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**DUAL PHASE TITANATE/TITANIA
PHOTOCATALYST FOR DEGRADATION OF
ORGANIC POLLUTANTS UNDER VISIBLE LIGHT**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2012

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UNDER VISIBLE LIGHT**

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“I almost wish I hadn't gone down that rabbit-hole, and yet, and yet--it's rather curious, you know, this sort of life.”

Alice's Adventures Underground

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List of Symbols, Abbreviations and Nomenclature

Symbol	Definition
UV	Ultraviolet
MB	Methylene blue
Vis	Visible
BET	Brunauer Emmett Teller
eV	Electron volt
HRTEM	High resolution transmission electron spectroscopy
EXAFS	Extended X-ray absorption fine structure
CB	Conduction band
VB	Valence band
XRD	X-ray diffraction

Abstract

This research focuses on the design and development of a unique efficient dual phase photocatalyst material suitable for efficient degradation of harmful organic pollutants under visible light. Existing photocatalyst materials are ineffective as they have poor surface adsorption, are only responsive to UV light and experience fast charge recombination which impedes breakdown of organic pollutants.

The thesis begins with a study on synthesis variations and its influence on the properties of the photocatalyst. The material that has high efficiency under visible light was determined to be a dual phase mixture of nanoscaled titanate and titania (anatase). Using a combination of theoretical and experimental techniques, the complete structure solution was achieved and the dual phase structure was confirmed by x-ray diffraction and high resolution transmission electron microscopy. Another key accomplishment of this thesis is the study of phase transition of the dual phase material and its evolution in crystal structure, surface area, optical absorption and chemical composition with change in synthesis temperature and duration. The titanate phase was found to dominate at lower temperatures and anatase phase at higher temperatures. This simple synthesis method also leads to doping of nitrogen in the titanate phase which effectively narrows its wide band-gap.

Photo-activity of the dual phase photocatalyst is demonstrated in a systematic study of methylene blue (MB) dye degradation under visible light. This work highlights the importance of surface adsorption and distinguishes its contribution in overall photo-degradation process. Dual phase photocatalyst S160 exhibited superior performance over a commercial reference, Degussa P25. Its efficiency stems from its synergistic

“adsorption- degradation” mechanism. In addition to capturing visible light, the titanate phase also plays the role of an adsorbent to attract organics such as MB molecules onto its surface. Intimate interfacial contact with the anatase phase allows easy band to band electron- hole transfer that retards charge recombination leading to faster degradation of organic compounds. In this study, demineralization of MB and its intermediates was studied in detail to make a distinction between dye sensitization and photocatalysis. Degradation of phenol under visible light was studied as well and the dual phase photocatalyst showed remarkable results compared to P25.

In summary, this thesis introduces the development of a nitrogen doped dual phase photocatalyst and demonstrates its use in efficiently breaking down two organic targets under visible light. Essentially, the experimental advances realized in this work will have a direct impact in functionalizing photocatalysis in practical solar- driven wastewater degradation of organic pollutants.

CHAPTER 1: INTRODUCTION

1.1 Sustainability, a global issue

Sustainability is defined as meeting the needs of society in ways that can continue indefinitely into the future without damaging or depleting natural resources.¹ Since the revolutionary age of industrialization in the 18th century, mankind has made tremendous progress in technology, standard of living and a general way of life. This however, created many problems for our environment as it takes the toll in obvious signs. According to renowned scientist James Lovelock the originator of Gaia theory, the earth's health has already gone beyond a point of no return.² One of the world's greatest environmental issues lies in our water resource. Water is a precious and limited resource and we have to deal with its scarcity, pollution and wastage. Industries are responsible for generating copious amounts of waste; much of which is toxic in nature and not biodegradable. The improper treatment of them results in the emission of harmful gases and chemicals into the atmosphere and into watercourses. This is particularly dangerous. Our global reserve of drinkable water is an estimated 1% and one in six people do not have access to potable water.³ Should the wastes in water be improperly treated and enter soils which then make their way back into our drinkable or usable water systems, ecosystems and public health will be at risk. The use of green technology has been popularized through the years and is being radically implemented into waste management with the aim to clean and recycle water. In targeting the root of waste management, we should aim to alleviate or reduce the effects on some of the other predicaments and help sustain our environment.

1.2 Challenges in sustaining our environment in wastewater treatment

The treatment of wastewaters is complex as it often requires the breakdown of complicated chemicals and organic compounds. The long list of contaminants in wastewater includes coloured dyes, phenolics, chlorinated solvents, pesticides, and so on. There are three main approaches to wastewater treatment and they are categorized as physical, chemical and energy-intensive methods. Physical methods refer to technologies that rely on filtration such as reverse osmosis and activated charcoal filters. Chemical methods involve using chemical interactions to either separate contaminants from water or aid in their destruction. Some examples include advanced oxidative technologies (AOTs), using chlorine and flocculation agents. Energy-intensive methods such as ozone, heat or ultraviolet light and are more commonly used as a means of sterilization. All these methods can be used as standalone technologies or integrated as a full treatment process. Even though the existing technologies are technologically effective in reducing wastewater, there is still much room for improvement. An important consideration is that these processes either incur high cost and energy or require the use of chemicals. Reverse osmosis uses fine and expensive membrane filters that are prone to attack by organic species and require frequent replacement. Activated charcoal filters, although useful in adsorbing chemicals and heavy metals, have to be re-activated by desorbing the adsorbed organics using a thermal regeneration technique, which also incurs high costs and energy.

Thus there is a need to search for new processes that are cost and energy effective and do not require the use of chemicals. To achieve this, we need to seek an improved solution for wastewater treatment so that the valuable waters can be reused. Photocatalysis is an emerging technology that makes use of solar energy to break down

toxic organic pollutants. It complements the current water treatment technology with its simplicity and ease of implementation. Importantly, photocatalysis operates under relatively low cost and energy overheads.

1.3 Motivation

Photocatalysts are semiconductor materials that are able to absorb light energy and translate that energy into useful chemical reactions to break down organic molecules. However to date, its full potential in practical applications has not been reached due to considerable challenges that have yet to be overcome. Some of these challenges include:

1. Most stable photocatalytic materials are only capable of absorbing ultraviolet (UV) light. Unfortunately, UV makes up a mere 5% of the entire solar spectrum. Therefore the technology is still not completely viable due to the ineffectiveness of present materials to capitalize on our freely abundant solar energy. Much work has been dedicated to extending the absorption of such materials into the visible light region but only limited success has been reported.
2. Photocatalytic materials face the problem of electron hole recombination. This backward reaction hinders useful photo reactions and contributes to inefficiency in the photocatalytic process.
3. The adsorption of chemical molecules in the degradation process is often not emphasized in photocatalytic research. The ability of a material to adsorb organic molecules onto its surface greatly enhances

the overall degradation process since it provides a shorter path for charge interaction. It is challenging to alter surfaces of photocatalytic materials to adapt this criterion.

The motivation of this thesis thus lies in developing a novel photocatalyst that has enhanced properties that will make it capable in degrading organic pollutants efficiently.

1.4 Hypothesis

A single material system is limited in the expansion of multiple ideal properties we look for in a photocatalyst. The adsorbent properties of titanates are compelling because good adsorption results in efficient interfacial charge transfer to and from the target organic molecules. The stability of TiO_2 is desired for safe usage and photocatalytic activity. Doped systems enhance visible light responsiveness and increase the photocatalyst's capacity to make use of a larger portion of our solar spectrum. It is therefore hypothesised that a multi phase system comprising of more than one phase will contribute to the overall effectiveness of photocatalysis and offer the following advantages:

1. Strong adsorption
2. Responsive to visible light
3. Electron transfer from one phase to another to reduce electron hole recombination and enhance photoactivity

1.5 Objective and Scope

The aim of this dissertation lies in seeking an energy efficient and environmentally friendly solution to treat harmful wastewater using photocatalysis. The process should enable the degradation of target organic contaminants in the wastewater. The scope encompasses the following milestones:

1. Development of a novel and efficient photocatalyst

A soft chemical low temperature synthesis procedure is established with the aim of doping to induce visible light photo-responsiveness as well as introduce high surface adsorption capacity in the synthesized material. This work proposes the incorporation of two intimate phases in the photocatalyst system- titanate and titania. Titanates are known for their superior adsorption abilities and are widely used as adsorbents for heavy metals and toxic organics.^{4, 5} Titania, in particular anatase, is the most widely studied photocatalyst due to its availability, stability, low toxicity and excellent photoactivity under UV light.⁶ The two phases also share common structural features (TiO_6 octahedras sharing four- edges and zigzag ribbons) which is important in creating compatible and intimate interfaces on nanoscale to facilitate charge transfer.^{7, 8} Combining these two phases might ideally merge the desired properties within one material system. This thesis reports for the first time, *a simple one pot* synthesis method for a dual phase titanate/ titania photocatalyst.

2. Detailed crystal structure characterization

Solving crystal structure of multi phase systems is a particularly tough challenge. In addition, the crystal structure of titanate has eluded a good deal of research focusing on this complex material. Much of the existing work makes vague references to the few known titanate structures. In this thesis, the crystal structure of the synthesized titanate is solved using a combination of theoretical and experimental techniques. Additionally, an in depth structural study comprising diffraction, imaging and spectroscopy techniques establishes the co-existence of titanate and anatase phases. These knowledge and methods contribute valuable insights into the vast field of research on titanate and multi phase systems.

3. Phase transformation study

By tailoring the synthesis conditions, a systematic phase transformation study can be conducted. Changes in the material properties such as crystal structure, surface area, composition, optical absorption and dopant concentrations will be assessed.

4. Photocatalytic activity evaluation

Photocatalytic activity for the synthesized materials is measured by testing two organic test pollutants; Methylene blue (MB) dye and phenol. They are chosen because their adsorption capacity and degradation mechanisms are radically different and allows for a fair assessment of the material's photocatalytic performance. Through the application, an important study highlighting the differences and contribution of adsorption and photo-

degradation will be made to provide a holistic account of photocatalytic reactions. This study emphasizes the synergistic actions of adsorption and photo-degradation in the as synthesized photocatalyst that makes it more efficient than commercial materials.

5. Study of photocatalytic reaction pathway

Thorough investigation of intermediate formation in both pollutants will also be performed. This understanding is useful in evaluating complete degradation efficiency, an important aspect which is lacking in existing literature. Particularly in dye degradation studies where most work associate the breakdown of dye with its decolouration, it is imperative that actual evidence of intermediate formation and breakdown be studied to provide a comprehensive evaluation of photocatalytic efficiency.

1.6 Organization of the Report

This report is divided into six chapters and each chapter is briefly discussed as follows:

Chapter 1 provides a brief introduction and background of the research focus as well as the motivation and objective of this work.

Chapter 2 presents a literature review which covers related topics such as fundamentals in photocatalysis, photocatalytic materials, fabrication techniques, titanates and adsorption concept.

Original work realized in this research is presented in Chapters 3 to 5.

Chapter 3 details the experimental methods and characterization techniques used throughout the research.

Chapter 4 presents the results of crystal structure solution of titanate and a comprehensive discussion of structure, chemical and optical properties of the dual phase systems across changes in the synthesis conditions.

Chapter 5 reports the photoactivity of the synthesized dual phase systems in degrading methylene blue and phenol under visible light. In methylene blue study, adsorption and photo-degradation are separately studied for their individual contributions and later combined to highlight the synergistic effect of both concepts in overall efficient degradation. The intermediate formation from MB degradation which is not commonly studied is also discussed. Phenol degradation was examined to further demonstrate the photo-responsiveness of the dual phase system under visible light. In all photo-activity tests, commercial reference Degussa P25 was used as a benchmark for comparison.

Finally, Chapter 6 summarizes the significant conclusions and proposes prospective work for future research.

CHAPTER 2: LITERATURE REVIEW

2.1 Overview of Photocatalysis

Photocatalysis is a promising technology in the field of green technology. This scientific concept was unveiled in 1972 when Honda and Fujishima demonstrated photocatalytic splitting of water. Using titanium oxide electrodes in a photo-electrochemical cell, they could split water into hydrogen and oxygen gases under UV light illumination (Figure 2.1).⁹ This work sparked wide interest in the potential of photocatalysis. Since then, much research has been performed to seek new materials or improve materials for better efficiency. Also, in terms of applications, photocatalysts have been applied extensively in areas such as energy production/ renewal, energy storage and more recently in environmental clean-up.

Figure 2. 1: The Honda Fujishima effect showing an electrochemical cell in which the TiO₂ electrode (label 1) is connected to a black platinum electrode (label 2).⁹

The term ‘photo-catalysis’ has long been in widespread use and encompasses other more narrowly defined terms such as photosensitization, photo-electrochemistry, artificial photosynthesis, etc. Some are more particular about differentiating the various

photo-processes. Photosensitization and photo-catalysis for example, both produce photo-reactions by the driving force of light. However, the difference lies in that if the initial photo-excitation process occurs in the absorbate molecule, which then interacts with the ground state of the catalyst substrate, the process is a “catalysed photoreaction” or “photo-catalysis”. Should the initial photo-excitation take place in the catalysed substrate and the photo-excited substrate then interacts with the ground state adsorbate molecule, the process is a “sensitized photoreaction” or “photosensitization”. Most water splitting processes are photosensitized reactions as the initial reaction takes place in the catalyzed substrate. However, it has been accepted that photo-catalysis is the generally favored term and is inclusive of the other terms. It should also be mentioned that majority of the work reported in this review involve heterogeneous catalysts, as are most of the work all over the world. In a heterogeneous reaction, the catalyst is in a different phase as the reactant.

2.2 Principle of Photocatalysis

Photocatalysis refers to the acceleration of a photoreaction by the presence of a catalyst.¹⁰ A *photo-catalytic* material acts in absorbing light of sufficient energy and converts the energy into chemical reactions within a medium. A photocatalyst is in fact a semiconductor. There are 2 classifications of semiconductors; intrinsic and extrinsic. The difference in the two classifications is that intrinsic semiconductors (or pure semiconductors) are undoped whereas extrinsic semiconductors are doped. Semiconductors are a unique class of materials as they can act as insulators or conductors depending on its state of excitation. For example, at 0K, under no thermal or optical

excitation, the material exists as an insulator. Under thermal or optical excitation, the material transforms into a conductor. Electrical conduction in solids only occurs via electrons in partially filled bands. Hence, conduction in pure semiconductors occurs only when electrons have been excited; into higher unfilled bands. At room temperature, a small proportion of electrons in the semiconductor will be thermally excited from the valance band into the next higher band, which is the conduction band. The ease at which these electrons can be excited in this way depends on the energy gap between the bands i.e. *band-gap*, E_g . It is the size of this very energy gap that defines a semiconductor and an insulator. Insulators have such a high energy gap that such excitation is inherently impossible and hence makes them unable to conduct electricity. Semiconductors are generally defined as having energy gaps of less than 4eV at room temperature.

In principle, conversion of solar energy into chemical energy can be obtained by means of any thermodynamically uphill reaction produced by visible-light excitation¹¹. The overall process of a semiconductor-sensitized/catalyzed reaction can be generalized as follows

where E_{bg} is the bandgap of the semiconductor photo-catalyst; D denotes donor and A, acceptor. Any photochemical conversion system based on a redox process must involve a light-induced electron-transfer. When a molecule of such a system absorbs a photon of suitable energy, an electronically excited state that is a better oxidant and reductant than

the ground state is obtained. An electron-transfer reaction between such an excited state and a suitable reaction partner may convert a fraction of absorbed light into chemical energy. Table 2.1 below shows examples of various photoreactions and the required Gibbs free energy.¹¹

Table 2. 1: Examples of TiO₂- sensitized photo-catalytic processes.¹¹

Reaction A + D	A⁻ + D⁺	Description	ΔG° (kJ mol ⁻¹)
<i>Photo-catalysis</i>			
$\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$		Water splitting	475
$2\text{CO}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{OH} + 3\text{O}_2$		Carbon dioxide reduction	1401
$2\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{NH}_3 + 3\text{O}_2$		Nitrogen reduction	1355
$3\text{O}_2 + 2\text{CH}_3\text{OH} \rightarrow 4\text{H}_2\text{O} + 2\text{CO}_2$		Methanol mineralization	-1401

These processes might be slow due to the multi-electron nature whereas the back electron-transfer reaction known as recombination is very fast. The catalyst has to be effective in speeding up the forward reaction and slowing down the back reaction.

Hence, when a photocatalyst particle is illuminated by light that has energy larger than its band-gap, an electron gains energy to make a jump across the band-gap into the conduction band, leaving behind a hole in the valence band. This is the formation of an electron hole pair. Subsequently, the electron and hole can be promoted to the surface of the particle to react with reactants. In Figure 2, the reactant demonstrated is methylene blue. Methylene blue is an organic dye that is commonly employed as a test vehicle to evaluate the effectiveness of a photocatalyst. It can be seen as an example or candidate for environmental pollutant. In this photocatalytic reaction, the photogenerated hole

produced reacts with methylene blue molecule ($C_{16}H_{18}N_3SCL$) and breaks it into simple components.

Figure 2. 2: A schematic displaying photocatalytic reaction for methylene blue degradation.

2.3 Materials in Photocatalysis

A material should fulfil several criteria to be suitable as a photocatalyst. The most basic of which require the material to be chemically stable in water, robust against photo-corrosion and low in toxicity. This ensures it is safe to use in environmental applications. Secondly, it should be able to capture free light energy from the solar system effectively. Our solar spectrum is made up of visible light (400- 700 nm), near infrared rays (700- 10^6 nm) and a small component of ultraviolet rays (100-400 nm) as shown in Figure 2.3. Since visible light makes up nearly half the solar spectrum, photocatalysts should ideally

have energy band-gaps between 1.5 to 3.1 eV to be able to capture this abundant source of energy. Another criterion is that the photocatalyst should possess high surface area. This is because photocatalytic reactions take place on the surface of the particle in contact with the reactant medium. Hence a high surface area provides more contact sites for reactions to take place and increases the efficiency of the reactions.

Figure 2. 3: Solar spectrum distribution.¹²

2.3.1 Titanium oxide, the prime choice

So far, titanium oxide (TiO_2) is the most popular choice of photo-catalyst and has been widely studied. It is stable, non toxic and relatively cheap to produce by a variety of methods.¹³ It has been used in a wide variety of commercial applications like cosmetics, sunscreen, whitening agents, green coatings for surfaces, etc. The material exists in many polymorphs but only 4 are commonly studied-anatase, rutile, TiO_2 (β) and brookite.

Studies have shown that anatase has the highest photo-activity amongst its polymorphs.¹⁴

¹⁵ Table 2.2 compares the crystal structure and properties of the 4 polymorphs.

Table 2. 2: Table comparing 4 polymorphs of TiO₂.

	Rutile (3.0 eV)	Anatase (3.2 eV)	TiO ₂ (β)	Brookite
Crystal System	Tetragonal	Tetragonal	Monoclinic	Orthorhombic
Space group	P42/mnm	I41/amd	C2/m	Pbca
a (Å)	4.5845	3.7842	12.1787	9.184
b (Å)			3.7412	5.447
c (Å)	2.9533	9.5416	6.5429	5.145
			107.06° (β)	

Titanium oxide has a band-gap between 3 to 3.2 eV which allows it to absorb only UV light. This makes the material less efficient under the solar spectrum. Any shift in the optical response of TiO₂ into the visible light region will have a positive impact on the efficiency of its light harvesting. Other properties such as crystallinity and surface area also influence photo-activity.

There are a variety of ways to synthesize titanium oxide. These include the physical methods, which are classified as top-down nanotechnology processes as well as wet chemical methods which are classified under the bottom-up category. Some examples of physical methods that are used in the fabrication of TiO₂ include physical/chemical vapour deposition techniques such as sputtering, pulsed laser ablation and other methods like mechano-synthesis and flame spray.¹⁶⁻¹⁸ Of the wet chemical routes, there is sol-gel, aqueous precipitation, hydrothermal and micro-emulsion.¹⁹⁻²¹ To date, many researchers have attempted and are still trying to improve titanium oxide by altering its

structure or tapering its surface in order to improve its photocatalytic performance by using different synthesis methods. For example, having a photocatalyst with small particle sizes makes for a large surface area which enhances photocatalytic interactions. The sol-gel technique gives excellent purity and is favourable for making powders which requires good particle size distribution and control over surface area.²² For applications that necessitate thin films or immobilized substrates, sputtering proves to be an effective method and allows straightforward manipulation of film thickness and composition.²³ Much work has also been done in the innovation of morphology; e.g. porous structures that effectively increase the surface area of the photocatalyst so as to increase the number of surface active sites and hence promote efficient photocatalysis.^{24, 25}

A different approach to tune the properties of TiO_2 is by introducing defects into it. Doping is a technique to introduce atoms from other elements into the structure of TiO_2 so as to improve its optical efficiency. Elements from all over the periodic table have been used as dopants as shown in Figure 2.4.²⁶ As it is, studies are still underway and different techniques used for doping²⁷ may also produce varying results. It is shown, like in the case of nitrogen doping as first performed by Sato, that the NO_x impurity contributes to the sensitization of visible light and leads to the desired band-gap narrowing.²⁸ Following this work, many other researchers have also tried to dope TiO_2 with nitrogen using a variety of methods such as ion implantation, adding nitrogen precursors, annealing in nitrogen-rich environments and so on.^{18, 29-33} Most of this research shows the successful red shifting of absorption band edge by varying degrees. However, the exact species of nitrogen bonding within TiO_2 matrix remains debatable since the nature of doped nitrogen is very much influenced by the doping process.^{34, 35}

With the present trend inclining towards non-metal dopants, anions such as sulfur and carbon are also heavily studied as potential candidates for TiO₂ doping.³⁵⁻³⁷ S- doped TiO₂ is commonly prepared by high temperature heating of titanium sulfide under controlled atmospheres.³⁸ These studies demonstrate that appropriate doping of non-metals can modify the electronic structure of pristine TiO₂.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		

i) : d⁰ ion
 ii) : d¹⁰ ion
 iii) : Non-metal
 iv) : to construct crystal structure and energy structure
 v) : to construct crystal structure but not energy structure
 vi) : to form impurity levels as dopants
 vii) : to be used for cocatalysts

Figure 2. 4: Elements constructing heterogeneous photocatalysts.²⁶

2.3.2 Emergence of other materials

Other materials that have been considered as photocatalyst candidates include ZnO ($E_g = 3.2\text{eV}$), SrTiO₃ ($E_g = 3.2\text{eV}$), WO₃ ($E_g = 2.8\text{eV}$) and ZnS ($E_g = 3.6\text{eV}$).³⁹⁻⁴² They also show good photo-stability but experience the same problem of limited light harvesting using solar light; just like TiO₂. Small to medium band-gap materials such as CdS, CdSe, MoS₂ and Cu₂O have suitable energy bands for efficient solar light harvesting but exhibit instability and are prone to severe photo-anodic

corrosion.^{43, 44} All these materials have been synthesized as powders, thin films and nano-structures, each of which are studied for their effectiveness in photo-reactions.

2.3.3 Titanates; a new contender

Titanates are a new family of photocatalytic materials that were introduced in the late 1990s and the research in this work only grew active in the recent years. They combine the properties of conventional TiO_2 with properties of layered materials (favourable for ion exchange). The discovery of carbon nanotubes in 1991 initiated a great amount of interest in non- carbon nanotubular structures.³⁶ TiO_2 was among other materials such as SiO_2 , Al_2O_3 , V_2O_5 and MoO_3 to be processed into nanotubes so as to obtain high performance TiO_2 with large surface area. Kasuga et al.³⁷ were the first to report titania nanotubes which they had prepared by treating amorphous TiO_2 with a concentrated solution of NaOH using an autoclave. They had characterized their product as anatase. As more studies emerged, it was found that the structure of the so- called titania nanotubes were more sophisticated than that of TiO_2 . In these early times when little was understood about these structures, the nanotubes were regarded as TiO_2 . Later on, these structures were formally termed titanates, layered titanates or protonated titanates as they were considered hydrated forms of TiO_2 . They have a chemical formula $\text{M}_2\text{Ti}_x\text{O}_{2x+1}$ ($\text{M} = \text{H}, \text{Na}, \text{K}, \text{etc}$). Figure 2.5 shows a simplified timeline by Bavykin et.al⁴⁵ to describe the development of TiO_2 and titanate related nanotubular structures. Mostly, people want to prepare titania nanotubes as they have higher surface area compared to other morphologies. In creating these nanotubes, titanate structure might first be attained; further processing can be done to convert the nanotubes into TiO_2

nanotubes.^{39, 40} Now, more attention is paid to titanates, not just as an intermediate structure, but as a candidate for photocatalytic or purification applications.

Figure 2. 5: Simplified timeline describing the development of TiO₂-related nanotubular structures.⁴⁵

There are 2 general approaches to create titanates; firstly via an alkaline hydrothermal route and secondly via pyrolysis (i.e. high temperature, solid-state reaction). It is worthwhile to understand these techniques in order to gain further understanding on the structure of these materials. Most studies adopt the alkaline hydrothermal approach because it is straightforward and uses low temperatures. The procedure usually involves mixing a readily available TiO₂ powder in an alkaline medium followed by hydrothermal treatment. By varying the concentration of alkaline medium, we can control the size, structure and shape of the nanotubes. As mentioned, Kasuga et al. used a similar method. The nanotubes formed by treatment of 10M NaOH

aqueous solution for 20 hours at 110 °C had a diameter of approximately 8nm and length of 100nm.⁴¹ The structure was identified as anatase. In 1999, they formulated that post-treatment washing was crucial to nanotube formation. They used HCl to wash the alkali-treated samples and concluded that the ion exchange of Na^+ by H^+ takes place during the washing and HCl treatment resulting in sheet-like particles⁴¹. Subsequent work done by Chen et. al. in 2002 opposed this; in their experiments using a single alkali treatment using 10M NaOH to treat commercial anatase in an autoclave at 130 °C for 72 hours, the nanotubes were found to form during alkali treatment and no acidic or other treatments was necessary.⁴² In fact, performing HCl treatment on their samples rendered no enhancement on the formation of nanotubes but introduced many defects instead.⁴⁶ They confirmed the structure to be a trititanate $\text{H}_2\text{Ti}_3\text{O}_7$ (monoclinic unit cell with $a= 1.603$, $b= 0.375$, $c= 0.919$ nm, and $\beta= 101.45^\circ$). Following their examples, many other papers also focused on exploring titanate microstructures as well as studying the effects of alkalinity and hydrothermal conditions.⁴⁷⁻⁵⁰

One of the earliest works to demonstrate understanding of crystal structure of titanates was performed by Sasaki et. al in 1992. In this paper, ion exchange was performed to produce a protonated pentatitanate with a monoclinic layer structure.⁴⁷ A parent compound of $\text{Cs}_2\text{Ti}_5\text{O}_{11}$ was treated with HCl so as to extract interlayer Cs ions and protonate the material. This parent compound had been earlier studied by Kwiatkowska and Grey where they provided detailed structure solution of the material.⁴⁸ The resulting structure was a layered titanate, $\text{H}_2\text{Ti}_5\text{O}_{11} \cdot 3\text{H}_2\text{O}$ (monoclinic, $a = 23.431$, $b = 3.749$, $c = 15.029$ Å and $\beta = 117.16^\circ$) where $[\text{Ti}_5\text{O}_{11}^{2-}]_\infty$ forms the host framework with an interlayer spacing occupied by water molecules and protonated species as shown in

Figure 2.8. This initiated more structural research on layered titanates, consequently more variations of the structure were discovered i.e. $\text{H}_2\text{Ti}_3\text{O}_7$ ⁵¹⁻⁵³, $\text{H}_2\text{Ti}_3\text{O}_7 \cdot x\text{H}_2\text{O}$ ⁴⁹, $\text{H}_2\text{Ti}_4\text{O}_9 \cdot x\text{H}_2\text{O}$ ^{54, 55}, $\text{H}_2\text{Ti}_5\text{O}_{11} \cdot x\text{H}_2\text{O}$ ⁵⁰, $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ ^{56, 57} and $\text{TiO}_2(\beta)$ ^{58, 59}.

Figure 2. 6: Idealized representation of $\text{H}_2\text{Ti}_5\text{O}_{11} \cdot 3\text{H}_2\text{O}$. The arrows point at possible oxygen atoms to be hydroxylated. The open and striped circles represent H_2O (or H_3O^+) at $y = 0$ and $\frac{1}{2}$ respectively.⁴⁷

A unique property of titanates is their strong physical adsorption capacity. Titanates generally have large surface areas ($> 200 \text{ m}^2/\text{g}$) and can adsorb organic species such as dyes on their surfaces.^{60, 61} Adsorption is an important property since photo-reactions take place at the surface of the photocatalyst. Good interfacial contact between photocatalyst and adsorbed species enhances electron-hole interaction and reduces the possibility of charge recombination. Previously, activated carbon was one of the few candidates to offer strong adsorption; it is however expensive to process and requires large energy for production and post-treatment. Recently more studies have revolved

around various titanate adsorbents as a cheaper and more efficient replacement for activated carbon.^{5, 50, 54, 62}

Another interesting application for titanates is in heavy ion removal.^{4, 63} The large interlayer spacing occupied by protonated species is ideal for intercalating alkaline ions (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+)⁶⁴ and some transition metals ions such as (Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+}).⁵¹ Titanates have even been coined “intelligent adsorbents” for radioactive ion removal.⁶³ Radioactive cations are preferentially exchanged with protons or sodium ions in the interlayer and a structural collapse takes place after a certain extent of ion exchange. This forms a stable solid that traps the radioactive ions permanently and makes it safe to dispose. Such an application is important in the efforts to reduce harmful environmental contamination.

Photocatalysis using titanates is also an emerging area of interest. Some researchers studied the photoactivity of titanates under UV light irradiation to degrade acetone⁶⁵, dyes⁶⁶ and split water⁶⁷. Titanates are responsive to UV light as they have been reported to possess wide band-gaps between 3.4 to 3.8 eV depending on the structure.^{40, 54} In efforts to extend its response into visible light, researchers have tried to dope them with elements such as nitrogen^{68, 69} and nickel⁷⁰. The results were encouraging; there was significant improvement in photo-activity measurements.

Although much progress has been made since the relatively short procession of titanates, some fundamentals have still not been completely unravelled. For example, many structures of titanates have emerged but not all crystal structures are well understood. The difficulties that are associated with establishing accurate crystal structure lie in the complexity of the layered material and relatively poorer crystallinity as a result

of low temperature hydrothermal conditions. In addition, most of the titanates are sized in the nano-range and cause broadening in the diffraction peaks leading to complications in refining the structure. It is also tough to pin down the exact locations of the protons and water molecules. So far, most research avoid crystal structure solutions and describe their titanates as “similar” to the 2 more widely known structures $\text{H}_2\text{Ti}_3\text{O}_7$ and $\text{H}_2\text{Ti}_5\text{O}_{11} \cdot x\text{H}_2\text{O}$. In addition, almost all the synthesis of hydrogen titanates up to now involve a top down wet chemistry approach; whereby the base material TiO_2 was transformed via alkaline hydrothermal treatment into sodium titanate followed by ion exchange with acid for the final hydrogen titanate as seen in Figure 2.7.⁴⁵ The process proves to be long, tedious, and difficult to control. Therefore, there is still much room for creativity and advancement for a young branch of materials such as titanate.

Figure 2. 7: Scheme of transformation of titanate and titania nanostructures.⁴⁵

2.3.4 Composite photocatalysts

Composites are also gaining popularity as photocatalysts. Since the recombination rate of electron and hole pairs play the dominant role in slowing down overall photoreaction, it is beneficial to promote their separation in order to promote the forward reactions useful for the intended application. This can be achieved via interfacial charge transfer in composites. Several methods and materials exist^{67, 71-73}. Early reports of “bi-functional catalysts” used in the photo-cleavage of water claims that quantum yield of hydrogen increased with the addition of Pt and RuO₂ nanoparticles to the surface of TiO₂ as shown in Figure 2.8⁷⁴. Pt and RuO₂ nanoparticles were deposited on the surface of TiO₂ powder and the 3 components form a closed circuit photo-electrochemical cell. Here, the Pt particle acts as an electron trap and the RuO₂ particle acts as the hole trap. As a result, electrons that migrate to the surface of Pt react with water and form H₂. Holes that migrate to the surface of RuO₂ react to form O₂. This actively intercepts the backward recombination reaction.

Figure 2. 8: Schematic illustration of the photoinduced events leading to water decomposition.⁷⁴

Another way of creating composite photo-catalysts is to couple 2 types of semiconductors together. This also works on improving the efficiency of a photo-catalytic process by increasing the charge separation and extending the energy range of photo-excitation for the system. Such an example is illustrated in Figure 2.9. The positions of the band edges are relative to the vacuum level. Should the energy of the excitation light be insufficient in exciting TiO_2 , it will be sufficient in exciting CdS (which has a smaller band-gap of 2.5 eV). Thus, an electron in the valence band of CdS jumps to conduction band upon light irradiation. Accordingly, the hole that is newly formed in the valence band remains there while the electron makes an energetically favorable jump to the conduction band of TiO_2 . This series of processes effectively enhances charge separation and allows the free electron and hole to react with adsorbents on the surface.⁷⁵

Figure 2. 9: Photoexcitation in semiconductor-semiconductor photocatalyst.⁷⁵

Titania composites can also be created by mixing different phases of TiO_2 together. The most famous success is the commercial powder Degussa P25. P25 is

manufactured by an Aerosil process in which titanium tetrachloride is subjected to hydrolysis at elevated temperature.⁷⁶ It has a composition of 70% anatase and 30% rutile phase and has been used as a benchmark for testing photo-activity in a large number of publications. Ohno et.al reported that the anatase and rutile phases exist as separate single crystalline particles where their average diameters were estimated to be 25 and 85 nm respectively. In solution, the anatase and rutile phases mix in such a way that the small anatase particles load onto the larger rutile particles and forms good contact.⁷⁷ It is understood that the difference between the conduction band edge of the two phases produces irreversible charge transfer between anatase (bandgap 3.2- 3.3 eV) to rutile (bandgap 3.0- 3.1 eV) since the anatase conduction band is aligned 0.2 eV higher than that of rutile. The photo- generated charges are efficiently separated and can take part in useful redox reactions. This mixed phase structure provides a synergistic effect (attributed to good crystallinity resulting in low count of defect centers and electron-hole separation due to interfacial charge transfer) for good photo-activity under UV irradiation. The understanding of such a system helps in designing an efficient photocatalyst since the theory should be applicable for other systems. The key is to construct a sufficient difference in the conduction band levels of the phases to create an irreversible charge transfer. Other studies have since emerged to study the interaction of mixed phases and their effectiveness.^{14, 26, 27}

Mixed phases of titanate and TiO_2 are also beginning to generate popular interest in photocatalysis. Studies have been performed in creating nano- composites of several kinds of titanate phases with titania. Zhu et. al grew anatase nanocrystals onto titanate nanofibers via a controlled reaction with dilute acid as shown in Figure 2.10.^{78, 79} The two

step process involved first fabricating sodium titanate nanofibers by hydrothermal reaction of titanium sulphate in concentrated NaOH solution. This was followed by ion exchange into hydrogen titanate nanofibers by washing in HCl solution. They demonstrated that phase transition of titanate and anatase could be achieved by controlling reaction conditions during ion exchange as shown in Figure 2.11.⁷⁹ The phase transition was thought to be a topochemical process where there was incomplete conversion of titanate to anatase at low temperatures. As hydrogen titanate nanofibers dehydrate from acid reaction, the TiO_6 structural units rearrange themselves to form anatase instead of titanate dissolving completely into individual atoms and recrystallizing into anatase. This composite fiber performed better than pure hydrogen titanate in the degradation of synthetic dye sulforhodamine (SRB) under UV irradiation. Although they did not provide clear justification behind the improved photocatalytic performance, this work provides a good platform and motivation in designing nanoscale titanate- anatase systems suitable for photocatalytic applications.

Figure 2. 10: HRTEM image of a titanate nanofiber covered with anatase crystals from a phase conversion reaction at 373 K.⁷⁸

Figure 2. 11: Scheme of phase transition between sodium and hydrogen titanates, anatase and rutile by the wet chemical process.⁷⁹

In another study, Zheng et. al. synthesized nanofibers with mixed phases of TiO_2 (β) and anatase by heating pre-made hydrogen titanate nanofibers via hydrothermal reaction between 300 to 700 °C.⁵³ During hydrothermal heating, TiO_2 (β) was converted into anatase and the phase composition was found to vary according to heating temperature. They also reported that all the mixed phase nanofibers exhibited higher photocatalytic activity in the degradation of SRB dye under UV light as compared to both of the pure phases. Such an improvement was due to efficient charge transfer between titanate TiO_2 (β) and anatase on a nanoscale level as shown in Figure 2.12. The stable interface was a result of the two phases having intimate and well matched lattice planes and sufficient difference in band-gap (where $\text{TiO}_2(\beta)$ bandgap(3- 3.22 eV) is slightly narrower than that of anatase (3.2- 3.3 eV)) as well as band edge.

Figure 2. 12: Schematic describing possible irreversible charge transfer process for mixed- phase $\text{TiO}_2(\beta)$ and anatase nanofibers under UV illumination. Process (I) shows the interfacial electron transfer from anatase conduction band to $\text{TiO}_2(\beta)$; Process (II) shows the interfacial hole transfer from anatase valence band to $\text{TiO}_2(\beta)$ and Process (III) shows the holes move to the surface of $\text{TiO}_2(\beta)$ to take part in oxidation reaction.⁵³

Such nanoscale composites demonstrate the importance in the design of mixed phase materials in order to exploit the huge advantage of interfacial charge transfer for efficient photoactivity. Up to now, most studies have only focused on the improvement in photoactivity under UV illumination since both titanate and titania are sensitive only to UV light.

2.4 Photocatalytic platforms and testing

There are many test vehicles used for photoactivity measurements. Commonly, coloured dye degradation offers a straightforward and visual method of detecting photoactivity. This was a popular method of testing photoactivity of TiO_2 under UV light.⁸⁰⁻⁸⁴ The degradation was tracked by spectroscopic measurement of the dye

absorption peak. The practical motivation behind dye degradation lies in the huge amount of waste dyes (about 15%) which is lost in the dyeing process. The improper disposal of this dye waste causes harm to the waters, environment and marine life as dye molecules are often complex and hard to break down.⁸⁵ The affinity between dyes and TiO_2 was also heightened by the usefulness of dye sensitized solar cells⁸⁶ whereby the dye, photo-excited by solar light, injects an electron into the conduction band of titanium oxide electrode. The dye itself is regenerated by electron donation from an electrolyte. Overall, the device generates electric power from light without suffering permanent chemical transformations.

As more progress in the advancement of TiO_2 was made, the application of dyes as a means to determine photo-activity became more of controversial. Much of the research began to focus on extending the absorption of TiO_2 from the UV into the visible light range in order to improve the effectiveness of TiO_2 photocatalysis under solar light. Yet, coloured dyes themselves absorb visible light and undergo photoexcitation. When photocatalysts are applied in these dyes under visible light, the excited dye molecule injects an electron into TiO_2 which is now excited to further catalyze the breakdown of the dye. The process is termed photo-sensitization and the process of dye breakdown becomes complicated and makes for a complex study.⁸⁷ Many previous studies also do not authenticate complete mineralization of MB but presume its breakdown by observing its discoloration. This may not be accurate as some dyes discolour upon photo-excitation but do not experience molecular breakdown.⁸⁸ Nevertheless, dyes remain a target for organic pollutant degradation especially for emerging surface adsorption studies.^{62, 89} The

key is to discern if the contribution towards enhanced photoactivity sources from the material itself or the sensitized dye and establishing evidence of its complete breakdown.

Other forms of photocatalytic testing breaks down other dangerous organic compounds such as phenols⁹⁰⁻⁹² and acids^{58, 59}, CO₂ reduction⁹⁰ and water splitting for hydrogen energy^{71, 91-93}, etc. Quoting renowned photocatalyst researcher Professor Bunsho Othani at the 14th TiO₂ Conference, *Niagra Falls*, “No photocatalyst is best at degrading every organic compound.” Because of the complexities behind a multi-faceted photocatalysis reaction, it is important to apply the suitable photocatalyst to a suitable pollutant in order to maximise efficiency and effectiveness.

2.5 Niche in current photocatalytis research

A photocatalytic material must be excited by light and thus produce electron hole pairs which must then engage in chemical reactions with the organic reactant. Hence, there are essentially two processes that govern a complete photocatalytic reaction. One of which is *photo-excitation*. This process has been paid more attention to. In tracking the history of photocatalysis developments, it is obvious that much of the initial research was fixated upon improving photo-excitation; an understandable justification, since the popularity of photocatalysis begun with TiO₂. This led researchers to capitalize on the material's effectiveness and extend its photo-excitation responsiveness to visible light as described previously. While this is a very practical strategy, photo-excitation is merely one of the two important focuses in photocatalysis. Following band excitation, the excited electron and hole have to remain separated to interact with organic molecules (target reactant species) in order to degrade them. This interaction must take place on the surface

of the photocatalyst particle as this is the closest point of contact available between electron/hole and reactants. Failing to reach them, the electron/ hole recombines. Thus, the process can be very much facilitated by modifying the surface of the photocatalyst to promote adsorption of the target organic molecules so as to enhance electron/hole interactions. Adsorption is thus the key to the second process which is *degradation*. TiO_2 does not easily adsorb organics. Mills showed that only 7.4% of methylene blue (10^{-5} mol/L) was adsorbed onto TiO_2 surface.⁸⁸ Hence the limiting factor to the final degradation of organics might lie in the adsorption quality of the surface. This factor is gaining more attention in the recent years. Among some interesting work is the use of activated carbon together with TiO_2 to form a composite material.⁹⁴⁻⁹⁷ Activated carbon is highly adsorptive due to its pore structure and high specific area. It plays the role of co-adsorbent to TiO_2 and provides a synergistic effect in adsorbing and degrading organic compounds.⁹⁵ However, most of the existing work uses commercial activated carbon which makes it difficult to modify or tune the structure or properties of the end product. Also, the synthesis often involves multiple processes which complicate production. Other co-adsorbents such as clays, silica, zeolites and alumina also emerged but none have shown much promising improvement in photo-degradation.^{98, 99}

It is important to learn from the rich pool of research. In summing up the developments as simply:

1. Modifying electronic structure of TiO_2 by doping
2. Developing new materials
3. Use of mix phases
4. Adding co-catalysts
5. Designing unique morphologies
6. Adding co-adsorbents

This guides us further in the persistent quest to seek a photocatalyst that is not only efficient in capturing visible light but at the same time, strongly adsorbs organic molecules and effectively channels the charge pair for efficient degradation reaction.

CHAPTER 3: SYNTHESIS AND MATERIAL CHARACTERIZATION OF DUAL PHASE TITANATE/TITANIA PHOTOCATALYST

3.1 Synthesis of layered titanate/ TiO₂ composite nanoparticles

A sol-gel approach was chosen to synthesize the photocatalysts for the reasons that it is easy to tailor the recipe, and operates at a low temperature. This chapter details the synthesis conditions and parameters as well as the characterization techniques and description of photocatalytic experiments. The results of characterization will be presented and discussed in the following chapter. The results and correlation of the photocatalytic experiments are presented in Chapter 5.

The approach is based on commonly known sol gel synthesis of TiO₂ powders. In designing this synthesis procedure, the focus was to attempt a simple and non-complicated process to construct mixed phases of titanate and anatase with good interfaces at nano-scale level since most of the current research on mixed titanate and anatase composites required top down multi step procedures. Existing work on the phase transition between titanate and anatase reveals that both materials have the same TiO₆ building blocks which can re-arrange themselves according to synthesis conditions applied to base TiO₂ powder as described in section 2.3.4. Particularly at low temperature hydrothermal processes, titanates were the predominant phase in the entire composition. As such in this work, it is believed that a bottom- up sol-gel process in the presence of a

suitable alkali could create mixed phases of nanocrystalline titanate and anatase controllable by synthesis conditions.

Generally in sol gel synthesis, a molecular precursor like titanium chloride, butoxide or fluoride is hydrolyzed by water.^{20, 100, 101} The reaction speed can be controlled by adjusting the pH. Alcohol is also added to facilitate the miscibility of alkoxide and water as well as to homogenize the mixture. Nitrogen doping has been widely studied due to its success in extending the visible light responsiveness of some TiO₂ materials. Although it is commonly used in its gaseous state such as sintering the TiO₂ sample in the presence of ammonium gas at elevated temperatures^{102, 103}, Burda et.al was one of the first to introduce triethylamine as nitrogen precursor into a prepared colloidal solution of TiO₂ nanocrystals.¹⁰⁴ They reported nitrogen doping up to 8 atomic percent in the TiO_{2-x}N_x samples and improved methylene blue decomposition under visible light excitation. The idea of a one step amination process using triethylamine is conceived in this work to present the following modified sol-gel recipe.

Chemicals and materials used for synthesis were titanium isopropoxide [Ti (OC₃H₇)₄, 99.5%, Aldrich], ethanol [technical grade, 95%], acetylacetone [C₅H₈O₂, 99.5%, Fluka], triethylamine [N(CH₂CH₃)₃, 99.5%, Aldrich] and deionized water. Ethanol and acetylacetone (ACAC) were mixed in molar proportion of 20:1. Next, titanium isopropoxide (TI) and triethylamine (TE) were added simultaneously dropwise in molar ratio of 1:4. Lastly, 3 mols of deionized water were added and the mixture was allowed to stir for 30 minutes. Following this, 50ml of this clear yellow solution was measured into a 125 ml capacity stainless steel autoclave for hydrothermal reaction. The autoclave was then heated in an ambient oven at a certain temperature and duration. The

autoclave was cooled under ambient conditions. Thereafter, the gel was dried in an oven at 80 °C. The extracted powder was cleaned repeatedly with ethanol and deionized water via centrifuging process to remove traces of organic waste left from previous process. Lastly, the powder was re-dried in ambient oven at 80 °C and collected.

The main variable in play is the temperature. In this study, the samples were hydrothermally heated between ranges of 100 to 200 °C for a fixed duration of 3 hours. The focus of this study is to observe a trend in phase transition of the material across the temperature range and to determine an optimum synthesis temperature which gives the best photocatalytic performance in degrading organic pollutant species. The structure of the synthesized powders will be explored in detail. All the samples are denoted accordingly to the hydrothermal temperature or time subset for the convenience of referencing. The samples in the temperature study heated for 3 hours are denoted S100, S130, S160, S170 and S200 as shown in Table 3.1.

Table 3. 1: Table of samples in Temperature Study.

Sample	S100	S130	S160	S170	S200
Temperature/ °C heated for 3 hours	100	130	160	170	200

In an extended study, synthesis duration was the parameter varied to study the effect of crystallinity on the structure and surface area. The samples were heated for duration of 1 week (168 hours) at several temperatures. The samples in the extended time study heated to 1 week are denoted T80, T100, T130 and T200 shown in Table 3.2.

Table 3. 2: Table of samples in Time Study.

Sample	T80	T100	T130	T200
Temperature/ °C heated for 168 hours	80	100	130	200

3.2 Material characterization

Crystal structure, chemical composition, surface morphology and optical properties are integral properties that constitute the material as shown in Figure 3.1. Much of the focus of this thesis lies in establishing a clear understanding of these properties and its influence on the photocatalyst's effectiveness. In particular, the crystal structure characterization of the layered titanate proved to be challenging as it is a reasonably new material and existing knowledge of its crystal structure is incomplete. This work contributes towards the knowledge of this material. An extensive range of characterization techniques were required to understand the unique composite material. The results of characterization are presented in the following chapter.

Figure 3. 1: Properties to be studied.

3.2.1 Crystal Structure

A few techniques were used in conjunction to study the crystal structure of the photocatalyst; namely, XRD, Rietveld analysis, TEM and computation.

X-ray diffraction patterns of the powders were recorded using a Shimadzu LabX-6000 diffractometer of CuK α radiation ($\lambda=1.5418^\circ \text{ \AA}$) equipped with a secondary graphite monochromator. A step size of 0.02° over 2θ ranging from 5 to 80° was used with scanning rate set at 0.2° per minute.

Computation was also used in conjunction with Rietveld as an iterative process to produce the best fitting structure. Electronic structure calculation of protonated titanate was performed within framework of Density functional theory (DFT) using CASTEP, which uses plane-waves basis and ultrasoft pseudopotentials. A kinetic energy cut-off of 400 eV was employed to describe the wave-functions. The generalized gradient approximation (GGA) with PBE functional is used for the exchange-correlation potentials. The self consistency criterion was set to SCF 10^{-6} eV . Symmetry constrained optimization of fractional co-ordinates and lattice parameters was carried out until the

forces on each atom reduce to 0.05 eV/Å and stress components reduce to 0.05 GPa. Monkhorst-Pack K point grid of $2 \times 3 \times 3$ was selected to plot the density of states (DOS) on the optimized geometries. The fractional coordinates of the protonated titanate discovered in this work has been known in existing literature.

In order to find out the stable fractional co-ordinates, $\text{Cs}_2\text{Ti}_5\text{O}_{11} \cdot (1+x)\text{H}_2\text{O}$ was selected as starting structure.¹⁰⁵ This material shows similar strongest diffraction peak to the synthesized photocatalyst. In addition, it is one of the well established titanate crystal structure available as reference and was used as a start up material for conversion into hydrogen titanate in earlier works.^{47, 106} The positions of Cs^+ ions were manually replaced by H^+ . A complete geometry optimization was performed to obtain a relaxed and stable structure configuration. Following which the cell parameters were constrained to that obtained by Le Bail approximation. This structure was re- inputted into TOPAS for further refinement until the structure converged.

HRTEM measurements were performed on Jeol 2100-F Transmission electron microscope operating at an accelerating voltage of 300 kV. The samples were carefully prepared by ultra-sonicating some composite powder in ethanol. The suspension was then dropped onto carbon coated copper grids and dried. Fast Fourier transform, FFT was processed using the high resolution images to study the diffraction patterns of the selected particles.

Extended X- ray absorption fine structure, EXAFS was performed using XDD beamline at the Singapore Synchrotron Light Source to further probe the local structure of the new material.

3.2.2 Chemical composition

Chemical compositions of the samples were probed using TGA, FTIR as well as XPS techniques.

Thermal analysis was carried out using TA Instruments HR 2950 Thermogravimetric Analyzer (TGA) under nitrogen gas flow. The thermal profile was fixed for all samples; first holding isothermal at ambient temperature for 240 minutes to dry off all surface moisture, followed by heating at 5 °C/min to 700 °C.

Fourier Transform spectroscopy, FTIR was also used to investigate surface properties of the powder using Perkin Elmer Instruments Spectrum GX FTIR Spectrometer. Powders were mixed with standard KBr and pressed into thin pellets. The spectral range was 400- 4000 cm^{-1} and a total of 30 scans were recorded at a resolution of 4 cm^{-1} averaging each spectrum.

The nature of dopant species were analyzed using X- ray photoelectron spectroscopy, XPS (Kratos Axis ULTRA). All binding energies were referenced to adventitious carbon C1s peak (284.1 eV). CASA XPS software was used for peak fitting.

3.2.3 Morphology and surface

Specific surface area was determined using a Micromeritics ASAP 2020 surface analyzer based on the Brunauer Emmett Teller, BET theory. The samples were outgassed under vacuum and heated to 100 °C.

The morphology of the photocatalyst particles were observed using HRTEM imaging.

3.2.4 Optical property

Optical properties of bulk powders were measured on Perkin Elmer Lambda 900 UV-Visible spectrometer in diffuse reflectance spectroscopy mode over the spectral range of 200- 800 nm.

3.2.5 Photocatalytic experiments

Methylene blue dye was chosen as primary candidate for photocatalytic degradation activity of the prepared powders in order to study both adsorption as well as degradation effects. Solutions of the dye were prepared by mixing with deionized water at 20 ppm concentration. 10 mg of photocatalyst powder was dispersed in 100 ml of each MB solution.

An adsorption isotherm test was carried out by varying concentrations of methylene blue from 5 to 50 mg L⁻¹ (5 to 50 ppm). For each test, 10 mg of adsorbent was added to 100 mL of MB solution. The equilibrium concentration was measured after adsorption saturation of each test was reached.

Control experiments were performed for mixtures in the dark as well as blank MB solutions under light irradiation. In addition, reference photocatalyst powder Degussa P25 TiO₂ was also tested as a platform for comparison of photocatalytic activity. The irradiation source was a 450W Newport Xenon Arc lamp with spectral range from 200-2500 nm. A short wave light filter was used to tune the transmission from 385 nm to 785 nm for near visible light irradiation to mimic solar spectrum. A cooling water filter was also attached to block IR-rays and prevent excessive heating. MB suspension was placed directly under the light source so that the irradiation was uniform over the surface of the

solution. During the experiment, the suspension was kept under stirring to ensure an aerobic environment for complete dye mineralization reaction.⁸⁸ Samples were taken at regular time intervals and underwent centrifuging. The spectral intensity measurements of the degraded dye were performed on a Shimadzu 2500 UV- Visible spectrometer. MALDI-TOF mass spectroscopy was performed to examine the intermediates formed during the reaction. It was recorded on a Shimadzu Biotech Axima ToF² MS instrument equipped with the delayed extraction option. Ionisation was achieved using N₂ laser source (337 nm). The analysis was performed in reflectron mode without addition of any matrix and the instrument was calibrated using small-cal-mix samples.

The second photocatalytic experiment involved the degradation of phenol. Since dyes are known to be photo- sensitizers, a target pollutant such as phenol that is neutral to visible light can be used to clearly demonstrate the enhancement of visible light absorption quality of the synthesized photocatalysts. Phenol is not easily adsorbed onto surfaces, thus setting it apart as a fairly different pollutant from Methylene blue dye and showcases the versatility of the synthesized material for differing applications.

Phenol solution (20ppm) was prepared in deionized water and the pH was kept neutral at pH 7. 100 mg of photocatalyst powder was dispersed in 100 ml of phenol solution along with 0.001 mol dm⁻³ of H₂O₂ solution. Commercial photocatalyst Degussa P25 was once more tested as a reference under the same conditions. During the experiment, the suspension was under constant stirring so as to ensure an aerobic environment for complete mineralization. The same light source and visible light filter for MB degradation was used for irradiation. Liquid samples were taken at regular time

intervals and centrifuged. Following which, the samples were filtered by a 0.2 μm cellulose membrane filter.

All samples were analyzed by HPLC and GC-MS. The phenol concentration and organic intermediates were quantified by HPLC (Agilent 1200 series) with a UV DAD detector. A RP-C18 column (Agilent Zorbax XDB C₁₈, 250 x 4.6 mm; 5 mm particles) was used as a stationary phase to separate the degradation products present in the reaction mixture. Mobile phase composed of Acetonitrile:water (60:40) with a flow rate of 1 mL min⁻¹ and the wavelength was adjusted to 269 nm.

Gas chromatography coupled with mass spectrometric analysis was carried out with Quattro micro GC Mass Spectrometer (RAB 241, Waters, USA) using DB-5 column (30 m x 250 μm x 0.25 μm) to identify the organic compounds present in the reaction mixture. Ultra pure helium was used as the carrier gas at a flow rate of 1.0 mL min⁻¹. The reaction mixture was initially in the aqueous form mixed with chloroform in order to extract the organic compounds from aqueous to organic phase and further taken into GC-MS analysis. The ramp of the analysis follows; initial column temperature was held for 2 min at 70 °C, ramped at 10 °C min⁻¹ to 280 °C, holding for two minutes at the same temperature. The sample was injected in the splitless mode. MS analysis was carried out with 70 eV as ionization energy, 6 kV accelerated voltage with solvent delay (3.5 minutes).

CHAPTER 4: RESULTS AND DISCUSSION- MATERIALS CHARACTERIZATION

The results of material characterization are presented in this chapter and discussed accordingly.

4.1 Crystal structure

Figure 4. 1: X-Ray diffraction patterns of samples treated at various temperatures (a) S100, (b) S130, (c) S160, (d) S170 and (e) S200. T denotes titanate and A denotes anatase phases.

Figure 4.1 presents the XRD patterns of the samples performed for temperature study varying from 100 °C to 200 °C. Across curves (a) to (c), the peaks appear to be

broad and have relatively low intensity; a characteristic of nano-sized crystals. The samples display low angle diffraction at 8.56° , 17.01° and 26.39° . As the hydrothermal temperature increases, the peaks grow sharper; an indication of improving crystallinity and nano-particle growth. Additional peaks at 37.78° , 48.77° and 62.86° also emerged in samples S130 (curve b) and S160 (curve c). No perfect match of the 3 strongest peaks can be found in existing database of crystal structures. However, the material is believed to be similar to a family of layered titanate materials that are generally known to diffract at low angles between 8 to 16° . Indeed, the first diffraction peak at 8.56° coincides well with first diffraction peak in a hydrated cesium titanate structure, $\text{Cs}_2\text{Ti}_5\text{O}_{11} \cdot 3\text{H}_2\text{O}$ (MATCH Entry number 00-038-0071) as shown in Figure 4.2.¹⁰⁵ Hence, it was believed that samples S100, S130 and S160 likely assimilated a form of hydrated titanate structure.

Figure 4. 2: Match profile of S160 sample with $\text{Cs}_2\text{Ti}_5\text{O}_{11}\cdot 3\text{H}_2\text{O}$.

Curve (d) of Figure 4.1 shows the crystal structure undergoing phase changes as the hydrothermal temperature increased to 170 °C for sample S170. The first two low angle peaks at 8.56° and 17.01° decreased and the third peak at 26.39° sharpened and shifted to 25.28°. Other distinct peaks also emerge. These peaks can be perfectly indexed to the well known anatase titanium oxide structure (PDF card #21-1272) having tetragonal system and lattice constants $a = 0.3785 \text{ nm}$, $c = 0.9614 \text{ nm}$. S170 is likely to assimilate a mixture of intermediate titanate phase evolving into anatase. Finally, in Figure 4.1e, the sample evolves completely into anatase at a temperature of 200 °C.

It is apparent that the crystal structure in samples treated at the low temperatures (S100, S130 and S160) was unique and presently not accounted for in existing works. In fact, most existing reports of titanates often reference structures to the few titanate

materials with known crystal structures stating that the structure is “similar” to the referenced titanate.^{39, 46, 65, 107} The lack of structural data of titanates is due to the complexity behind structure calculation as a result of their complicated atomic arrangements.

There are two challenges in solving the titanate crystal structure. This is due firstly to poor crystallinity and broad reflections. Secondly, the titanate peaks overlap with anatase, creating more difficulty in structure solution as compared to a pure phase material. As sample S160 displayed the best crystallinity, it was selected for further heat treatment to improve the quality of its diffraction peaks. The as-synthesized powder was pressed into pellets and vacuum sealed in a quartz tube. They were then heated to a temperature of 120 °C for 1 week. After which, the pellets were grounded into fine powder once more. The same as-synthesized sample was also calcined in an open crucible at 500 °C.

Figure 4. 3: X-ray diffraction profile of (a) as-synthesized S160, (b) S160 after vacuum heat treatment and (c) transformation into anatase after annealing. T denotes titanate phase and A denotes anatase phase.

The XRD result of the S160 vacuum heat treated powder in Figure 4.3b shows the emergence of strong crystalline peaks from $2\theta = 25.28^\circ$ onwards; this matches well with the known data of anatase mentioned above. The results indicate a growth in crystallinity of anatase in the presence of the low angle titanate phase. It is important to note that the integrity of the titanate phase was well preserved despite the heating process whereas calcination at 500°C causes the titanate structure to transform completely into anatase TiO_2 as shown in Figure 4.3c.

The vacuum heat treatment not only successfully improved the crystallinity, but also ascertained the presence of 2 phases. The pressing of the powder in pellet form enhanced the sintering process for dramatic improvement of crystallinity in the anatase phase that previously gave broad low intensity diffraction peaks. In another experiment, heating the as synthesized S160 powder at 120°C in an open furnace for the same

duration rendered no change in the crystal structure. It is believed that the pressure from the sealed environment enhanced the sintering of the nano-crystallite anatase phase. In addition to that, it helped in retaining the moisture in the hydrated titanate phase which preserves the integrity of its crystal structure. The same vacuum heat treatment was applied to samples S100 and S130 but no obvious changes were observed in the diffraction patterns.

The diffraction pattern obtained from vacuum heat treatment in Figure 4.3b was utilized for structure solution of the titanate phase and to determine the phase ratio of the 2 phases.

4.2 Hydrated layered titanate structural solution

As described in Chapter 3, a known structure of hydrated cesium titanate was used as a start up model to give a theoretical prediction of the crystal structure of the layered titanate in this work. Most titanates form layered structures from the ribbons of TiO_6 octahedras connected by their edges (Figure 2.6). Using CASTEP, the Cs ions were replaced by H ions and geometry optimization was performed on the structure. The optimized cell parameters obtained were $a = 2.431 \text{ nm}$, $b = 0.375 \text{ nm}$, $c = 1.503 \text{ nm}$ and $\beta = 117.16^\circ$. Figure 4.4 shows the model of $\text{H}_2\text{Ti}_5\text{O}_{11} \cdot 3\text{H}_2\text{O}$ after geometry optimization.

Figure 4. 4: Model of $\text{H}_2\text{Ti}_5\text{O}_{11} \cdot 3\text{H}_2\text{O}$ after geometry optimization performed using CASTEP.

Rietveld refinement using TOPAS was performed on the vacuum heat treated sample in Figure 4.3b. Le Bail “pre-fitting” delivered a preliminary approximation of the titanate unit cell. As Le Bail fitting concerns itself with fitting a “structure-less” profile, it gives a good calculation of the unit cell without the complication of the added structure contents. The parameters obtained were $a = 2.343 \text{ nm}$, $b = 0.375 \text{ nm}$, $c = 0.908 \text{ nm}$ and $\beta = 117.16^\circ$ in monoclinic arrangement. Figure 4.5 shows the Rietveld fitting for the preliminary refinement assessment.

Figure 4. 5: Rietveld refinement of the S160 under vacuum heat treatment. The observed pattern is presented in blue, the calculated pattern in red and the difference plot is given in grey.

Comparison between computation and refinement cell parameter results reveal that the a and b parameters were in close agreement. However, the c parameter of the computed structure was obviously too large in comparison to the calculated rietveld value. From Figure 4.4, it is observed that the c parameter of the monoclinic cell is governed by the number of TiO_6 octahedra units connected within the cell. By calculation, only 3 octahedra units could fit within the predicted rietveld structure. Following which, the model was recreated within CASTEP to accommodate 3 octahedra units. Geometry optimization was again performed to verify if the structure converged close to the predicted cell parameters. Careful measures were also taken to restraint the water molecule as a single molecule. Finally, the structure was relaxed to ensure the atoms were in their least free energy states.

The iterative process between computation and Rietveld refinement to solve the titanate structure continued. The final structure was fitted together with anatase TiO_2 and this gave a good fit in Rietveld refinement. Only the scale factors, lattice parameters, size broadening, strain broadening and an overall isothermal parameter for each phase were released as the analysis was impeded by the nanocrystalline and multiphase nature of the material, which resulted in broad, strongly overlapping reflections of both crystalline phases and a structured background. This indicates the presence of an amorphous phase or disorder in both phases. Figure 4.6 shows the final Rietveld plot. The 2 phases were confirmed to be hydrated layered titanate $\text{H}_2\text{Ti}_3\text{O}_7 \cdot x\text{H}_2\text{O}$ and anatase TiO_2 in a weight phase ratio of approximately 1 to 1.

Figure 4. 6: Final Rietveld refinement of the dual phase S160 photocatalyst under vacuum heat treatment conditions. The observed pattern is presented in grey, the calculated pattern and the difference plot are given in black.

Table 4.1 shows the lattice parameters and the Rietveld indices of the new hydrated layered titanate crystal structure. Figure 4.7 shows an extract of the proposed structure in [010] projection. It features corner- and edge- sharing TiO₆ and TiO₅ polyhedra which form infinite layers in the (011) plane, and are stacked in the [100] direction. The protons and the water are intercalated between these layers which also may accommodate reactants during the photocatalytic processes. The atomic parameters of this material are presented in Table 4.2. This crystal structure has been submitted to ICSD (Inorganic Crystal Structure Database) under the depository number CSD-422026.

Table 4. 1: Lattice Parameters and Rietveld indices of $\text{H}_2\text{Ti}_3\text{O}_7 \cdot x\text{H}_2\text{O}$.

Space-group	$C 2/m$ (12)
a	24.931(33) Å
b	3.7079(56) Å
c	10.255(23) Å
β	123.11(14)°
V	794.06(270) Å ³
R_{wp}	9.1 %
R_{p}	7.1 %
R_{exp}	4.5 %
R_{bragg}	3.9 %

Figure 4. 7: [010] projection of the crystal structure of $\text{H}_2\text{Ti}_3\text{O}_7 \cdot x\text{H}_2\text{O}$.

Table 4. 2: Atomic Parameters of $\text{H}_2\text{Ti}_3\text{O}_7 \times \text{H}_2\text{O}$.

Atom	Wyck.	x/a	y/b	z/c
H1	4i	0.41595	0	0.99762
H2	4i	0.45048	0	0.56749
Ti1	4i	0.23241	0	0.22797
Ti2	4i	0.18620	0	0.48041
Ti3	4i	0.15643	0	0.80512
O1	4i	0.18919	0	1.01820
O2	4i	0.33080	0	0.25864
O3	4i	0.16821	0	0.26659
O4	4i	0.27893	0	0.48729
O5	4i	0.10872	0	0.44156
O6	4i	0.22866	0	0.71562
O7	4i	0.07743	0	0.71948
O8	4i	0.04144	0	0.14419
H3	4i	0.08191	0	0.24410
H4	4i	0.01232	0	0.18308

The anatase phase is believed to form from the rearrangement of TiO_6 octahedra in the titanate phase and therefore shows poorer crystallinity, resulting in low XRD intensity peaks. HRTEM further confirms the presence of 2 phases in the as synthesized S160 photocatalyst. Figure 4.8 shows the S160 HRTEM image of a single particle. Many interfaces can be observed within the particle, indicating the presence of multiple phases in intimate contact.

Figure 4. 8: HRTEM image of S160 displaying the presence of multiple crystalline interfaces.

A fast fourier transformation study of a larger area in the same particle shows two sets of diffraction pattern (Figure 4.9 inset). The two patterns match well with tetragonal anatase TiO_2 (strong spots) and the calculated structure of monoclinic hydrated layered titanate (weak spots) formulated in the earlier section. Color imaging clearly illustrates the presence of both phases interspersed within the particle. From Figure 4.9, it is also observed that the anatase (cyan color) and titanate phases (red color) appear to be present in fairly equal proportions and the nanocrystallites share intimate interfaces. Therefore, both TEM and XRD reveal a dual phase structure of titanate and titania in the S160 photocatalyst. It can be noted that titanate and antase both possess common structural

features in that their crystal lattices consists of octahedras sharing four edges and zig-zag ribbons thus the two phases can have well-matched interfaces.⁷⁹

Figure 4. 9: HRTEM image of S160 with two phases distinguishable by color. The inset shows the diffraction pattern obtained from the FFT study of monoclinic titanate (weak spots) and tetragonal anatase (strong spots) phases.

XANES and EXAFS analysis was carried out to further probe the bonding structure of the dual phase material. Anatase TiO_2 , Barium orthotitanate Ba_2TiO_4 and Fresnoite $\text{Ba}_2\text{TiSi}_2\text{O}_8$ were used as references to investigate the Ti coordination geometry

in the S160 sample. TiO_2 contains Ti in sixfold- coordination, $\text{Ba}_2\text{TiSi}_2\text{O}_8$ has Ti in fivefold coordination and Ba_2TiO_4 in fourfold coordination. Pre- edge structure of Ti K-edge X- ray absorption near- edge structure (XANES) spectras of Ba_2TiO_4 , $\text{Ba}_2\text{TiSi}_2\text{O}_8$, TiO_2 and dual phase S160 are shown in Figure 4.10. The pre- peak in S160 sample differs from the other peaks. This suggests that the Ti bonding is not limited to one type of bonding and indicates a non centro- symmetric geometry likely to be Ti-5O, Ti-4O or some form of distorted structure.

Figure 4. 10: Pre- edge Ti K-edge XANES spectra of Ba_2TiO_4 , $\text{Ba}_2\text{TiSi}_2\text{O}_8$, TiO_2 and dual phase S160.

EXAFs analysis was performed by applying Fourier transformation (FT) on the Ti K-edge of S160. The resultant peaks in FT give the distance (R) between the absorber Ti and the backscatters O. Only the first peak representing the first coordination sphere was fitted with the theoretical data of the references. Figure 4.11 shows the Fourier transforms and least square fittings of the first coordination spheres after back Fourier transforms of TiO_2 (Fig 4.11 a,b), $\text{Ba}_2\text{TiSi}_2\text{O}_8$ (Fig 4.11 c,d) and BaTiO_3 (Fig 4.11 e,f).

Figure 4. 11: (LEFT) Fourier transforms of pre- edge Ti K-edge of Dual phase S160 fitted with (a) TiO_2 (c) $\text{Ba}_2\text{TiSi}_2\text{O}_8$ and (e) BaTiO_3 . (RIGHT) Corresponding least square fitting back Fourier transforms with (b) TiO_2 (d) $\text{Ba}_2\text{TiSi}_2\text{O}_8$ and (f) BaTiO_3 .

All least square fitting were performed using theoretical phase shift and amplitude of the reference. The results show that all the fitting for Ti purely in 6, 5 and 4-

coordination were poor; reconfirming previous presumption from pre-peak analysis that the structure is distorted or in mixed coordination. In particular, it is observed in Figure 4.11 (a) that the sample peak shifts to a lower R value compared to the peak for Ti in sixfold- coordination. A mixture of sixfold (path one) and fivefold (path two) - coordination was considered and the results are shown in Figure 4.12.

Figure 4. 12: (a) Fourier transforms of pre- edge Ti K-edge of Dual phase S160 fitted with TiO₂ and Ba₂TiSi₂O₈. (b) Corresponding least square fitting back Fourier transforms.

Both pre-edge fitting (Figure 4.12 (a)) and least square fitting (Figure 4.12 (b)) show good fits. XANES and EXAFS analysis agree well with the structure calculated in previous refinement section where the structure shows TiO₅ and TiO₆ polyhedras within the titanate crystal (Figure 4.7). The anatase phase also has sixfold- coordination. The experimental and theoretical R values from Fourier transformation are also in close agreement and are shown in Table 4.3.

Table 4. 3: Comparison between theoretical subshell values from sixfold (TiO_2) and fivefold ($\text{Ba}_2\text{TiSi}_2\text{O}_8$) coordination to experimental values for dual phase S160.

Paths	R [$\text{\AA}$]	R [$\text{\AA}$] theory
First subshell Ti-O from TiO_2	1.879 (± 0.078)	1.9465
Second subshell Ti-O from $\text{Ba}_2\text{TiSi}_2\text{O}_8$	1.950(± 0.052)	2.0014

Upon establishing the titanate structure in S160 as $\text{H}_2\text{Ti}_3\text{O}_7 \cdot x\text{H}_2\text{O}$, TGA was performed on the dual phase sample S160 to estimate the degree of hydration of the sample in the as-prepared state. Since the titanate ultimately degrades to anatase, with the loss of water and correcting for the roughly equal weight of each phase present, the degree of hydration (implicitly associated with the titanate phase) can be related to the measured weight loss.

Figure 4. 13: TGA analysis of weight loss for sample S160.

According to the thermogram (as shown in Figure 4.13), the small initial decrease in weight at low temperature constitutes loss of surface moisture due to pre-drying in flowing N₂. The main loss occurs in two distinct stages; from 50-150 °C and 200-450 °C, in roughly a 1:2 weight proportion. The 1st stage is probably due to loss of some crystal water, while the second stage presumably corresponds to loss of any residual crystal water as well as degradation of the titanate structure, with loss of an additional molecule of constituent water (*vide infra*). The weight change totals up to ~15%. It is difficult to verify exact number of water molecules present due to two uncertainties. Firstly, the evaluated composition of titanate and titania in approximately 50:50 phase proportion represents only the crystalline phases. There could be certain amorphous phases which are unaccounted and contribute to partial weight loss. Secondly, there might be trace organics residual from synthesis which burn off during TGA analysis and also contribute to weight loss. Hence, it is postulated that the final formula unit be H₂Ti₃O₇.*x*H₂O where 1<*x*<3. The basis of this recommendation is referenced to similar work on pure titanates⁴⁷.

4.4 Effect of synthesis parameters on surface area, crystallinity and phase transition

It was observed earlier in this chapter that varying hydrothermal temperature caused changes in the crystallinity and phase content. BET technique was employed to measure the surface areas of the as-synthesized samples. High surface area is regularly suggestive of enhanced photocatalytic performances since it presents more active sites for photoreactions to take place upon. The results are as seen in Table 4.4.

Table 4. 4: BET surface area for as synthesized powders.

Sample	S100	S130	S160	S170	S200
Specific Surface area (m ² /g)	224.7	234.2	179.7	121.9	75.1

Pure titanates typically have high surface areas ranging from 130 to 300 m²/g^{60, 61} whereas anatase samples tend to possess low surface areas ranging from 10 to less than 100 m²/g.^{108, 109} P25 was measured to be 51.4 m²/g. Hence as far as estimating the phase content goes, a high surface area is indicative of more titanate being present and a low surface area suggests that more anatase is present. The results show that as the hydrothermal processing temperature increased, surface area gradually decreased; signifying the titanate phase decreased in phase ratio and the anatase phase increased accordingly. S100 and S130 displayed close to equal surface area, indicating that the samples did not undergo much transition at the low temperature range between 100 to 130 °C. Both samples are titanate rich and the phase contents should be approximately the same. The surface area for S160 decreased to 179.7 m²/g; demonstrating a significant transition from dominating titanate phase to more anatase phase emerging. From previous structure solution, the post vacuum heat-treated sample was found to have titanate and anatase in approximately equal ratios. It is not expected that the as synthesized S160 possess the same phase content as the former since the added process might have altered crystallinity and helped in some anatase transformation process. However, it is believed that S160 phase content should not deviate too much from this ratio since the XRD

comparison of the strongest titanate peak intensities were similar (see Appendix I for comparison of diffraction peak).

An additional set of experiments was performed whereby hydrothermal heating duration was extended to 168 hours. The purpose of extending to such a considerably long duration was to ensure adequate time for the particles to grow and crystallize at the particular temperature ensuring maximum crystallinity could be reached. By comparing the surface areas of the samples heated for 3 hours and that heated for 168 hours, a relation between phase content, surface area and crystallinity can be made. Table 4.5 shows the results for BET surface area in the time study and the accompanying XRD profiles are displayed in Figure 4.14.

Table 4. 5: BET surface area for additional set of synthesis conditions.

Sample	S80	T80	T100	T130
Specific surface area (m ² /g)	197.3	287.0	237.6	63.1

Figure 4. 14: XRD diffraction profiles of time study BET samples (a) T80, (b) T100, (c) T130 and (d) T200.

Sample S80 was synthesized at 80 °C for 3 hours. Its surface area was found to be 197.3 m²/g, lower than all the other samples. It is deduced that the sample was highly amorphous due to the low synthesis temperature and short hydrothermal heating duration. T80 underwent the hydrothermal process at temperature of 80 °C but the duration was extended to 168 hours. This ensures greater crystallinity to be obtained at the specified temperature. The surface area for T80 was found to be 287.0 m²/g; the highest of all the samples. The high surface area is characteristic of pure titanate materials.

T100 was also hydrothermally treated for 168 hours at 100 °C and the surface area deviated very little from S100 that was heated for 3 hours. A shorter heating condition was sufficient to achieve maximum crystallinity at 100 °C; also observed with similar XRD profiles. T130 was treated at 130 °C for 168 hours and the surface area dropped to 63.1 m²/g. Its XRD profile shows that it has transformed into pure anatase phase; the extended heating duration provided sufficient time and energy for a complete rearrangement into anatase phase.

From the BET surface area results, an estimation of titanate and anatase phase composition can be made in Figure 4.15. It is clear that the as synthesized materials exists as dual phase structures from 100 to 170 °C in decreasing titanate phase content. The possibility of applying Rietveld refinement for predicting exact phase composition is nearly impossible for the as synthesized samples due to the less than ideal degree of crystallinity and likely presence of amorphous phases. This study can be applied as a qualitative guide for the estimation of phases in the samples and the highlight remains on the nature of the dual phases present and their synergetic cooperation in photocatalytic reactions.

Figure 4. 15: Estimation of titanate and anatase phase composition from BET surface area.

4.3 Optical absorption

Figure 4.16a displays a visual comparison of the as synthesized powders in the original temperature study set. From observation, S100, S130 and S160 appears to be a similar shade of deep yellowish orange which is a characteristic feature of N doped samples.^{104, 110} S170 appeared brownish in color and S200 was a light shade of beige. The changes in color of the powders point towards a shift in light absorption as shown in diffuse reflectance spectroscopy results in Figure 4.16b. S100, S130 and S160 show comparable absorption curves that extends into most of the visible light region. S170 displays a kink in the curve at approximately 380nm and continues to absorb in the visible region but lesser than the former powders. S200 shows typical absorption edge of

TiO₂ anatase which absorbs strongly in the UV region albeit exhibiting some tailing from 400 nm into 700 nm.

Figure 4. 16: Visual comparison of as synthesized powders (b) Diffuse reflectance spectroscopy curves displaying absorbance of corresponding powders.

The interesting results suggest some form of doping in the crystal structures which arises in the ability of the material to capture visible light energy. In the one pot sol gel synthesis process, hydrolysis and condensation reactions take place:

Upon the addition of water, hydrolysis reaction takes place whereby the hydroxyl group undergoes nucleophilic substitution giving rise to the exchange of alkyl (OR) group. Following this, condensation reaction takes place to form Ti-O-Ti bonds. It is predicted that in the presence of amines, O-Ti-N bonds may also form from substitutional replacement of oxygen by nitrogen atom.¹¹¹ Alkaline and basic mediums have been known to encourage the formation of titanates at low synthesis temperatures.⁷⁹ Thus, it is believed that the oxynitride forms in the titanate phase which is the more abundant and favoured phase to evolve at low hydrothermal temperatures. More complicated bonds may form and this is studied in detail in the following section where FTIR and XPS are used to probe chemical bonding on the surface and the dopant concentration of the synthesized photocatalysts.

4.3 Surface bonding

Figure 4.17 shows the FTIR spectra results. The features appearing between 400 to 1250 cm⁻¹ are characteristic of the lattice absorption of O- Ti- O bonding in the samples. Samples S100, S130 and S160 displays broad adsorption band from 2900 to 3600 cm⁻¹ attributed to O- H stretch region. S170 shows a shallower O-H stretch

adsorption peak. The samples also exhibit peak at 1630 cm^{-1} due to $\delta_{\text{H-O-H}}$ (O- H bending) of adsorbed water molecules. The O-H peaks are less pronounced in S200 and P25 sample which indicates that little moisture is present in the samples. 2 peaks at 1457 and 1393 cm^{-1} observed in S100, S130 and S160 can be referenced to the presence of nitrogen affiliated to NH groups or nitro compounds^{112, 113}. A band was also detected at 1060 cm^{-1} for samples S100, S130 and S160. The appearance of this band is attributed to carbon species in titanium and oxygen environments.⁹⁴

The typical surface NO_2 peaks that emerge at 1618 , 1318 and 750 cm^{-1} are not observed. At the same time, the peaks of triethylamine at 2950 , and 1000 to 1200 cm^{-1} are not seen; thus indicating there are no traces of amine residues contaminating the surface.¹¹⁰ It is important that the surfaces are free of organic contamination as the residues may complicate the actual organic waste degradation in later applications.

The position of O- Ti- O transmission feature at 1241 cm^{-1} sits at lower energy for the first 3 samples. This could be due to structural changes in the Ti- O lattices caused by nitrogen inclusion and difference in bonding for the dual phase samples. S170 shows a slight shift in this peak to the right indicating a change in Ti-O bonding. As mentioned in previous XRD findings, S170 is likely a mixture of 2 phases- an anatase phase and an intermediate titanate phase that is transforming into anatase due to the increase in heating temperature. The FTIR results agree well with that since the O-Ti-O adsorption peak sits between S160 and S200. S200 and P25 show similar O-Ti-O peak at 1104 cm^{-1} . OH groups present on surface of sample S100, S130, and S160 can facilitate the adsorption or trapping of charged species that aids in organic waste degradation.¹¹⁴

Figure 4. 17: FTIR transmission spectrums of (a) S100, S130, S160, S170 and S200.

4.4 Dopant formation and chemical composition

XPS study was also performed to probe the dopant species and concentration. All peaks were calibrated to carbon C 1s peak at 284.6 eV (adventitious carbon). Figure 4.18 illustrates the high resolution spectras of elements present in the samples nitrogen (Figure 4.18 a), oxygen (Figure 4.18 b) and titanium (Figure 4.18 c). Similar to diffuse reflectance UV-Vis absorption results shared previously, samples S100, S130 and S160 displayed comparable high resolution spectra profiles for all the elements. It can be inferred that the bond nature of all the elements are alike in these 3 samples. Obvious changes in the elemental profiles of S170 was observed. Nitrogen peak was not apparent indicating the absense of nitrogen in the sample. Oxygen and titanium both showed the emergence of strong peaks at 531.3 and 460.3 eV respectively. The differences in peak positions and broadening is due to the transition whereby the dual phase material undergoes major phase change from titanate rich to anatase rich composition supported by other chacterization described earlier. The titanate structure is futher destroyed to re-arrange into anatase thus resulting in the changes in binding energy; presenting S170 as an intermediate structure whereby phase transformation is incomplete. O 1s and Ti 2p peaks were oberved to have shifted to lower binding energy and narrowed in peak width.

Figure 4. 18: High resolution XPS spectrums of (a) nitrogen N1s, (b) oxygen O1s and (c) titanium Ti 2p for samples S100, S130, S160, S170 and S200.

Fitting was performed on all the elemental profiles. The peak fits of S100, S130 and S160 are also in close approximation. Nitrogen was found to be present in these three dual phase materials. Figure 4.19 shows peak fits of single N 1s peak with binding energy centering at 401.27eV for S100 (Figure 4.19 a), 401.48 eV for S130 (Figure 4.19 b) and 401.55 eV for S160 (Figure 4.19 c), likely attributed to oxynitride bonding that is a consistent feature of nitridation process.^{104, 115} It is unlikely that Ti- N bonds are formed as N 1s found in TiN typically measures at 397.2 eV.¹¹⁶ These values are notably larger than the typical value of 397.2 eV in TiN as N 1s binding energy becomes higher if the formal charge of N is more positive such as in NaNO_3 (408 eV) as compared to a negative charge as in NH_3 (398.8 eV).¹¹⁵ Prokes et. al presented similar findings of N 1s peak at 401.3 eV and attributed it to Ti-O-N bonding.¹¹⁷ In addition to the O1 s peak at

530 eV (Ti-O bonding in TiO_2), they also reported an additional O 1s peak at a higher binding energy of 531.5 eV, which is a result of the nitridation process. Similarly, this higher binding energy peak was also observed in the deconvolution of the O 1s signals in S100, S130 and S160 as seen in Figure 4.20. This suggests an oxynitride formation and the successful inclusion of nitrogen into the Ti-O lattice, which in turn enhances visible light absorption.¹¹¹ Although it is shared in literature that the inclusion of a nitrogen atom as a dopant in place of oxygen in anatase reduces the valence state of titanium from Ti^{4+} to Ti^{3+} which is observed by a lower shift in Ti 2p binding energy, the same was not observed in this case. This is because the binding energies of titanate Ti 2p peaks are typically higher than that of titania.¹¹⁸ The Ti $2p_{3/2}$ peaks were found to be 458.57, 458.69 and 458.61 eV with separation energies of 5.73, 5.75 and 5.72 eV for the same samples S100, S130 and S160 as shown in Figure 4.21 (a), (b) and (c). This is consistent with earlier research and confirms that Ti exists solely as Ti(IV) in the synthesized samples.¹¹⁹

Figure 4. 19: Fitting of components for nitrogen N 1s for samples (a) S100, (b) S130, and (c) S160.

Figure 4. 20: Fitting of components for oxygen 1s for samples (a) S100, (b) S130, and (c) S160, (d) S170 and (d) S200.

The nitrogen dopant concentration was found to be 3.84, 3.59 and 3.75 atomic percent for S100, S130 and S160. The little fluctuation in the nitrogen concentration marks the stability of nitrogen doping up to temperature of 160 °C. Overall, visible light

absorption is markedly enhanced, as seen in the diffuse reflectance spectras previously where all three powders displayed similar absorption spectras extending into the visible light region.³² It is believed that the doping of nitrogen yields this effect. Liu et. al. reported that the space between the titanate interlayers encourages nitrogen species to migrate through to replace O in TiO_6 octahedras steadily and uniformly; a different process from N-doping in 3-dimensional anatase particles.⁶⁸ They detected a similar N 1s peak at 401 eV. Using density of states calculation, they found that the bandgap of protonated hydrogen titanate was reduced from 3.47 to 2.85 eV due to an upshift in valence band maxima from a mixture of N 2p and O 2p states. A similar conclusion could be drawn here. In this respect, the system is slightly more complicated with the presence of two phases. Possibly, it is the titanate phase that is nitrated since N 1s signal was lost from sample S170 and S200 due to the increase in temperature causing the transformation of titanate (Figure 4.18 a). On the whole, in addition to nitrogen species playing a predominant role in narrowing bandgap, the system benefits with the additional phase of anatase that encourages electron transfer and slows down the recombination effect. This will potentially improve its photocatalytic efficiency which will be discussed in the following chapter.

S170, an intermediate material displayed 2 sets of doublets with Ti $2p_{3/2}$ values at 458.36 and 460.27 eV (Figure 4.21 d). The separation energies were 5.82 and 5.57 eV respectively. As compared to the previous titanate rich samples (S100, S130 and S160), the significant changes in peaks could be due to the unstability of the Ti-O bonds which are broken and undergo rearrangement from titanate to titania. For S200, the temperature was sufficient to render a complete phase transformation into a stable anatase. Seo's

group also showed that heating titanate at an elevated temperature caused it to transform into anatase and resulted in a decrease in Ti 2p_{3/2} binding energy to 458.1 eV.¹¹⁸ In this work Ti 2p_{3/2} peak for S200 (Figure 4.21 e) was detected at 458.06 eV (separation energy of 5.7 eV) which is in close agreement to the referenced work. Samples S170 and S200 do not show any signs of nitridation since no nitrogen peak was detected (Figure 4.18 b). Hence, it is expected that oxygen bonding of S170 and S200 would differ from that of the 3 nitrided samples. In Figure 4.20 (d), it is observed that the raw oxygen scan displays 2 peaks where the peak fit at 531.30 eV appears well defined and cleaves away from Ti-O 529.57 eV fit. This contrasts S160 where the raw scan appears to be a summation of the Ti-O and Ti-O-N peak and overlaps both fittings. The oxygen peaks found at 531 and 533-534 eV in S170 (Figure 4.20 d) and S200 (Figure 4.20 e) are attributed to lattice oxygen surface groups. These surface groups are related to oxygen defects or vacancies respectively¹²⁰. The visible light absorption of these 2 samples also was not as remarkable as the previous three samples.

Figure 4. 21: Fitting of components for titanium Ti 2p, (a) S100, (b) S130, (c) S160, (d) S170 and (e) S200.

4.5 Band structure prediction

First principle calculations were performed in order to predict the band structure of the dual phase S160 to provide understanding to its superior photocatalytic performance.

Existing literature suggests nitrogen doping to be effective in reducing bandgaps of several TiO_2 and titanate systems.^{34, 121} In the previous XPS analysis, the dual phase material was determined to be doped with nitrogen in the titanate phase. Therefore in this computation, nitrogen doping was simulated in the titanate phase. Although the experimental structure in this study was hydrated ($\text{H}_2\text{Ti}_3\text{O}_7 \cdot x\text{H}_2\text{O}$), for simplicity and conciseness of computation, $\text{H}_2\text{Ti}_3\text{O}_7$ was computed since Liu et.al had previously reported that nitrogen doping had negligible effect on interlayer spacings of titanate structures and the reverse is assumed to hold true.⁶⁸ Figure 4.22 shows the substitutional doping of 1 nitrogen atom over an oxygen atom in $\text{H}_2\text{Ti}_3\text{O}_7$ in a super- cell of $1 \times 2 \times 1$. Substitutional N doping was done by replacing one of the oxygen ions which is the equivalent of 1.04 atomic percent. Although substitution at different O sites is possible and likely to have different effects on the band structure, only one case is considered in the present study.

Figure 4. 22: Substitutional N doping in the proposed structure of $\text{H}_2\text{Ti}_3\text{O}_7$, the spheres in red (O), light blue (H), grey (Ti), blue (N) represent the atomic position inside the cell.

Partial densities of states (PDOS) of pure and N doped $\text{H}_2\text{Ti}_3\text{O}_7$ are shown in Figure 4.23a and 4.23b respectively. The bandgap of pure $\text{H}_2\text{Ti}_3\text{O}_7$ obtained from DFT calculation is 3.0 eV, close to reported values of similar structures.¹²² Experimental bandgaps of titanates are reported to range from 3.44 to 3.84 eV.^{54, 93} It is well known that calculated band values are typically underestimated from experimental value.¹²³

Figure 4. 23: Partial (orbital decomposed) density of states of (a) $\text{H}_2\text{Ti}_3\text{O}_7$ and (b) N doped $\text{H}_2\text{Ti}_3\text{O}_7$.

Comparing the computed band structures of pure and doped titanates, a bandgap narrowing of 0.68 eV is observed in N doped titanate. An additional small shoulder appears in between the bandgap and the VB is effectively shifted upwards as shown in Figure 4.23b. For a detailed analysis of the N– doped band structure, Figure 4.24 shows the site projected DOS whereby the new valence band is observed to be mainly composed of N 2p state that mixes with O 2p states. It is worth noting that unlike N doped TiO_2 , the bandgap narrowing is significantly larger. Nitrogen induced states are not discrete mid-gap states. A similar gap narrowing of 0.62 eV was observed in the case of $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_4$ and $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_{4-x}\text{N}_x$.⁶⁸ The nitrogen induced states introduced a narrowed bandgap and

shifted the valence band to a more negative value. This provides effective band to band transition which is preferable to the more common but less effective mode of nitrogen doping that result in localized nitrogen states forming within the bandgap usually found in TiO_2 systems.^{34, 121, 124-126}

Figure 4. 24: Site projected density of states of N doped $\text{H}_2\text{Ti}_3\text{O}_7$ on (a) N (b) Ti (nearest) (c) O (nearest).

Based on the DOS analysis, a schematic band diagram of N doped pure and doped titanates is proposed in Figure 4.25. Pure anatase and titanate CB positions were measured with reference to NHE (Normalized Hydrogen Electrode) at pH 7. The

experimental bandgap of pure anatase and titanate were referenced from literature to be 3.2 eV and 3.47 eV respectively.⁶⁸ Although DFT calculation underestimates the absolute bandgap for semiconductors (in the case of titanate there is an underestimation of 0.47 eV), relative values are adequate for comparison. The nitrogen doping is predicted to narrow the modified titanate bandgap to 2.85 eV.

Figure 4. 25: Proposed band diagram of anatase and titanate.

In a dual phase system such as S160, the newly proposed VB comprising of mixed N and O 2p states allows the titanate phase to capture visible light energy whereby the photoexcited electron makes a jump from its VB to its CB. Due to the favourable positioning of titanate CB above that of anatase, the electron should be able to make a transfer to the CB of anatase, thereby enhancing electron and hole separation so that the charged species may interact with target reactants within a waste solution.

4.5 Chapter summary

In this study, we characterized the properties of as-synthesized photocatalysts across a hydrothermal synthesis temperature range of 100 to 200 °C. Using a combination of theoretical and experimental approach, the as-synthesized photocatalysts were determined to be a unique dual phase material comprising of a hydrated titanate and anatase titania phase. We utilized DFT calculation in conjunction with rietveld refinement to establish the crystal solution of the titanate phase as $\text{H}_2\text{Ti}_3\text{O}_{7-x}\text{H}_2\text{O}$. HRTEM and EXAFs were further employed to verify the dual phase nature of a particularly crystalline sample S160. The crystal structure of the photocatalysts was observed to evolve with the increase in temperature; whereby the titanate phase dominated at lower hydrothermal synthesis temperatures and anatase dominated at higher temperatures. Surface area studies were also consistent in validating the phase transition across the temperature range. In addition, we also performed another succinct study by varying the hydrothermal synthesis duration to observe its correlation to crystal structure, crystallinity and surface area. The dual phase samples S100, S130 and S160 displayed a greatly enhanced optical absorbance in the visible light region. We present for the first time doping of nitrogen in a dual phase titanate/ titania photocatalyst that is sensitive to visible light. Theoretical bandgap calculation was also performed to predict the extent of band-narrowing in the titanate phase and the effect on overall charge transfer in a mixed phase system such as S160. This unique material shows strong potential for use in visible light photocatalytic environmental applications.

CHAPTER 5: RESULTS AND DISCUSSION-

PHOTOCATALYTIC TESTING

5.1 Methylene Blue photocatalytic degradation

The photocatalytic activity of the as-synthesized samples was evaluated by measuring the decomposition of methylene blue (MB). The pH of the MB solutions were measured to be 4.9 before and after the experiments. Reference photocatalyst P25 (Degussa) was tested under the same conditions as a comparison. UV-Vis spectroscopy was used as a measurement of the concentration of MB by tracking changes in its characteristic 664 nm absorption peak throughout the reactions. Visual decolourization of the blue dyes was also observed (see Appendix I). The decomposition of MB was tested under the dark as well as under light irradiation. The purpose of the study was to distinguish between adsorption kinetics and light activated degradation kinetics and finally the synergy of the two components in enhancing overall MB decomposition.

5.1.1 Adsorption of MB under the dark

Figure 5.1 shows the results of the change in concentration (C) normalized to initial concentration (C_0) of MB under the dark across samples S100, S130, S160, S170, S200, P25 and blank MB solution. The experiment was repeated 3 times for S160 under dark (as well as light) and the respective mean standard deviation graphs are included in Appendix I.

Figure 5. 1: Adsorption of methylene blue under dark using photocatalyst samples P25, S100, S130, S160, S170 and S200.

P25 shows little or no dark response, indicating poor adsorption of MB molecules onto its surface. Similarly S200, which was found to be anatase TiO_2 (Chapter 4) also shows little adsorption. These results are typical of TiO_2 materials which are known to adsorb poorly.⁸⁸ The dual phase samples show progressive improvement in adsorbing MB with increase in hydrothermal heating temperature. This is attributed to strong adsorption from titanate phase which is reported to adsorb organic species well.^{60, 62, 127} S160 fared the best in adsorption over all the other samples. This is likely due to its improved crystallinity compared to samples S100 and S130 that were treated at lower temperatures. In a study relating synthesis temperature on the dye adsorption of titanate nanotubes, Chung et. al discovered that the adsorption capacity of nanotubes increased for two basic dyes (BG5 and BV10) with increase in synthesis temperature.⁵⁵ The MB

concentration level of S160 dropped rapidly in the first hour and eventually tunnelled out, suggestive of an adsorption isotherm to saturation. S170 showed some adsorption but lower than the other samples. This observation can be correlated to its structure whereby most of the titanate phase underwent a transformation into anatase hence the decrease in adsorption completely for S200. Figure 5.2 shows a clear comparison of the MB left in the solution after 28 hours of complete adsorption in the dark.

Figure 5. 2: Concentration of methylene blue present after 28 hours of adsorption under the dark.

As the adsorption performance of S160 was evidently the best, it is interesting to understand the kinetics behind its unique activity. An adsorption isotherm of S160 was plotted across MB concentrations ranging from 0 to 20 mg L⁻¹. Figure 5.3 presents the adsorption isotherm of S160.

Figure 5. 3: Adsorption isotherm of S160.

The adsorption isotherm curve was fitted to well known Freundlich and Langmuir adsorption models which are described as

$$\text{Freundlich: } q = K_f C_e^{\frac{1}{n}} \quad (5.1)$$

$$\text{Langmuir: } q = \frac{q_m KC_e}{1 + KC_e} \quad (5.2)$$

where q (mg g⁻¹) is the amount of adsorbed MB, C_e the concentration of MB at equilibrium, q_m (mg g⁻¹) the maximum adsorption capacity, K_f and n are Freundlich constants and K is the Langmuir constant. The amount of MB adsorbed onto the photocatalyst q can be given by:

$$q = \frac{(C_0 - C_f)V}{M} \quad (5.3)$$

where C_0 and C_f represent the initial and final concentrations of MB in the solution, V is the volume of MB solution (L) and M is the mass of photocatalyst added (g). The Freundlich and Langmuir models can be linearised as such:

$$\text{Freundlich: } \ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (5.4)$$

$$\text{Langmuir: } \frac{1}{q_e} = \frac{1}{q_{\max} K_L C_e} + \frac{1}{q_{\max}} \quad (5.5)$$

The Langmuir model describes monolayer adsorption whereas the Freundlich model describes a heterogeneous surface binding. The results of fitting can be seen in Table 5.1 and the fits can be found in Appendix I. A relatively high regression coefficient (R^2) is an indicator that the model successfully describes the kinetics of adsorption.¹²⁸ The Langmuir adsorption model was found to fit S160 very well where R^2 value was found to be closer to unity. The value of q_m derived theoretically was also in close agreement to the experimental value. Hence, the adsorption of MB is determined as monolayer adsorption; whereby a layer of MB molecules form over the surface of dual phase S160. The MB adsorbed for S160 (q_m) was found to be 162.19 L mg^{-1} and fared comparatively higher in adsorption as compared to other reported adsorbents such as rice husk (40.58 L mg^{-1})¹²⁹, raw date pits (80.29 L mg^{-1})¹³⁰ and titanate nanotubes (133.33 L mg^{-1})⁶⁰.

Table 5. 1: Langmuir and Freundlich isotherm parameters for MB adsorption on S160.

Langmuir				Freundlich		
$q_{m \text{ experimental}}^a$	K^b	q_m	R^2	K_F^c	n	R^2
162.19	5.764	163.66	0.89541	114.5	5.995	0.41422

^a q_m ($L \text{ mg}^{-1}$). ^b K ($L \text{ mg}^{-1}$). ^c K_F ($\text{mg}^{1-n} L^{-n} \text{ g}^{-1}$).

5.1.2 Degradation of MB under visible light

Photocatalytic activity of MB decomposition under visible light irradiation is presented in Figure 5.4. A filter was used to cut off all wavelengths under 420 nm thus exposing only visible light.

Figure 5. 4: Photocatalytic degradation of methylene blue under visible light using samples P25, Blank MB solution, S100, S130, S160, S170 and S200.

Once more, S160 shows the best activity; nearly all the MB disappears in 6 hours. S160 was found to be successfully doped with nitrogen and showed enhanced visible light absorption in the previous chapter. Although the surface area of this sample was not the highest, it had the best crystallinity which contributes to less defect states that promote electron hole recombination. In addition, the intimately matched interfaces of titanate and anatase on nanoscale promote charge transfer that further reduces electron hole recombination. Blank MB shows some decomposition under visible light which is due to the effect of direct photolytic breakdown of MB.¹³¹ P25 does not demonstrate much visible light activity since both the anatase and rutile phases within the sample absorb only in the UV region. The weak photo-activity shown is presumably a result of photolysis or dye sensitization effect which is lesser than that of blank MB due to suspended P25 particles blocking the penetration of light into the solution. Pure anatase S200 displayed a similar trend line, its poor surface adsorption does not facilitate in the photo-degradation process. In addition, pure anatase absorbs little visible light; hence there is little marked improvement in MB decomposition. In later sections, a study distinguishing dye sensitization from visible light photocatalysis affirms the origins of photo- activity in P25 and the dual phase photocatalyst. S100 showed little improvement over blank MB irradiation, likely due to the poorly crystalline phases which contain defect sites that trap electrons and holes formed to impede the degradation rate. Comparatively, S170 and S130 fared much better under visible light irradiation; S130 showed 60% decrease in concentration. Its visible light degradation performance is a result of successful nitrogen inclusion in the titanate phase. S170 demonstrated 50% decrease in concentration. S170 is known to be an intermediate structure due to

incomplete transformation from titanate to anatase phase. It is presumed that the interfaces remain intimately matched during this transformation and aid in electron-hole separation that forms from excitation of the dye under visible light.

Figure 5.5 shows the comparison of MB left in the solution after 6 hours of visible light irradiation.

Figure 5. 5: Concentration of methylene blue present after 6 hours of visible light irradiation.

The kinetics of methylene blue degradation is presented in Figure 5.6 by plotting the logarithm of the normalized dye concentration against irradiation time. Fairly good linear relationships were observed thus establishing the degradation to follow a modified Langmuir-Hinshelwood mechanism:

$$\frac{dC}{dt} = \frac{k_r K_e C}{1 + k_e C} \quad (5.6)$$

expressed in integral form gives:

$$t = \frac{1}{K_e k_r} \ln \frac{C}{C_0} + \frac{1}{k_r} (C_0 - C) \quad (5.7)$$

when the concentration of the dye is adequately low ($\ll 10^{-3}$) as is the condition of the experiment, the equation can be expressed as:

$$\ln \frac{C}{C_0} = k_r K_e t = k' t \quad (5.8)$$

where C and C_0 represent the concentration of MB at time t and initial concentration, k_r is the apparent reaction rate constant, K_e is the apparent equilibrium constant for the dye to adsorb onto the photocatalyst and k' represents the overall rate constant.

Figure 5. 6: First order degradation rates for P25, Blank MB, S100, S130, S160, S170 and S200 under visible light irradiation.

The results show that degradation of all samples was well described by the pseudo first order kinetic model. All the linear plots have R^2 values close to unity. S160 again fares the best in degradation; giving the highest R^2 and rate constant k' of 0.99455 and 0.63438. This gives a reaction rate constant that is approximately 21 times that of P25 under visible light irradiation. The degradation curve for S160 was less linear than its counterparts, which is indicative that the overall degradation over the sample could be influenced by both adsorption and degradation reactions.

5.1.3 Synergy in adsorption and degradation

Since S160 consistently exhibits enhanced activity in adsorption as well as light activated degradation, it is motivating to study the synergetic effects of adsorption and degradation in this optimized sample. Figure 5.7 combines the time extended dark and light MB experiments of S160 with P25 as a comparison.

Figure 5. 7: Degradation of methylene blue under visible light (solid lines) and dark conditions (dotted lines) using photocatalyst sample S160 and reference P25.

It is interesting to observe that under direct visible light irradiation using S160, the adsorption process appears to dominate the kinetics initially for the first hour where both the dark and light curves exhibit similar trend-line. Following which, the MB level drops quite rapidly to zero for the light experiment whereas the dark experiment levels

out into saturation. The comparison between the dark and light experiment suggests genuine degradation of MB by the dual phase material under visible light, enhanced by simultaneous adsorption, a clear pre-requisite for efficient charge transfer during photodegradation. HRTEM images of S160 are displayed in Figure 5.8.

Figure 5. 8: HRTEM image of S160 (a) particles display cubic morphology and good size dispersity. (b) Particles are porous and crystalline in nature.

Figure 5.8 (a) shows the particles having a cubic morphology which is characteristic of hydrothermal processes. The particles also exhibit a unique porosity with a “bumpy” surface. Undoubtedly the bumpy porous surface facilitates in the adsorption process as it increases the interaction sites between the particle and adsorbate. There is good size dispersity among all the particles and they average 15- 20 nm in size. The high magnification image in Figure 5.8 (b) confirms that the particles are highly crystalline and still retain the porous nature. Both crystallinity and porosity are crucial for photocatalytic efficiency.

The proposed photocatalytic process is illustrated in Figure 5.9. The titanate phase undergoes band narrowing and absorbs visible light as mentioned in XPS and bandgap computation discussion in the previous chapter. The electrons produced by light excitation can jump from the titanate conduction band into the titania conduction band thus enhancing electron hole separation. The produced electrons can be captured by O_2 molecules to yield $O_2^{\bullet-}$ radicals. Similarly, the produced holes decompose water or react with OH^- to form hydroxyl radicals ($OH^{\bullet}$). Hydroxyl radicals are strong, non selective oxidants which can mineralize several organic chemicals.¹³² The radicals react with MB molecules adsorbed on the surface of the titanate phase and mineralizes them into intermediates that will further breakdown into CO_2 .

Figure 5. 9: Scheme of proposed photocatalytic process for dual phase titanate/titania in MB aqueous suspension.

In comparison, P25 took 5 times longer to come close to degradation as shown in Figure 5.7 where the light reaction extended to 24 hours. P25 composes of a mixture of rutile and anatase TiO_2 and is only excitable by UV light, not visible light. The degradation activity shown by P25 is expected to be due to dye sensitization effect. In

dye sensitization, the MB molecule gets excited by visible light and injects an electron into P25 TiO₂ particles. The TiO₂ then gets excited and produces electrons which proceed to form active oxygen species from reducing dioxygen and the holes react with MB to break it down as shown in the following equations.

The dye sensitization process operates as a different mechanism from photocatalysis. In this case, TiO₂ itself gets photoexcited by light irradiation and produces electrons and holes that react in subsequent reactions. However in both cases, the complete mineralization must be accompanied by the formation of intermediates and finally CO₂. Zhang et. al reported important observations for complete degradation of MB dye; the degradation of MB causes N- demethylation that is accompanied by a hypsochromic effect. They observed that as the absorbance $\lambda_{\max}$ of MB at 664 nm decreases, there was also broadening and blue shifting of the peak due to the N- demethylated analogs of MB produced.^{82, 87} These analogs include Azure B, Azure A, Azure C and Thionine which have absorption bands in the region of 654 to 602.5 nm. The broadening and blue shifting of $\lambda_{\max}$ is a good indicator that MB N- demethylation is concomitant with the degradation of its phenothiazine structure.

The spectroscopic data of MB degradation for S160 and P25 under visible light irradiation (of Figure 5.7) can be analyzed in Figure 5.10. Figure 5.10(a) shows the MB $\lambda_{\max}$ at 664 nm decrease with time using S160. As mentioned, in the first hour, the adsorption phenomenon dominates the kinetics and there is only altitude decrease in $\lambda_{\max}$. After this initial adsorption process, $\lambda_{\max}$ starts to display blue shifting and gradual broadening at 1.5 hours. This observation continues until all the MB in the solution gets degraded into the demethylated intermediates and the absorption maxima shifts to 654

nm. The inset displays clearly the progression of absorption maxima $\lambda_{\max}$ shift according to irradiation time. The absorbance results for P25 are shown in Figure 5.10 (b) and its corresponding $\lambda_{\max}$ shift data with respect to irradiation time is shown in the inset. There is no change in the $\lambda_{\max}$ position and no signs of peak broadening even after 8 hours of irradiation. Since P25 does not exhibit any surface adsorption, the initial decrease in $\lambda_{\max}$ could be due to photolysis effect which is not a genuine dye breakdown and is not accompanied by hypsochromic shift. The dye sensitization reaction takes place at a much slower rate when the excited MB injects electrons into P25's TiO_2 conduction band. This is sufficient for it to produce an electron which reacts with surface adsorbed O_2 molecules to yield $\text{O}_2^{\bullet-}$ radical anions that protonate into $\text{HOO}^{\bullet}$ radical. Following this, H_2O_2 forms by disproportion of $\text{O}_2^{\bullet-}/\text{HOO}^{\bullet}$ and can further be reduced by electrons to generate $\text{OH}^{\bullet}$ to decompose the dye under visible light.¹³³

After 8 hours of irradiation, the intermediates start forming, observed by the blue shifting of $\lambda_{\max}$ and its gradual broadening. In comparison, S160 was much more efficient in forming intermediates, thus demonstrating its effectiveness in complete mineralization of MB.

Figure 5. 10: Absorption spectral patterns of MB during visible light irradiation reactions (of Figure 5.7) using (a) S160 and (b) P25.

To evaluate the effective dye degradation mechanism behind S160, a dark-to-light experiment was performed. Figure 5.11 (a) displays the change in concentration of MB with time. Following full adsorption to equilibrium over 16 hours in the dark, the solution was then irradiated with visible light until MB completely disappeared. Corresponding spectroscopic curves in Figure 5.11 (b) shows that the MB absorption band maximum (λ_{max}) at 664 nm only decreases in altitude during the adsorption process. Upon visible irradiation, λ_{max} begins to blue shift and broaden within the first hour and progresses extensively until λ_{max} approaches 636 nm and all the MB in the solution is depleted. As compared to the reaction under direct irradiation, there is less competing kinetics of adsorption and degradation. In this reaction, the MB molecules were first adsorbed onto the surface of S160 particles and formed a monolayer whereby the surface was completely covered and adsorption saturation limit was reached. MB gets adsorbed onto the material's surface through its nitrogen atoms that bind to surface hydroxyl groups.⁸² When irradiation begins, the S160 photocatalyst absorbs the visible light and gets excited to deliver holes to the MB molecules that were pre-adsorbed onto its surface. This makes for efficient charge transport to reduce electron hole recombination. The formation of intermediates is also more effective as indicated by the deeper hypsochromic shift effect signifying more N-demethylated analogs forming for a more complete mineralization.^{87,}

Figure 5. 11: (a) Change in concentration of MB using S160 under dark for 16 hours followed by light irradiation; (b) Corresponding MB absorption spectroscopy tracking decrease of MB and change in λ_{max} wrt time (inset).

To further validate the mineralization process, MALDI-TOF was used to investigate the intermediate formation of MB degradation under direct visible light. The initial concentration of MB was raised to 50 ppm to enhance quantitative accuracy. Figure 5.12 shows the MALDI-TOF result of blank MB under visible light irradiation.

Figure 5. 12: MALDI-TOF spectra of Blank MB under visible light degradation at 0, 6, 8 and 9 hours.

The peak at $m/z = 286.47$ corresponds to the molecular weight of pure MB. Subsequently, it is the only peak detected even after 9 hours of visible light irradiation. Previous UV-Vis spectroscopy results showed that blank MB absorbance decreased with light irradiation due to photolysis effect. It is evident here that MB concentration does not change and no intermediates form in the absence of any photocatalyst. This is an

important finding as it resolves the controversy over the contribution of photolysis in visible light reactions; most work merely endorse “degradation” by presenting UV-Vis data.

Figure 5.13 (a) displays the MALDI-TOF results of degradation of MB over S160. Similar to preceding UV-Vis spectroscopy discussion, it can be seen that the intermediates start to form early into the reaction after 2 hours. The first step of the MB degradation process is demethylation whereby the intermediate that forms corresponds to the demethylated ring structure which has a methyl group cleaved from the MB molecule ($m/z = 270.29$). It is believed that the hole and electron produced from band-gap excitation could reduce $C=N$ and $C=S+-C$ in the central aromatic ring to simpler $C-N$ and $C-S$ bonds.¹³⁴ Following which, more demethylated analogs emerged as the reaction progressed until there was destabilization in the ring structure and the ring completely breaks up into simpler substances. After the 6th hour, most of the intermediates were also broken down into lesser concentrations. This mineralization process is likely to continue until all the MB is converted and the intermediates broken down. Comparatively, the results of P25 shown in Figure 5.13 (b) shows that there was little intermediate forming after the 4th hour under visible light irradiation such that it was close to negligible ($m/z = 270.40$). All the results are in close agreement with the UV-Vis discussion and this suggests genuine photocatalytic efficiency of the synthesized S160 over P25. In photocatalysis, complete mineralization is of utmost importance since the intermediates formed could also pose as a dangerous pollutant. For the first time to our knowledge, we demonstrate that MALDI-TOF can be an effective tool in verifying the complete mineralization of MB under visible light photocatalysis. Previously, it is commonly

agreed that the detection of CO₂ using gas chromatography or total organic carbon (TOC) measurements was the primary way of ensuring true mineralization.^{85, 88} This method proves to be simpler and informative compared to previous techniques.

Figure 5. 13: MALDI-TOF spectra of (a) S160, (b) P25 for MB degradation under visible light degradation at 0, 1, 2, 3, 4, 5, 6 hours.

5.1.4 Effect of crystallinity on photocatalytic dye degradation

A study focusing on the crystallinity effect was carried out. Figure 5.14 shows results of varying hydrothermal synthesis duration of the samples previously described in the Chapter 4.4. The sample denoted by “T” indicates that hydrothermal heating duration was extended to 168 hours. In addition, the experiments were also performed under a different light filter cutting on 385 nm enabling part UV and visible light exposure. A trend can be identified whereby all the samples that underwent extended heat treatment fared better than their counterparts that were heated at 3 hours. Only S130 and T130 was the exception. This is due to the fact that T130 had completely transformed into 100% anatase as indicated in Chapter 4. Thus its absorption ability is markedly poorer than S130 which is a mixture of titanate and anatase phase. In addition to that, the dual phase also promotes electron transfer which enhances the MB degradation; which is lacking in the single phase system in T130. Observing the samples heated at 200°C, even though S200 was already crystalline anatase, extended heating helps it to further improve in crystallinity and there was particular improvement in the UV + Vis light degradation. Not much change was observed between S200 and T200 under visible light degradation since anatase is not that active under visible light. Comparing the results between the 2 light filters, most of the dual phase samples fared better under UV + Visible light. Under pure visible light, only the doped titanate phase is excited and transfers its electrons into the anatase phase. The anatase phase then releases another electron to further react and breakdown methylene blue. With the addition of UV light, the anatase phase can also be excited, hence both phases are actively at work. Overall, S160 still performed the best of all the samples under both UV + Visible and visible light.

Figure 5. 14: Comparison of concentration of MB present after 6 hours using (a) S80 and T80, (b) S100 and T100, (c) S130 and T130, (d) S200 and T200 and (e) S160 and P25 under UV + Visible (grey color) and Visible light (yellow color).

The dye degradation process is undoubtedly a very complicated process and has been a feature of many studies.^{38, 85, 133, 135-142} In this study, it is shown that the as synthesized dual phase material S160 is much more effective than the commercial P25 TiO₂ counterpart in degrading dye; mainly attributed to its competent adsorption and visible light activated degradation that performs synergistically. While there are several reports that debate the appropriateness of using organic dyes to showcase visible light photocatalytic activity due to implications of dye sensitization,^{88, 143, 144} the complete breakdown of MB and its intermediates were investigated such that genuine degradation was accounted for. Moreover, the degradation of organic dyes and colorant pollutants is very much a significant focus of environmental remediation. Visible light driven materials such as this study would greatly facilitate this important application. To provide a clean study on the visible light responsiveness of dual phase S160, another probe species which is not sensitive to visible light was chosen.

5.2 Phenol degradation

Phenol and its derivatives are common organic pollutants that exist as intermediate molecules in organic synthesis of plastics, pesticides, etc.¹⁴⁵ It is not sensitive to visible light and therefore it is chosen as an additional probe species to test the visible light responsiveness of the best photocatalyst sample, S160.

Fig 5.15 shows the percentage of phenol remaining upon degradation from HPLC analysis with respect to irradiation time. H_2O_2 was added to all samples and visible light (>420 nm) was irradiated on the solutions. Blank phenol solution without addition of any photocatalyst shows no significant degradation under visible light even with the addition of H_2O_2 . It is very clear that among the catalysts, S160 showed better activity and complete mineralization of phenol. By the 6th hour, phenol was completely degraded. A parallel experiment for S160 was performed in the dark with the addition of H_2O_2 as well. The result shows insignificant change in the concentration even after 10 hours (see Appendix I). This eliminates adsorption effects from the visible light degradation. In comparison, phenol was still present after 6h of reaction time over P25 photocatalyst. At the 8 hour mark, the degradation saturation limit was reached where approximately 30% of phenol remained un-degraded. The degradation of phenol under visible light with the reference P25 is believed to be based on the action of $\cdot\text{OH}$ radicals from dissociation of H_2O_2 via surface complexes. Li et. al. demonstrated that H_2O_2 molecule adsorbed on TiO_2 surface formed surface titanium- (IV) hydrogen peroxide complexes ($\equiv\text{Ti}^{\text{IV}}\text{-OOH}$) which were photoresponsive to visible light. As this surface complex gets excited by the visible light, electron is released and transferred to TiO_2 conduction band, then dissociates H_2O_2 to give $\cdot\text{OH}$ radicals resulting in the further photooxidation of salicylic

acid.¹⁴⁶ This is presumable true in the P25/phenol/H₂O₂ system as well. Degradation in this system finally discontinues when all the H₂O₂ is depleted from the solution. P25 is primarily a mixture of anatase and rutile and can not be excited by visible light irradiation, thus, there is no further enhancement towards degradation except by H₂O₂. In comparison, S160 absorbs visible light (as shown in diffuse reflectance data above) whereby it becomes photo-excited and releases electrons and holes to dissociate H₂O₂ and water molecules within the solution. This creates more [•]OH radicals that enhances and sustains phenol degradation for complete mineralization.

Figure 5. 15: Degradation of Phenol in the presence of H₂O₂ for (a) Blank phenol, (b) P25, (c) S160 under visible light.

To further validate this point, the same degradation experiment was performed under visible light without the addition of H_2O_2 . The results in Figure 5.16 show that sample S160 degrades phenol steadily albeit at a slower rate as compared to previous experiment with addition of H_2O_2 . After 8 hours of reaction, approximately 50% of the phenol was degraded. P25 shows little degradation in the absence of H_2O_2 . This confirms the photo-activity of S160 under visible light. In addition to this, the dual phase material is also likely to promote electron- hole charge separation since there can be irreversible charge transfer between the intimate interface of the two phases.^{53, 147} This prevents the electrons and holes from recombining and accelerates the phenol degradation reaction.

Figure 5. 16: Degradation of Phenol without H_2O_2 for (a) S160 under visible light, (b) P25 under visible light.

HPLC was used to analyze the degradation efficiency of phenol under heterogeneous photocatalytic condition. Figure 5.17 displays the HPLC peaks of the reaction solution using sample S160 under visible light with the addition of H_2O_2 . The phenol peak observed at 3.12 RT (retention time) in the HPLC chromatogram is seen to decrease steadily and finally disappears after 6 hours. Various oxidized compounds were observed from HPLC at different time intervals. Finally at the 9th hour, all the oxidized compounds disappeared; this gives a complete breakdown of phenol and sub-compounds into CO_2 .^{148, 149}

Figure 5. 17: HPLC peaks of the reaction solution using sample S160 under visible light with the addition of H_2O_2 .

The intermediates were identified in GC-MS and tabulated in Table 5.2. A plausible scheme for phenol degradation is given in Table 5.2 below.

Table 5. 2: Intermediates of phenol degradation reaction.

Compound	Structure of the molecule	Mass	Molecular fragmentation	Retention time
Phenol		94	94(M ⁺), 66, 55, 39	8.91
Di-hydroxybenzene		110	110(M ⁺), 92, 81, 64, 53, 27, 18	8.09
1,2,3-trihydroxybenzene		126	126(M ⁺), 108, 97, 80, 52, 39	13.55
Hydroxy propanoic acid		90	90(M ⁺), 73, 72, 60, 55, 45, 43, 42, 31, 29, 27	11.84
benzoquinone		108	108(M ⁺), 82, 69, 54, 38, 32, 26	8.04

Maleic acid		116	116(M ⁺), 98, 88, 81, 71, 53, 45, 27	13.22
Oxalic acid		90	90(M ⁺), 45, 29, 18	10.21
Acetic acid		60	60(M ⁺), 45, 43, 29, 15	9.37

The GC-MS analysis results of phenol degradation samples showed the presence phenol as well as its destructed compounds. Intermediates such as di- and tri- hydroxy benzenes, Benzoquinone, n-propanoic acid, glycerol, etc., were detected. Traces of organic acids such as maleic/ fumaric, oxalic and acetic acids were also detected. The postulated mechanism of the photodegradation of phenol has been given in Figure 5.18. By assuming that $\cdot\text{OH}$ radicals attack the phenyl ring, yielding di-hydroxy benzenes, what follows is the further oxidation into tri-hydroxy benzenes, ring opening compounds and short chain organic acids. The products finally break down into CO_2 . The synthesized sample S160 was also able to photoexcite under visible light to create electron-hole pairs and further dissociate water molecules to give more $\cdot\text{OH}$ radicals. In addition, within the material, the layered structure of the titanate phase is likely to be able to trap $\cdot\text{OH}$ radicals and electrons due to its hydrated surface. Szczepankiewicz et. al showed that the annihilation of charged carriers were suppressed by increasing surface hydration as does

the total concentration of available charged traps.¹¹⁴ Overall, the lifetime of $\cdot\text{OH}$ radicals is extended and electron-hole recombination may be reduced and this facilitates the efficient degradation of phenol.

Figure 5. 18: Scheme of postulated mechanism of the photodegradation of phenol.

5.4 Chapter Summary

In summary, this chapter demonstrates the use of as-synthesized photocatalysts S100, S130, S160, S170 and S200 in methylene blue degradation under visible light. Commercial photocatalyst, Degussa P25 was employed throughout as a benchmark for comparing photoactivity. In this work, we wanted to distinguish the contribution between two important aspects of photocatalysis, namely adsorption and degradation. The experiments were performed independently under dark and light conditions. Sample S160 consistently performed the best in both adsorption and degradation tests. Adsorption studies concluded that S160 was best described by Langmuir adsorption model. We carried out a detailed study focusing on S160 under dark- to- light conditions so as to highlight the synergistic “adsorption and degradation” effect which is behind the efficient breakdown of methylene blue. Another focal point of the work involved an investigation of MB and its intermediates throughout the degradation reaction using MALDI. Through this, we were able to account for a complete genuine breakdown of MB which is lacking in existing studies. The effect of dye sensitization was described as well. An additional study varying the hydrothermal duration showed that the photocatalytic performance was correlated to the crystallinity of the material. We also conducted degradation test for S160 and P25 on phenol under visible light and confirmed that S160 excelled in performance. The degradation mechanism of phenol using as synthesized dual phase material was described in detail. The results imply that our doped dual phase material possess immense potential in visible light photocatalytic applications.

CHAPTER 6: CONCLUSION AND FUTURE WORK

This thesis made progress in developing a suitable visible light photocatalyst that can be used to efficiently degrade harmful organic waste in the environment. A simple one-pot synthesis of a novel dual phase photocatalyst has been successfully achieved. Its potential to degrade two organic pollutants under visible light has been demonstrated. The new catalyst has been shown to be a nanoscale intergrowth of a layered titanate phase with anatase. The former phase contributes by adsorbing the organic substrate as well as visible light absorption. The close proximity of both phases allows an efficient electron hole transfer onto the organic substrate before recombination takes place. This leads to a unique synergism of adsorption and photocatalysis and thereby the excellent properties of the new material. The key findings are:

1. Developed a novel route to synthesize visible light active dual phase photocatalyst

In this work, we have established a novel soft chemical recipe that produces a dual phase material comprising of titanate and anatase. The simplicity and energy competency of this technique gives it a competitive edge over existing dual phase materials that require multiple synthesis steps and high temperature processing. The technique also incorporates nitrogen doping within its one-pot procedure. The successful inclusion of nitrogen dopants has been studied in detail using XPS and is now understood to enable band-gap narrowing of the titanate phase. This results in

the titanate phase absorbing visible light. A further advantage to the dual phase structure is that intimate contacts between adjacent well distributed phases shown by HRTEM imaging create good interfaces for electron transfer that enhances photocatalysis. This unique doping mechanism could be a useful platform for synthesizing related material systems.

2. Determined the crystal structure of hydrated layered titanate

We report the crystal structure of the hydrated layered titanate in this dual phase material. A systematic loop between experimental and theoretical techniques was employed. DFT calculation was used to predict a rough framework of the titanate model. Rietveld refinement was then used to refine the simulated structure. The iterative procedure enabled us to formulate a good prediction of the titanate crystal structure model. HRTEM diffraction was also used to verify the accuracy of the model. This information will undoubtedly be valuable amidst the limited knowledge of crystal structure among titanate materials and suggests a systematic approach that can be applicable to any crystal structure particularly complicated multi- phase ones.

3. Evaluated phase transformation of dual phase photocatalyst through methodical temperature and time study

By varying the temperature and time parameters, we were able to study the transformation of titanate and anatase phases. We found that increasing temperature caused the material to transform from titanate rich to anatase dominating until there was complete transformation to anatase at 200 °C. While the titanate features layers

of TiO_5 -pyramids and TiO_6 -octahedra, anatase consists of a 3D framework of TiO_6 -octahedra. Therefore the transformation from titanate to anatase involved the octahedras breaking up and rearranging themselves. Through the time study, we discovered the improvement in crystallinity over various temperatures that improved the material's photocatalytic performance. Extensive characterization on the surface, optical and chemical properties was also accomplished to co- relate the changes in phase transformation.

4. Demonstrated efficient photocatalytic degradation of MB and phenol under visible light

From the phase transformation study, we recommend sample S160 to be a potential photocatalyst candidate for promising environmental applications relying on solar energy. This dual phase material possessed good crystallinity and ideal mixture of titanate and anatase phase such that it was the most efficient in degrading methylene blue and phenol under visible light. It also performed much better than commercial Degussa P25, which is a classic benchmark of reference. In particular for the MB study, we propose a synergistic “adsorption and degradation” mechanism whereby the titanate phase attracts MB molecules and adsorbs them on the particle's surface. This creates a short pathway for the photo- excited electrons to react with the dye molecule. In phenol degradation, the dual phase S160 is also efficient in producing $\cdot\text{OH}$ radicals to breakdown phenol. The titanate phase also traps these $\cdot\text{OH}$ radicals to prolong their lifetime for effective reaction. The anatase phase plays the role of inhibiting electron- hole recombination.

5. Investigated intermediate formation in MB and phenol degradation

We performed a comprehensive study of intermediates formed during MB and Phenol degradation and established their mechanism of breakdown. Importantly in the field of photocatalysis, there are many studies emerging using MB as a convenient module to demonstrate visible light photo-activity. However, many of these works did not take into consideration the dye sensitization and photolysis effect which induces the same artificial decoloration but fails in actual breakdown of MB and its intermediate components. To our knowledge, it is the first time MALDI- TOF is used to verify photocatalytic demethylation of MB under visible light. We also demonstrate that the MB intermediates are further broken down throughout the reaction and renders true photocatalytic activity. In addition, we establish that photo- sensitization, although produces the same visual discoloration, does not contribute to breakdown of MB and its intermediates as demonstrated in the blank and P25 tests. The same was confirmed for phenol degradation and we suggest a breakdown pathway for phenol and its intermediates. This study stresses the importance of presenting accurate and reliable photocatalysis results through thorough study of intermediate formation. We also suggest MALDI- TOF as a technique for future studies involving MB as a target species.

Recommendations for future work include further study on the following areas:

1. Further optimization of synthesis parameters

Intricate efforts have been made in this work to study the effect of temperature and time on the composition, structure, optical absorbance and photo-activity of the synthesized materials. Seeing as there is already a great potential in S160 for visible light degradation of organic pollutants, it would be worthwhile to further fine tune parameters such as synthesis time, hydrothermal pressure and dopant concentration so as to achieve an even better dual phase photocatalyst with higher crystallinity and establish added control over doping. Accomplishing this may also facilitate the determination of phase content with high degree of accuracy. In this respect, a thorough optimization may yield a much more promising material for practical applications.

2. Electronic band structure measurement

In this work, we simulated nitrogen doping in DFT calculations to predict the extent of band narrowing induced by a single nitrogen atom in a 1x2x1 titanate supercell. Although the theoretical model shows good agreement to the hypothesized effect induced by nitrogen doping in titanate, it is still vague in describing the actual model which consists of nitrogen dopants in a hydrated titanate environment. Therefore, a new theoretical model should be built to better describe the crystal structure of the doped titanate in the dual phase material. This allows for a more accurate assessment of the modified bandgap. The numerous permutations involving available occupancy sites for the dopants might prove to be a computation challenge; however, it is a

meaningful study that might facilitate the design of new doping systems in other materials.

3. Solar stimulated degradation of organic pollutants using dual phase photocatalyst

While the materials synthesized in this work shows excellent pollutant degradation activity under simulated visible light, they have not yet been tested under solar light. To be truly useful, photocatalysts should be able to absorb solar energy so as to tap on the free and abundant resource. We demonstrate that the dual phase material absorbs visible light which accounts for approximately half of the solar spectrum. As such, testing the organic degradation under a solar simulator could provide a realistic perspective of the practicality of the application.

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APPENDIX I: SUPPLEMENTARY INFORMATION

Figure A.1: XRD diffraction profiles of S160 S160 as synthesized (red) and vacuum heat treated sample (black). All the peaks were callibrated relative to strongest titanate peak

T200 at a relative value of 1000.

Figure A.2: Visual observation of methylene blue decolourization as a result of visible light degradation using photocatalyst S160.

Figure A.3: Degradation of methylene blue under dark using S160 displaying mean standard error of 3 experiments.

Figure A.4: Degradation of methylene blue under visible light using S160 displaying mean standard error of 3 experiments.

Figure A.5: Plot of Freundlich fitting to adsorption isotherm of S160.

Figure A.6: Plot of Langmuir fitting to adsorption isotherm of S160.

Figure A.7: Degradation of Phenol in the dark in the presence of H_2O_2 .

APPENDIX II: LIST OF AUTHOR'S PUBLICATIONS

Journal Publications

1. **Y. H. Cheng**, *Y. Z. Huang, P. D. Kanhere, V. P. Subramaniam, D. G. Gong, S. Zhang, J. Highfield, M. K. Schreyer, and Z. Chen*, "Dual-Phase Titanate/Anatase with Nitrogen Doping for Enhanced Degradation of Organic Dye under Visible Light.", *Chemistry A European. Journal*, 2011, **17**: p. 2575. (Published)
2. **Y. H. Cheng**, *V. P. Subramaniam, D. Gong, Y. Tang, J. X. Lim, O. Wijaya, J. Highfield, S. Pehkonen, M. K. Schreyer, Z. Chen*, "Dual phase Titanate/ Titania doped with Nitrogen for Visible Light Phenol Degradation". (In preparation)
3. **Y. H. Cheng**, *V. P. Subramaniam, D. Gong, Y. Tang, J. X. Lim, O. Wijaya, J. Highfield, M. K. Schreyer, Z. Chen*, "Nitrogen doped dual Phase Titanate/ Titania for Visible Light Methylene Blue Degradation: A Study of the Influence of Temperature on Phase transition." (In preparation)
4. *Y. Tang, V.P. Subramaniam, T.H. Lau, Y. Lai, D. Gong, P. D. Kanhere, Y. H. Cheng, Z. Chen, Z. Dong*, "In situ formation of large scale Ag/ AgCl nanoparticles on layered titanate honeycomb by gas phases reaction for visible light degradation of phenol solution." *Applied Catalysis B: Environmental*, 2011, **106**, 577. (Published)
5. *Y. W. L. Lim, Y. Tang, Y. H. Cheng, Z. Chen*, "Morphology, crystal structure and adsorption performance of hydrothermally synthesized titania and titanate nanostructures." *Nanoscale*, 2010. **2**: p. 2751. (Published)

Patent

1. “One-Step Low-Temperature Synthesis of Protonated Titanate / Titania Composite Nanoparticle Photocatalyst”, US patent filed

International Conferences

1. Oral presentation; **Y. H. Cheng**, *Z. Chen*, “One-step low-temperature synthesis of protonated titanate/ titania composite nanoparticle photocatalyst”, 14th International conference for TiO₂ Photocatalysis: Fundamentals and Applications, October 5-8, 2009, *Niagara Falls, USA*
2. Poster presentation; **Y. H. Cheng**, *Z. Chen*, “Synthesis of hydrogen titanium oxide hydrate using a low temperature solution process for the application of photocatalysis”, *MRS (Materials Research Society) Fall Meeting: December 1-5, 2008, Boston, USA*
3. Oral presentation; **Y. H. Cheng**, *T. An, Z. Chen*, “Optical Studies of N-doped Titanium oxide Thin Films For Near Visible Light Photo-catalytic Applications”, *ICMAT 2007 (International Conference on Materials for Advanced Technologies): July 1 - 6, 2007, Singapore.*