallites, identical to those observed in the tausonite sample. The curves of Sr 3d region can be deconvoluted into two peaks for Sr $3d_{5/2}$ and Sr $3d_{3/2}$, located at around 133.0 eV and 135.0 eV respectively. The peak at 133.0 eV is in accordance with those reported for SrTiO_3 perovskite material, and the higher energy peak can be attributed to SrO complexes (Vasquez 1991, Yang 1999). Observations of the Ti 2p spectra from the 3 samples show that apart from peaks arising from SrTiO_3 and TiO_2 , no other peaks from partially oxidized Ti^{3+} , Ti^{2+} were detected. Two peaks of O 1s, centered at around 529.6 eV and 531.0 eV, can be observed in all 3 samples. The first peak is inherent from O atoms bounded to metals such as Ti and Sr (Atuchin et al. 2006), while the latter peak reveal possible surface contamination by hydroxyl species. One additional peak at 532.5 eV exists only in samples containing SrTiO_3 , which may be attributed to presence of surface carbonate species (Yang 1999).

The Kubelka-Munk function was applied to convert diffusive reflectance measurements into the equivalent absorption coefficients (Serpone et al. 1995b).

$$\alpha = \frac{(1 - R)^2}{2R} \quad (7.5)$$

where α is optical absorption coefficient neat the absorption edge for indirect interband transitions, R is the reflectance of the semiconductor, $R = 10^{-A}$, A is the an optical absorbance.

$$\alpha h\nu = C_1 (h\nu - E_g)^2 \quad (7.6)$$

$$h\nu = \frac{1240}{\lambda} \quad (7.7)$$

Where C_1 is the absorption constant for an indirect transition, $h\nu$ is the photon energy, E_g is the indirect bandgap energy (eV) and λ is wavelength (nm).

Figure 7.12. UV-vis diffuse reflectance spectra of the as-prepared photocatalysts. Inset shows the corresponding Kubelka-Munk transformed reflectance spectra.

The inset of Figure 7.12 is plotted using $(\alpha h\nu)^{1/2}$ against $h\nu$, and the vertical segment of the spectra is extended to intersect the $h\nu$ axis (x-axis) in obtaining the indirect band gap (E_g) value of the measured sample. The tausonite sample characterized an indirect bandgap of 3.75 eV and the indirect bandgap recorded for the hetero sample of $\text{TiO}_2/\text{SrTiO}_3$ was 3.47. As apparent from Figure 7.12, the presence of TiO_2 in the hetero sample contributed to a red shift of absorption edge, narrowing the bandgap of the tausonite sample. It is evident that formation of $\text{TiO}_2/\text{SrTiO}_3$ heterojunctions has modified the electronic structures of the pristine semiconductors. On the other hand, band gap of the anatase sample was obtained to be 3.25, consistent with reported literature of titania (Michalow et al. 2009).

7.2.2 Hydrogen Generation

Figure 7.13. GC spectra of gas product collected from the photocatalytic reaction.

Figure 7.13 presents a typical GC analysis spectrum of the gas collected from the photocatalytic reaction. Owing to the limitation of off-line GC analysis, air trespass is inevitable, leading to viewable peaks of O_2 and N_2 . However, since the ratio of detected O_2 and N_2 corresponded exactly to that of ambient surrounding air and neither O_2 nor N_2 is produced during the photocatalytic reaction, both gases were deemed adventitious and the concentration of H_2 was calculated without their due consideration. Note that helium was used as the carrier gas; hence H_2 peak is negative and relatively small. However, after calibration using the standard H_2 gas, H_2 was identified as the core component in the collected gas.

As illustrated from the results of Figure 7.14, hydrogen generation of the hetero sample was evidently more superior as compared to the 2 pristine samples of SrTiO_3 and TiO_2 . Blank photolysis experiments that were carried out under the same irradiation intensity revealed negligible H_2 generation.

Figure 7.14. Photocatalytic hydrogen evolution over an irradiated surface area of 18 cm^2 per photocatalyst. Inset: Rate of hydrogen evolution from the respective photocatalysts over 300 min.

Figure 7.15. Schematic diagram illustrating the respective band positions (pH 1) and spatial separation of photogenerated interparticle charges during photocatalytic activation of the heterostructured $\text{TiO}_2/\text{SrTiO}_3$ catalyst, with a negative shift in its Fermi level.

The presence of TiO₂/SrTiO₃ heterojunctions enhances the photocatalytic activity by a mechanistic separation of photogenerated electrons and holes as illustrated in Figure 7.15. Based on the calculated band gap of the as-synthesized TiO₂ (3.25 eV) and SrTiO₃ (3.75 eV), the supplied UV irradiation with a primary wavelength of 254 nm is suffice in activating both semiconductors. Upon UV irradiation, electrons from the valence bands (VB) of TiO₂ and SrTiO₃ were excited and subsequently promoted to their corresponding conduction bands (CB), leaving behind holes which are consumed by the sacrificial reagent (Jin et al. 2007). Due to the lower (more positive) conduction band level of TiO₂ by 200 mV (Burnside et al. 1999, Niishiro et al. 2005, Wrighton et al. 1976), the promoted electrons from the CB of SrTiO₃ are then transferred to the CB of TiO₂, and the accumulation of excess electrons in TiO₂ causes a negative shift in its Fermi level. From a previous photocatalytic study involving titanium oxide-perovskite type composite particles, it was inferred that the electrons flow to the CB of TiO₂ through a pn-junction, an interface where the p-type acceptor perovskite compound (SrTiO₃) and n-type TiO₂ connect electronically (Omata and Otsuka-Yao-Matsuo 2003, Ueda and Otsuka-Yao-Matsuo 2004). The charge flow through the pn-junction may induce an efficient spatial separation of the photogenerated interparticle charges and form highly reduced states of TiO₂/SrTiO₃ that are stable even under oxygen saturated conditions, thus improving photocatalytic water splitting performance (Jin et al. 2007, Omata and Otsuka-Yao-Matsuo 2003). The Fermi level of the undoped, intrinsic n-type TiO₂ semiconductor lies at the minimum of its CB range and coupling of SrTiO₃ elevates this Fermi-energy level to assume a more negative redox potential against H⁺/H₂ (0 V vs. NHE), resulting in an overall higher work function for water reduction reactions (Chakraborty et al. 2003, Jin et al. 2007, Kudo and Miseki 2009). The negative shift in Fermi level is indicative of a large accumulation of electrons at the heterojunctions of TiO₂ and SrTiO₃, reflecting a decrease in recombination of charges (Zhang et al. 2010). For efficient water splitting to produce H₂, the CB level should be sufficiently higher (more negative) than the reduction potential of H₂O, and the theoretical minimum band gap for water splitting was calculated to be 1.23 eV (Kudo et al. 2004). It is expected that

the $\text{TiO}_2/\text{SrTiO}_3$ heterojunctions can optimize light harvesting abilities with the incorporation of anatase and tausonite crystallites. With an effective charge separation at the heterojunctions, as well as a highly negative redox potential, hydrogen generation rate of the hetero sample was discovered to be highest among the 3 samples, at $386.6 \mu\text{mol/h}$; while the tausonite and anatase samples respectively yielded an average rate of 200.4 and $85 \mu\text{mol/h}$ across a 5 h reaction. Apparent quantum yield of the respective as-prepared samples was calculated based on the following equation.

$$\text{Apparent Quantum Yield} = \frac{\text{Number of H}_2 \text{ molecules evolved} \times 2}{\text{Number of incident photons}} \quad (7.8)$$

Table 7.1. Photocatalytic hydrogen production and apparent quantum yield of the as-prepared samples over a 5-h reaction.

Photocatalyst	Indirect Bandgap [eV]	H ₂ Production Rate [$\mu\text{mol/h}$]	Apparent Quantum Yield [%]
Hetero	3.47	386.6	42.6
Tausonite	3.75	200.4	22.2
Anatase	3.25	85.0	9.4

It is apparent from Table 7.1 that both photocatalytic hydrogen production and apparent quantum yield figures attest to the reported trend that a lower intensity of the PL spectra leads to higher quantum efficiencies and higher photocatalytic activity (Liu et al. 2007, Yu et al. 2002, Zhang et al. 2000). On the contrary, the low quantum yield of intrinsic TiO_2 has been a widely reported obstacle hampering practical applications (Tamura et al. 1977), and is primarily caused by the accentuated recombination of photogenerated electrons and holes (Yang et al. 1997). Previous research work has proven that the perovskite cubic SrTiO_3 offers a greater potential than pristine TiO_2 in terms of photocatalytic formation of hydrogen

and oxygen, and this is consonant with the results presented in Figure 7.14 (Qin et al. 2007, Yang et al. 2006).

The experiments of photocatalytic H_2 generation using the as-prepared photocatalysts were carried out triplicates. The range of results from the triplicate tests was within a variation range of $\leq 5\%$, suggesting the high confidence of experimental reproducibility. Please refer to Appendix (II) for the calculation of apparent quantum yield of the as-prepared samples for H_2 production.

7.2.3 Photocatalytic degradation of AO7

Figure 7.16. Photocatalytic degradation of AO7 upon the prepared photocatalysts.

The photocatalytic activities of the prepared photocatalysts were also investigated for AO7 degradation. As shown in Figure 7.16, the three photocatalysts exhibited high efficiencies for AO7 degradation because of their highly ordered nanostructures. In particular, the heterojunctioned $\text{TiO}_2/\text{SrTiO}_3$ thin film showed the enhanced activity for AO7 degradation, owing to the more efficient separation of charge carriers in the system.

7.3 Conclusion

A heterojunctioned TiO₂/SrTiO₃ thin film was successfully synthesized via facile hydrothermal techniques. The SrTiO₃ nanocubes were grown from underlying TiO₂ nanowires by an in-situ dissolution-precipitation pathway and the growth mechanism of the nanocrystallites was in good agreement with the classic LaMer model. Experimental results have revealed that the coupling of TiO₂ and SrTiO₃ bestowed positive energetics and synergies in attaining spatial delocalization of photogenerated electrons and holes. The negative shift in Fermi level has also reinforced reduction of hydroxide ions, thus increasing hydrogen gas production over pristine TiO₂ and SrTiO₃. The unique heterojunctions formed at interphases between the 2 dissimilar semiconductors of unequal bandgaps aid in facilitating interfacial electron transfer and act as potential traps for the photogenerated electrons. Subsequently reaction lifetimes of electron and hole pairs are prolonged.

This work is the first to report the successful photocatalytic cleavage of water using a hybrid TiO₂/SrTiO₃ thin film. Results have shown remarkable efficiency in hydrogen generation, primarily attributed to the unique TiO₂/SrTiO₃ heterojunctions.

CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

This PhD work presented the development of immobilized TiO₂-based nanostructured epitaxial film photocatalysts to treat recalcitrant, emerging contaminants and pathogens that are commonly present in water bodies (AO7, *E. coli* cells and BPA) with the production of photogenerated holes and oxidative radicals. The later phase of this research work encompasses utilization of free electrons that are produced from the photocatalytic reduction half-reaction. The electrons are harvested for the reduction of hydroxide ions present in the treated water to generate hydrogen gas, a source of clean energy.

The controllable fabrication of immobilized TiO₂-based nanostructured epitaxial photocatalysts developed from this research work, represent a significant advance in environmental remediation and green energy (hydrogen) production through photocatalytic water splitting. This PhD work is a culmination of multidisciplinary sciences - encompassing the assimilation of nanomaterials chemistry to engineer various dimensionalities and morphologies of TiO₂ in manipulating crystallographic and photocatalytic properties, and thus optimizing efficiencies in photocatalytic oxidation and water splitting reactions. Hierarchical nanostructures provide large interfacial areas and channels for excited electrons to effectively dissociate. This would effectively reduce the phenomena of promoted electrons from the valence band to recombine with photogenerated holes, causing impediment in production of reactive radical species and thus leading to low quantum efficiency, which is another paramount issue restraining the engineering potential of TiO₂ in practical applications.

The disinfection efficacy of surface water using anodic TiO₂ films was investigated in the first part of this research work. The as-prepared photocatalyst demonstrated

excellent photocatalytic disinfection of *E. coli* cells. The free-standing and self-organized TiO₂ nanotube arrays are synthesized via a facile electrochemical anodization method, prior to calcination. Over 95% of the initial 10⁶ cpu/mL *E. coli* cells were inactivated within 50 mins of UV-A photocatalytic disinfection, despite influence from various ionic species and organic compounds commonly present in ground water. This was justified by the unique double-walled nanotubular structure of the TiO₂ photocatalyst, which provided a moderate surface area of 28.97 m²/g, with an efficient delocalization of electron carriers and advocated anti-recombination of photogenerated pairs of electron and hole. Based on the experimental results obtained, cations enhanced the overall disinfection process while anions had an inhibitory effect on the disinfection rates. The photocatalyst exhibited high efficiency in terms of photocatalytic disinfection of *E. coli* cells present in ground water. The as-fabricated nanotube photocatalyst offers promising potential for applications in drinking water treatment applications, owing to its superior disinfection performance, as well as high settleability which promotes recovery and reuse of the catalyst. Incidentally, this study was also the first to be reported in the application of anodic TiO₂ nanotubular films for *E. coli* disinfection and represents great significance for all self-cleaning and water treatment applications, particularly in applications where particle separation from the treated media is technologically difficult and costly.

The next phase of study involved growth of well-crystallized and ultralong 1D anatase nanowhisker arrays from a Ti substrate via a template-free technique developed from an anodization process and subsequent hydrothermal treatment. Progressive morphological and crystallographic evolution of highly ordered anodic nanotubes to radially-aligned nanowhisker arrays was clearly elucidated. The morphology, crystallinity and optical properties of the final nanowhiskers were extensively investigated using XRD, FESEM, TEM, UV-Vis spectroscopy and photoluminescence techniques. A prolonged hydrothermal reaction successfully removed inherent crystal defects of the titanate nanowhiskers, and calcination in air at 500 °C recrystallized the hydrothermally-prepared titanate into an anatase

polymorph, without altering its 1D morphology. The nanowhisker architecture demonstrates high thermal stability, without experiencing morphological change under extended hydrothermal durations (24 h) and calcination (500 °C). As evidenced from HRTEM and SAED images, the TiO₂ nanowhisker film exhibits a single crystalline anatase polymorph with almost defect-free lattice characteristics. The as-synthesized nanowhisker photocatalyst also exhibited excellent photodegradation of AO7, a common dye used in textile industries, under UV-A irradiation. The photocatalytic performance was evaluated against other TiO₂ films of various 1D nanostructures, and benchmarked against a Degussa P25 TiO₂ coated film. Owing to its unique morphology and monocrystalline defect-free lattice structure, the nanowhisker sample exhibited highest photocatalytic efficiency. Its inherent 1D morphology has resulted in high quantum yield, hence reiterating a strong ability to suppress recombination of photogenerated electrons and holes. In view of the experimental results, the 1D hierarchical nanowhisker architecture may find a variety of potential applications in solar cells, endoscopy and photonic devices, etc.

The synthesis of an anatase thin film bearing a unique, hierarchical nanofungus-like structure was also reported in the subsequent chapter. The nanostructures were directly grown from a Ti substrate via a facile, one-pot hydrothermal reaction, thus rendering ease of catalyst separation, recycle and reuse. High-resolution images of FESEM indicated presence of small titania nanoparticulates of *c.a.* 20 nm on the nanoflakes, which constitute to the final overall nanofungus-like morphology. Hydrothermal duration-progressive FESEM images illustrated evolution of the nanofungus-structure and provided some evidence of the probable mechanism in obtaining the final nanostructure. The crystallographic phases and orientation of the photocatalyst were investigated by XRD and TEM and we can conclude that the highly crystallized NF10 product characterizes the body-centred tetragonal anatase phase and is polycrystalline. The typical HRTEM lattice images indicate that the nanocrystallites of NF10 characterized a predominant crystallographic growth along the (101) crystal plane. Nitrogen adsorption-desorption isotherm indicated that the

as-prepared catalyst possessed a mesoporous structure and a large BET surface area of $102.1 \text{ m}^2/\text{g}$, thus extremely favourable for diffusion and adsorption of BPA pollutant molecules. It should be noted that the porosity and textural properties of the sample play important roles in the interaction of photocatalyst with external fluid and solid media in achieving high removal efficiencies. Greater light absorbance as shown from the UV-vis diffuse reflectance spectra, denoted enhanced light harvesting effects for UV penetration, possibly induced by inherent mesopores. Surface elemental analysis by means of XPS and EDX underlined the purity of the titania sample with detected presence of only Ti and O in the sample; and high resolution XPS scan of F 1s region revealed presence of fluoride ions adsorbed on the surface of TiO_2 , which promoted etching and surface fluorination within the acidic hydrothermal environment. The photocatalyst exhibited superior photocatalytic degradation of Bisphenol A under UV-A irradiation, in comparison with a Degussa P25 TiO_2 coated film, which presents a significant advance as commercial Degussa P25 is widely regarded as a benchmark reference photocatalyst in photocatalysis research. It can thus be concluded that the excellent photocatalytic performance of NF10 stems from the synergistic effects of a unique hierarchical morphology, large BET surface area, mesoporosity, high crystallinity, extended optical absorbance and increased active surface sites available.

The mechanism behind UV photocatalytic degradation of BPA over TiO_2 was elucidated using charge-trapping and interfering scavenging species as diagnostic tools and evidence have manifested hydroxyl radicals ($\bullet\text{OH}$) to be the predominant active species in associated oxidation processes. Photocatalytic removal of BPA was curtailed to some extent by scavengers of photogenerated h^+ and $\text{O}_2^{\bullet-}$, implying peripheral roles of the 2 oxygen radicals, while the role of $^1\text{O}_2$ was largely inconsequential during photocatalytic degradation of BPA.

The one-pot hydrothermal synthesis method in preparing a novel nanofungus-like morphology of anatase TiO_2 catalyst offers an easy method to prepare highly crystallized, mesoporous anatase TiO_2 photocatalyst. The facile fabrication method offers easy scale-up for mass production. The nanostructures constructed in this

study were directly grown on the Ti substrate thus rendering ease of catalyst separation, recycle and reuse. Despite being used for 10 continuous cycles, photocatalytic efficiency of BPA did not attenuate more than 2%. In view of the above, this photocatalyst can be a promising candidate for treatment of wastewater in an engineering scale.

In the final chapter of this PhD research work, a unique morphology of SrTiO_3 nanocubes precipitated on TiO_2 nanowires in the form of a thin film heterojunctioned $\text{TiO}_2/\text{SrTiO}_3$ photocatalyst was successfully prepared by facile hydrothermal techniques. The epitaxial crystallization and growth of the heterojunctioned $\text{TiO}_2/\text{SrTiO}_3$ photocatalyst from Ti substrates resulted in an immobilized and highly stable film structure anchored on a support, therefore not requiring a post-separation stage for the spent catalysts. The formation mechanisms of the synthesized photocatalysts are meticulously studied and described. Growth of SrTiO_3 single crystal nanocubes (~50 nm in width) from underlying anatase polycrystalline nanowires follows an in-situ dissolution-precipitation pathway. This is consonant with the classic LaMer model. By analyzing the results of FESEM, FETEM, XRD, EDX, XPS and UV-vis spectrophotometry, a comprehensive structural and morphological characterization of the photocatalysts is established. FESEM images reveal that the anatase film comprises mainly of nanowires bristles while the tausonite film is primarily made up of nanocube aggregations. In comparison to the respective pristine semiconductor photocatalysts, the heterostructured photocatalyst demonstrates the highest efficiency in photocatalytic splitting of water to produce H_2 - 4.9 times that of TiO_2 and 2.1 times that of SrTiO_3 . The enhanced photocatalytic efficiency is largely attributed to the efficient separation of photogenerated charges at heterojunctions of the 2 dissimilar semiconductors, as well as a negative redox potential shift in Fermi level which acted as potential traps for electrons and reinforced reduction of hydroxide ions present in water. This is also the first report on the successful photocatalytic cleavage of water over a novel hybridized architecture of nanowire and nanocubic $\text{TiO}_2/\text{SrTiO}_3$ thin film.

In view of the wide spectrum of engineering applications which semiconductor nanostructures can potentially excel in, the synthesis procedures reported herein could herald an emerging generation of immobilized single-crystalline nanostructured assembly with high quantum yields for other metal oxides, particularly in nanophotonics, single cell endoscopy and solar-to-fuel conversion devices. The exciting possibilities of assembling these "nano-architectures" on different flexible and transparent substrates are added impetus in developing the future of nanotechnology.

8.2 Recommendations for future works

In this PhD study, a variety of immobilized titania films was developed via epitaxial crystalline growth over a Ti substrate and by manipulating experimental parameters, modify and construct various forms of nanostructures via hybrid synthetic procedures. The various forms of nanostructures are expected to enhance photocatalytic activities by different mechanistic behaviours of charge migration and transport. Charges, in particular photogenerated electron and hole pairs from a photocatalytic system, can be more efficiently transported, thereby lengthening their reaction lifetime and reactivities. Correlation between photoreactivity and charge-carriers recombination dynamics have been extensively reported in literature and it is an established fact that the recombination of photogenerated electron and hole pairs is a critical factor in the attenuation of photocatalytic efficiencies.

Design and morphological control of crystal facets can optimize performance of various crystalline semiconductor catalysts. Precise morphological control can influence reactivity in heterogeneous reactions by tuning surface atomic structure configuration and coordination. Large, high surface energy facets with higher percentage of undercoordinated atoms are usually more reactive, thus some facets have shown superior photocatalytic performances over others. Precise morphological control of synthesized nanostructures is able to achieve predominant growth of crystal facets with higher heterogeneous reactivity, therefore detailed

mechanistic studies on preferential growth of crystallographic facet development and orientation may be carried out to achieve enhanced photocatalytic efficiencies.

Application of the fabricated photocatalysts for degradation of endocrine hormonal-disruptor compounds or pharmaceutical active compounds such as antibiotics, atrazine, caffeine and ibuprofen can be explored to tap on the immense potential and mileage of photocatalysis in environmental engineering. The heterojunctioned nanocomposites can also be employed in dye-sensitized solar cells and in photocatalytic generation of hydrocarbon fuels from atmospheric CO₂ and H₂O. Since the nanostructured photocatalysts possess extremely large surface area and thus increased reaction sites, equilibrium studies in sorption kinetics of heavy metal such as cadmium, or radioactive ions such as cesium and iodide at the catalyst-water interface may be performed. Leveraging on the immobilized fixed bed system of the synthesized photocatalysts from this research work, photocatalytic remediation of airborne aerosol pollutants, in the form of indoor volatile organic compounds, formaldehyde, oxides of nitrogen and sulphur (NO_x, SO_x), polycyclic aromatic hydrocarbons and other phenolic/benzene compounds that are carcinogenic and have been reported to develop adverse health effects when exposed to humans. Mechanistic reaction pathways of pollutant degradation could also be elucidated by means of chromatography techniques to analyze the different forms of organic intermediates that may be produced as the photocatalytic reaction proceeds.

Different experimental and conditional factors as well as aqueous matrix influences can be investigated on their influence on photocatalytic oxidation reactivity. The below list are some variable factors that can be considered for future work to expand this thesis. These terms include, but are not limited to, catalyst dosage, initial pollutant concentration, initial pH of system, level of dissolved oxygen, presence of different cations and anions, temperature effect, light intensity/wattage of irradiation, wavelength of irradiation, presence of external oxidants such as H₂O₂, presence of photocatalysis inhibitors/radical scavengers/organic anions,

photostability under extended periods of irradiation and repeated cycles of photocatalyst usage.

To improve on photocatalytic efficiencies, a comprehensive and more detailed investigation on photocatalytic reaction mechanisms, for e.g. the generation of specific reactive oxygen species and their respective interaction and contributory roles in the photocatalytic system, should be studied with great interest and detail. Empirical and inferred tests (as reported in Chapter 6) by applications of hole/radical scavengers or probe species to scavenge photogenerated holes or radicals may not be deemed sufficient or accurate. Direct evidence, by means of electron paramagnetic resonance or electron spin resonance spectroscopy, to qualitatively and quantitatively detect the generation of free radicals would be a more accurate and precise procedure. This would allow better understanding of the underlying photocatalytic mechanisms, to effectively embark on optimizing reaction efficiencies by modifying or tuning physicochemical properties of the photocatalysts.

The simultaneous hydrogen production and photocatalytic oxidation of recalcitrant pollutants may be explored on the synthesized $\text{TiO}_2/\text{SrTiO}_3$ photocatalyst. By virtue of the unique heterojunctions created at the interface crystal boundaries of 2 dissimilar semiconductors of unequal bandgaps, in this instance TiO_2 and SrTiO_3 , interfacial electron transfer was facilitated and the negative shift in Fermi level reinforced reduction of hydroxide ions, hence enhancing hydrogen gas production. Photocatalytic reduction/removal of toxic heavy metal ions, such as ionic reduction of As(V) to As(III) or Cr(VI) to Cr(III) in treating industrial wastewaters rich in heavy metal concentrations before discharge, are some of the potentially viable applications in environmental remediation. Simultaneous oxidation and reduction water treatment can therefore be proposed on grounds of positive synergies attained by the spatial delocalization of photogenerated electron and hole pairs, as well as the negative shift in Fermi level which would enhance the photocatalytic reduction half reaction and act as potential traps/sinks for photogenerated electrons, therefore prolonging the reaction lifetimes of the electron and hole pairs.

It is worthy to note that the synthesized photocatalysts immobilized on stable substrates do not require separation or recovery from the treated effluent, and can be conveniently recycled (regenerated under UV irradiation and then reused). Integration of a photocatalysis system incorporated within a fixed bed reactor by layered film coatings on the exposed reactor surfaces can be considered via addition of such a modular stage in the conventional water treatment process train. With the ability to concurrently generate hydrogen gas as a source of clean energy; this would be embarking a large step towards a self-sustainable future of clean energy production and water treatment applications.

Higher activities of hydrogen production may be achieved by metal ion-doping, such as Cu components, which have been proven to enhance photocatalytic reduction and water splitting reactions under sacrificial conditions to produce H₂. The Cu compounds are able to facilitate charge separation and provide reduction sites for H₂ generation. Cu-incorporated TiO₂ is also comparatively more cost-effective as compared to noble metal-loaded TiO₂, such as Pt or Au. Moreover, several Cu compounds have been reported to undergo kinetic transformation in chemical states and distribution on TiO₂ and are regarded active in photocatalytic hydrogen generation.

Heterogeneous semiconductor photocatalytic reactions are based on the fundamental principles of in-situ production of hole and electron that are generated when the photocatalyst is activated under irradiation of light source that can be absorbed by the photocatalyst based on its intrinsic or modified bandgap. A significantly promising future research area that has been envisioned to leverage on the existing framework of study in this PhD work, is developing the concurrent ability of utilizing photogenerated positive holes from the valence band for photocatalytic oxidative degradation of aqueous organic contaminants and pathogens (AO7, *E. coli* cells and BPA), while simultaneously, tapping the reductive electron from conduction band to reduce hydroxide ions of the aqueous bulk solution, to photocatalytically-generate H₂ from water. With such a mechanism in place, potential synergy can be derived for photocatalytic oxidation and reduction

half reactions, enhancing the anti-recombination of charge-carriers and prolonging reaction lifetimes of the electron-hole pairs. In the process, energy resource derived from the concurrent generation of high energy H_2 gas may be tapped to address or offset energy consumption and operational costs for the process of water decontamination. This holistic concept can potentially close the energy loop within a water treatment system, with production of clean energy. Carbon footprint is also substantially reduced with the introduction of green energy in the form of hydrogen. There will not be a need to invest in large capital and developmental costs to co-locate different process trains in order to tap on unutilized energy resources. With this in mind, there are strong motivational incentives for the future of photocatalysis in the environment and water industry.

APPENDIX (I)

Received the First Place Award in the Materials Research Society (MRS) Annual Science As Art Competition 2011 at the *MRS Fall Meeting & Exhibit, Boston, United States, 28th Nov – 2nd Dec 2011*.

My entry was entitled "**Autumn's Drought**". The scattered "autumn leaves" are anatase TiO₂ nanorods self-assembled to form bundles of dendrites. The leaves are embedded on a substrate of congregated nanocubic structures in the form of tausonite SrTiO₃ crystallites. This unique architecture of hybrid heterojunctioned TiO₂/SrTiO₃ was engineered by a 2-step hydrothermal pathway and the image was obtained via a field-emission scanning electron microscope with its colours digitally modified using Adobe Photoshop.

The image is a portrayal and rendition of a paradoxical relationship between scientific research and environmental challenges surrounding us. It is known that the earth is besieged by environmental impacts many of which are anthropogenic in nature. Amongst countless of such issues are pollution, climate change, overpopulation, fresh water shortage, land degradation, famines and droughts. The design philosophy and inspiration of the submission image was to be impactful and unique, while conveying a cogent and stark environmental message across. It is envisioned that the image has to offer ample imaginative space for the viewers to ruminate and ponder upon their initial impressions. It is also noteworthy that heavy emphasis was placed on a strong themed title, as well as to the use of striking and contrasting colours splashed across the overview to stimulate and evoke reflections.

You may have noticed that the title itself is contradictory in nature. Autumn is not a typical season of the year that one would associate with droughts but indeed due to climate change and global warming, the weather is increasingly becoming more unpredictable these days. We are living in a warmer world with increasing levels of carbon dioxide, and unbalanced evaporation rates have severely disrupted normal hydrological cycles. We are thus experiencing longer periods of unyielding

droughts that extend into autumns and even winters, and if such trends are allowed to continue, unknowingly to many yet alarmingly, the widespread consequences that follow may be a lesser capacity to sequester carbon on land, less ability to produce biofuels and a less secure food supply aggravated by the current state of unrelenting global population boom.

The vibrant red leaves signify the aspiring hopes and promise that this novel hybrid nanostructured photocatalyst can endeavour to a barren land in dire deprivation of aqua. The contrasting colours used: blood red autumn leaves epitomize vitality, longevity and dynamism harnessed from the energy of sustainable research to mitigate environmental challenges; grayscale monochrome background illustrates an air of gloom and worry, in the knowledge that climate change is indeed real and is manifesting as we speak. It personifies the reality of global warming and the harsh consequences if we continue to turn a blind eye to the relentless tell-tale signs of the Earth. The long, deep cracks of dry earth from the picture serve to remind us about the fragilities of our environment and that natural resources on earth are not inexhaustible; obviously there isn't enough to sustain our lavish and extravagant lifestyles. It is high time we stop taking everything that Nature has bestowed upon us for granted.

In general, the image exemplifies the significant and compelling roles of fundamental scientific research and advancing technology in the midst of massive urbanization and stimulating economic growth today. The essence is to put things into perspective and the rationale of introducing vivid imaging contrast via mechanisms of depth, colour and connotations further empower the message to be driven across. The core objective of utilizing contrasting elements is purposeful; it accentuates stress and significance, and projects the sustainability and resolute conviction of scientific research (blood red autumn leaves) standing out strongly during times of uncertainty and environmental crisis (grayscale backdrop of cracked barren ground).

APPENDIX (II)

The calculation of apparent quantum yield of the as-prepared samples for H₂ production

$$\text{Apparent Quantum Yield} = \frac{\text{Number of H}_2 \text{ molecules evolved} \times 2}{\text{Number of incident photons}} \quad (7.8)$$

The number of incident photons can be determined with the following equation:

$$\text{No. of incident photons} = \frac{I \times S}{hc/\lambda} \quad (7.9)$$

where I is the light intensity measured using UV radiometer (Cole-parmer, VLX-3W, USA), S is the irradiated area, h is the Plank's constant (6.62×10^{-34} J.s), c is the speed of light in vacuum (3×10^8 m/s), λ is the wavelength of emitted light (254 nm).

Note: Quantum yield calculations were made based on 4 sets of UV lamps (254 nm) which were employed to irradiate the as-prepared samples. Apparent quantum yield was calculated instead of the actual quantum yield, due to limitation of measuring the exact number of absorbed photons that were utilized by the catalyst for reaction; thus total number of supplied photons emitted from the 4 lamps was used instead.

For the heterojunctioned TiO₂/SrTiO₃,

The rate of H₂ molecules evolved = Rate of H₂ evolved * Avogadro's Constant

$$= 386.6 \text{ } [\mu\text{mol/h}] * 1/3600 \text{ [h/s]} * 10^{-6} \text{ [mol/}\mu\text{mol]} * 6.02 \times 10^{23} \text{ [molecules/mol]}$$

$$= 6.465 \times 10^{16} \text{ [molecules/s]}$$

$$\begin{aligned} \text{Energy of one 254 nm photon, } E &= hc/\lambda = 6.626 \times 10^{-34} \text{ [J/s]} * 2.998 \times 10^8 \text{ [m/s]} / \\ 254 \times 10^{-9} \text{ [m]} &= 7.82077 \times 10^{-19} \text{ [J]} \end{aligned}$$

The rate of incident photons = $4 * 5400 \text{ } [\mu\text{W}/\text{cm}^2] * (3.142 * 19.12 * 10^{-2}) \text{ } [\text{cm}^2] * 10^{-6} \text{ } [\text{W}/\mu\text{W}] / 7.82077 * 10^{-19} = 3.029 * 10^{17} \text{ } [\text{einstein/s}]$

Therefore, apparent quantum yield for the sample $\text{TiO}_2/\text{SrTiO}_3$

$$= 2 * 6.465 * 10^{16} \text{ } [\text{molecules/s}] / 3.029 * 10^{17} \text{ } [\text{photons/s}] * 100\%$$

$$= 42.6\%$$

The apparent quantum yields of tausonite and anatase samples are 22.2% and 9.4% respectively.

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