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GREEN PREPARATION OF VISIBLE LIGHT ACTIVE TITANIUM DIOXIDE FILMS

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GREEN PREPARATION OF VISIBLE LIGHT ACTIVE TITANIUM DIOXIDE FILMS

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ABSTRACT

The thesis focuses on the fabrication of visible light active TiO_2 -based thin film photocatalyst, via a green method, for self-cleaning and potentially other solar energy harvesting applications. TiO_2 is chosen due to its attractive attributes of being inexpensive, nontoxic, photocatalytically active, chemically stable and broad application especially in degrading organic pollutants. However, TiO_2 can only be activated under UV light due to the wide band gap of TiO_2 (3.2 eV). This limits its widespread applications since ultraviolet is only a small part of solar energy (approximately 4%) and almost non-existent in indoor lighting.

Transparent, uniform, crack free and visible light-activated single element doped TiO_2 films (N-doped TiO_2 and Fe-doped TiO_2) were successfully fabricated. The precursors were prepared using a “green” aqueous Peroxo Titanic Acid (PTA) solution approach and coated on the glass substrate using hydrophilicity-assisted method. The optimal photocatalytic activity of the N- doped TiO_2 films was about 9.5 and 13.6 times higher than that of un-doped TiO_2 coated glass and commercial self-cleaning glass, respectively. The optimal photocatalytic activity of the Fe-doped TiO_2 films was about 4 times higher than that of un-doped TiO_2 . The improvement of photocatalytic activity was mainly due to enhanced visible light absorption by N or Fe doping which is attributed to bandgap narrowing as observed from absorption redshift.

We extended the PTA approach to prepare C-N-codoped TiO_2 films. The optimal visible light photocatalytic activity observed for C-N-codoped TiO_2 film was at 10.0 wt.% C, which was more than double that of N-doped TiO_2 film. This enhancement was attributed to linear contributions of carbon and nitrogen. Both carbon and nitrogen dopant states work hand-in-hand to increase the photogenerated electrons and holes thus leading to an increase of visible light photocatalytic activity. However, beyond optimal carbon concentration, reduced photocatalytic activity was attributed to the decrease of nitrogen dopant.

Another promising way to improve visible light photocatalytic activity of TiO_2 is by coupling with a visible light-activated semiconductor. Bi_2WO_6 under-layers with high surface roughness were prepared by a hydrophilicity-assisted method. The optimal visible light photocatalytic activity of the $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ film was 7.4 and 15.7 times higher than that of unmodified Bi_2WO_6 and TiO_2 films respectively, attributed to enhanced charge separation efficiency. The improvement in photoelectrochemical and photocatalytic performances was attributed to the porous film structure and facilitation of higher charge separation efficiency, the latter evidenced by photoluminescence (PL) and current-voltage (I-V) analyses.

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List of Publications

Journal Publications

- (1) **Diana V. Wellia**; Qing-chi Xu; Kok Hwa Lim; Mahasin Alam Sk; Tuti Mariana Lim; Timothy Thatt Yang Tan, Experimental and Theoretical Studies of Fe-doped TiO₂ Films Prepared by Peroxo Sol-Gel Method. Applied Catalysis A: General, **2011**, 401, 98-105. (*chapter 6*)
- (2) Qing Chi Xu*, **Diana V. Wellia***, Rose Amal, Dai Wei Liao, Joachim Say Chye Low and Timothy Thatt Yang Tan. Superhydrophilicity-Assisted Preparation of Transparent and Visible Light Activated N-doped Titania Film. Nanoscale, **2010**, 2, 1122-1127. (*chapter 4*)
- (3) Qing Chi Xu*, **Diana V. Wellia***, Dai Wei Liao, Tuti Mariana Lim, Timothy Thatt Yang Tan. Enhanced Photocatalytic Activity of C-N-codoped TiO₂ Films Prepared via an Organic-free Approach. Journal of Hazardous Materials, **2011**, 188, 172-180. (*chapter 5*)
- (4) Qing Chi Xu*, **Diana V. Wellia***, Yun Hau Ng, Rose Amal, Timothy Thatt Yang Tan, Synthesis of Porous and Visible-light Absorbing Bi₂WO₆/TiO₂ Heterojunction Films with Improved Photoelectrochemical and Photocatalytic Performances. Journal of Physical Chemistry C, **2011** 115, 7419–7428. (*chapter 7*)

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Conference Proceedings

- (1) **Diana V. Wellia**, Tan, T. T. Y, and Lim, T. M, Investigation of Nanotitania Synthesized via a Modified Sol-Gel Route as Self-Cleaning Surface Materials, Regional Symposium on Chemical Engineering (RSCE), Dec 2007, Yogyakarta, Indonesia.

- (2) **Diana V. Wellia**, Tan, T. T. Y, and Lim, T. M, Investigation of Various Types of Unmodified and Modified Titania as Self-Cleaning Surface, The International Symposium on Advance Bio, Nano, and Pharmaceutical Science and Technology 2009, May 2009, Beijing, China.
- (3) **Diana V. Wellia**, Tan, T. T. Y, and Lim, T. M, Preparation and Study of the Fe-doped TiO₂ Films Prepared by Peroxo Sol-Gel Method for Visible Light Activated Self-Cleaning Applications, The International Symposium on Exploring the Frontiers of Chemical and Biomedical Engineering, May 2010, Singapore.

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NOMENCLATURE

Acronyms

3D	three dimensional
AACVD	aerosol-assisted chemical vapor deposition
AES	Auger electron spectroscopy
AFM	atomic force microscopy
ALD	atomic layer deposition
BET	Brunauer-Emmet-Teller
CB	conduction band
CA	contact angle
CVD	chemical vapor deposition
CVI	chemical vapor infiltration
DOS	densities of states
DTA	different thermal analysis
DT-TGA	Differential Thermal and Thermogravimetric Analysis
e^-	electron
EDS	energy-dispersive X-ray spectroscopy
EDX	energy-dispersive X-ray spectroscopy
EISA	evaporation-induced self-assembly
EVD	electrochemical vapour deposition
FESEM	field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
FTO	fluorine doped tin oxide

h^+	hole
IPCE	incident-photon-to-current efficiency
IR	infra red
ITO	indium tin oxide
MB	methylene blue
MBE	molecular beam epitaxy
MOCVD	metalorganic chemical vapor deposition
NHE	normal hydrogen electrode
O	orthorhombic
PEC	photoelectrochemical cells
PECVD	plasma enhanced chemical vapor deposition
PEG	polyethylene glycol
PL	photoluminescence
PTA	peroxo titanate acid
PVD	physical vapor deposition
RHEED	reflection high energy electron diffraction
SEM	scanning electron microscopy
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
UV	ultraviolet
VB	valence band
VIS	visible
WDX	wavelength-dispersive X-ray spectroscopy
XPS	X-ray photoelectron spectroscopy

XRD X-ray diffraction

Variable Names

θ	diffraction angle
ε	molar absorptivity at a given wavelength
η	viscosity
ρ	density
Φ_s	work function term
λ	wavelength
A	absorbance
C	molar concentration (part 3.3.2), BET constant (part 3.3.9)
d	crystal plane distance
E	energy
E_B	binding energy
E_{bg}	bandgap energy
E_{kin}	kinetic energy
g	gravitational force
H	film thickness
I_t	intensity of the transmitted light
n_{ad}	amount of adsorbate
P	pressure
T	transmittance
Uo	withdrawal speed

Unit of Measurement

Å	angstrom
μA	micro ampere
μm	micrometer
μl	microliter
at. %	atomic percentage
C	celsius
cm	centimeter
eV	electron volt
g	gram
h	hour
K	kelvin
m	meter
min	minute
mL	milliliter
nm	nanometer
n _m	number of moles of adsorbate
pm	picometer
s	second
V	volt
W	watt
w	frequency
wt. %	weight percentage

CHAPTER 1

Introduction

1.1 Background

The application of TiO_2 as a photocatalyst has received much attention due to its attractive attributes of being inexpensive, nontoxic, photocatalytically active and chemically stable especially in the degradation of organic pollutants.^[1,2]

Since TiO_2 has a wide band gap of 3.2 eV, it can only be activated under the UV light which is only a small part of the solar spectrum (approximately 3-4 %).^[3] Tremendous efforts have been made to produce TiO_2 photocatalyst that is capable of effective utilization of visible light. One way is to activate TiO_2 in the visible light region by depressing the TiO_2 band gap via doping with either metal ions (Fe ,^[4-5] Cr ,^[6-7] Co ,^[8-9] Cu ,^[9] and V ^[10]) or non metal species such as C ,^[11, 12] N ,^[13, 14] F ,^[15, 16] B ,^[17] and S ^[18, 19]. Other methods include co-doping TiO_2 with two or more elements such as N-S ,^[20-22] W-N ,^[23] B-N ,^[24, 25] F-N ,^[26-28] and Ce-N ^[29, 30] as well as coupling TiO_2 with other narrow band gap semiconductor such as CdS ,^[31] WO_3 ,^[32, 33] and Bi_2WO_6 .^[34, 35]

TiO_2 can be applied in suspended form or immobilized on a substrate as thin film. The use of suspension form is efficient due to the large surface area of the suspended TiO_2 particles. However, post-operation separation of the photocatalyst is required, which can be an expensive and challenging process. The expensive running costs and the limitation of depth of light encountered in the suspension system can be overcome by

the immobilized system. It has been suggested that the immobilized system is superior to the suspension system.^[36]

Several chemical and physical techniques can be used to prepare TiO₂ coatings, such as sol-gel, sputtering, chemical vapor deposition (CVD), spray pyrolysis, pulsed laser deposition, ion-assisted electron beam evaporation, and atomic layer deposition.^[37]

Among all the afore-mentioned techniques, the sol-gel method is the most widely used as it presents many advantages such as the use of very simple equipment and low capital investment, the high homogeneity of thin films, the possibility of using different substrates, and the ability to control the microstructure and density of thin films.^[37-39] However, conventional sol-gel method suffers from several disadvantages

such as the use of organometallic precursors that are expensive and easily hydrated in air.^[40] Besides, this method also requires acid or base to stabilize the prepared sol, making it difficult to apply on corrosive substrate.^[41] The peroxo sol-gel method is a promising approach to overcome these issues in the preparation of TiO₂ thin film.^[42]

The peroxo sol-gel method also offers other advantages such as neutral pH condition^[41-43], low material cost^[42, 43] and is environmentally friendly as it uses aqueous instead of organic solvents^[43], and hence this method can be considered green.

However, the peroxo sol-gel method requires the use of polyethylene glycol (PEG) to stabilize the obtained peroxo titanic acid (PTA).

For thin film preparation using PTA method, it is challenging to form uniform and transparent thin film on smooth glass substrate without forming cracks when typical coating techniques such as dip-coating and spin-coating are used. This is due to the

high surface tension of the water based PTA solution, such that it cannot disperse on the glass uniformly and hence resulting in cracks after calcinations, as reported by Ge et al.^[44] and Yuan et al.^[45]

This thesis reports a “green” route of synthesizing transparent, uniform, crack-free and visible light active TiO₂ thin films via an organic-free peroxo sol-gel approach without the addition of a stabilizer. This thesis also reports an alternative method of producing superhydrophilic TiO₂ thin film via a hydrophilicity-assisted method, which utilizes hydrophilic glass as a substrate for coating. The photocatalytic activity of these modified TiO₂ thin films was evaluated using stearic acid as a model organic compound and is reported in this thesis. In one aspect of this thesis, the photoelectrochemical properties of Bi₂WO₆/TiO₂ composite nanostructured film are also reported.

1.2 Purpose of the Project

This aim of this project is to synthesize visible light responsive TiO₂ thin films, via a “green method”, that are capable of exhibiting oxidizing properties under visible light irradiation, such that they may be applied in solar organic pollutant degradation and other solar harvesting applications such as solar fuels production.

In this thesis dissertation, the preparation of single-phase anatase sols using peroxo sol-gel process under ambient conditions is reported. The synthesis of N-doped TiO₂, C-N-codoped TiO₂, Fe-doped TiO₂ and composite Bi₂WO₆/TiO₂ heterojunction films is

presented, and their properties and performances optimized using various precursors and dopant concentrations, pH values and synthesis temperature are also reported.

1.3 Scope of the Project

This thesis has been subdivided into the following sections. Following this introduction, a literature review will be presented in Chapter 2, which discusses the crystal structures of TiO_2 and its application in photocatalysis, TiO_2 thin films and a brief review about their current fabrication methods, followed by a detail explanation about conventional and peroxo sol-gel method, photo-induced hydrophilicity and visible light-activated photocatalysts.

The methodology, the basic principle of different materials characterization techniques used throughout the study, the procedure for photocatalytic evaluation and photoelectrochemical study are presented in Chapter 3.

Chapter 4 describes the synthesis and characterizations of N-doped TiO_2 thin films and their photocatalytic activity evaluation under 24 h visible light illuminations. The aim of this study is to investigate the effect of pH on nitrogen doping concentration in TiO_2 films and obtain an optimal nitrogen concentration. It was observed that the pH has a direct correlation with doped nitrogen concentration and affects the visible light absorption and photocatalytic activity.

Chapter 5 presents the fabrication, characterization and evaluation of photocatalytic activity of C-N-codoped TiO_2 . The calcination temperature and carbon doping

concentrations were varied to optimize for highest visible light photocatalytic activity. It was observed that all C-N-codoped TiO_2 films showed an excellent visible light absorption and enhanced photocatalytic activity compared to that of un-doped TiO_2 , and single element C-doped and N-doped TiO_2 .

Chapter 6 describes another visible light active photocatalyst: Fe-doped TiO_2 . The preparation method, characterizations and photocatalytic activity evaluation of stearic acid degradation are discussed. The objective of this study is to find the optimal Fe^{3+} concentration for the best photocatalytic activity under visible light region. It was observed that all samples show red-shift absorption and are photocatalytically active under visible light illumination.

A simple technique to prepare porous composite $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ thin films is reported in Chapter 7. Some characterizations, photocatalytic activity and photoelectrochemical properties are studied. Bi_2WO_6 film as an under layer had high surface roughness, resulting in a great increase in the interfacial area of the $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ bi-layer film. Bi_2WO_6 concentrations were optimized and all the samples showed enhancement of visible light absorption. The photoelectrochemical and photocatalytic performances were improved.

Chapter 8 concludes the current study, with recommendations for future works.

CHAPTER 2

Literature Review

2.1 Introduction

Titanium dioxide (TiO_2), both as powdered photocatalyst or thin films have received significant attention due to its widespread applications.^[47] Photoactivity of TiO_2 has been reported since 1938 with a report on the photobleaching of dyes by TiO_2 both *in vacuo* and in oxygen. In the early 1970s, Honda et al. used TiO_2 for water photoelectrolysis. Since then, numerous research works have focused on TiO_2 with reports on photocatalytic H_2 production in the 1980s and photocatalysis and hydrophilicity of TiO_2 film in the 1990s. By end of the 1990, the results of these basic researches were commercialized for the first time. The research in this area is still ongoing to date particularly in the improvement on molecular and applications aspects. The milestones of the TiO_2 research development is shown in Table 2.1.^[48]

As mentioned above, the application of TiO_2 as a photocatalyst is very wide including self-cleaning, water treatment, deodorizing and air purification, anti-fogging function, anti bacterial effect (self-sterilizing) and photocatalytic cancer treatment.^[2, 48, 49] Among these applications, self-cleaning has gained significant attentions as it has wider market potential such as self-cleaning materials for residential and office buildings, indoor and outdoor lamps and related systems, materials for roads, tent materials, hospital garments, spray coating for cars, etc.^[2] In addition, nowadays, TiO_2 become a promising photocatalyst on hydrogen production application from water

splitting.^[50-51] A clean, renewable and storable energy obtained from hydrogen production become a solution for high energy demand and other environmental problems.^[52-53]

Table 2.1 Milestones of TiO₂ research development.^[48]

No	Year	Researcher	Contribution
1	1938	C. F. Doodeve, J. A. Kitchener	Photobleaching of dyes by TiO ₂ <i>in vacuo</i> and in oxygen.
2	1956	Mashio et al.	Autooxidation of organic solvents by TiO ₂ and simultaneous formation of H ₂ O ₂ under ambient conditions.
3	Late 1960s	Akira Fujishima	Investigation of the photoelectrolysis of water by TiO ₂ using a single crystal n-type TiO ₂ (rutile) semiconductor electrode.
4	1969	Akira Fujishima et al.	The first example of solar photoelectrolysis.
5	1972	A. Fujishima and K. Honda	Electrochemical photolysis of water (published in Nature).
6	Late 1970s		Photocatalytic approach for the problem of light-assisted water splitting.
7	1977	Frank and Bard	Decomposition of cyanide in the presence of aqueous TiO ₂ suspensions.
8	1980	Kawai and Sakata	Purification of waste water and polluted air by powdered TiO ₂ .
9	Late 1980s	R. W. Matthews	Immobilization of TiO ₂ powders on supports.

No	Year	Researcher	Contribution
10	1992	T. Watanabe, K. Hashimoto, A. Fujishima	Photocatalytic cleaning material with a ceramic tile.
11	1995	TOTO Ltd	Manufacturing of antibacterial ceramic tile coated with photocatalytic TiO ₂ containing Cu and/or Ag.
12	After 21 st century		Research study to improve TiO ₂ photocatalyst is still being carried out.

2.2 Crystal Structure of TiO₂

TiO₂ exhibits three different crystal forms, namely brookite (orthorhombic), rutile (tetragonal) and anatase (tetragonal). Rutile is the only stable phase, whereas anatase and brookite are metastable at all temperatures and transform into rutile at high temperature^[54] and pressure.^[55] However, in solution-phase methods for TiO₂ formation, it generally favors the anatase structure because the surface energy of anatase is lower than rutile and brookite.^[56]

The detailed structure of anatase, rutile and brookite are shown in Fig. 2.1 and the crystal structure data are summarized in Table 2.1. The structure of rutile and anatase can be described in terms of chains of TiO₆ octahedral, whereas brookite has a more complicated structure. It has eight formula units in the orthorhombic cell.^[57] However, the structures of all three polymorphs are similar in that the Ti atom is octahedrally coordinated, but the linkage of these TiO₂ octahedral is differed.^[55] Each Ti atoms in anatase and rutile is surrounded by an octahedron of six O atoms and each O atom is

surrounded by three Ti atoms. The octahedron in rutile and anatase are not regular; showing a slight distortion with two Ti-O bonds slightly greater than the other four and some of the Ti-O-Ti bond angles deviate from 90° .^[57] The distortion in anatase is greater than in rutile, and it is the greatest in brookite.^[58] The Ti-O distances in anatase are shorter than in rutile ($1.937 - 1.965$ Å in anatase vs. $1.949 - 1.98$ Å in rutile), whereas the distance in brookite is ranging from $1.87 - 2.04$ Å.^[57] These differences in lattice structure cause different mass densities and electronic band structures among the three forms of TiO_2 .^[59]

Figure 2.1 Structure of TiO_2 : (a) Rutile, (b) Anatase and (c) Brookite.^[57]

As mentioned above, rutile, anatase and brookite differ in their octahedral linkage. In rutile, two edges of each octahedron are shared, whereas three and four are shared in brookite and anatase, respectively.^[55] The densities of these crystals depend on the number of the edges shared: if the number of edges shared in the structure increases, the density decreases. So, it can be seen in Table 2.2 that rutile with the smallest amount of edges shared has the highest density followed by brookite and anatase, respectively.^[55]

Table 2.2 Crystal structure data of TiO₂.^[55, 57]

	Rutile	Anatase	Brookite
Crystal structure	Tetragonal	tetragonal	orthorhombic
Lattice constant (Å)	a=4.5936 c=2.9587	a=3.784 c=9.515	a=9.184 b=5.447 c=5.145
Space group	<i>P4₂/mnm</i>	<i>I4₁/amd</i>	<i>Pbca</i>
Molecule/cell	2	4	8
Volume/molecule (Å ³)	31.216	34.061	32.172
Density (g/cm ³)	4.13	3.79	3.99
Ti-O bond length (Å)	1.949 (4) 1.98 (2)	1.937 (4) 1.965 (2)	1.87 ~ 2.04
O-Ti-O bond angle	81.2° 90°	77.7° 92.6°	77° ~ 105°
The mean nearest-neighbor Ti-Ti distance (Å)	2.959	3.039	3.024

TiO₂ is a semiconductor with sufficient band-gap energy to catalyze a chemical reaction.^[60] The band gap is defined as the void region which extends from the top of the filled valence band to the bottom of the vacant conduction band. The excitation occurs across the band gap, creating electron-hole pairs to undergo photocatalysis reaction.^[59]

The band gap energy (E_{bg}) of anatase is larger than that of rutile (3.23 and 3.02 eV, respectively) while the band gap of brookite is slightly higher than anatase. In photocatalysis, anatase and rutile are commonly used, whereas anatase is more photochemically active than rutile^[47] due to the higher surface area of anatase crystal structure to allow for greater photocatalytic efficiency^[61] and its potentially higher

conduction-band edge energy.^[62] On the contrary, the photocatalytic activity of brookite has never been reported either in liquid-solid or in gas-solid systems due to the difficulty to synthesize pure brookite because the brookite is the metastable modification of TiO_2 ^[63] and usually forms as secondary minority phase along with rutile and/or anatase, depending on the experimental conditions.^[64]

2.3 Titanium Dioxide Photocatalysis

2.3.1 General Principle of Photocatalysis

Photocatalysis involves light and a catalyst to bring about a chemical reaction. In photocatalysis, the catalyst is activated by the absorption of photons of light to overcome the activation energy. The charge is effectively transferred from the reactant to the product via a reduction oxidation (redox) reaction through a semiconductor as the photocatalyst.^[65]

2.3.2 Mechanism of TiO_2 photocatalysis

Fig. 2.2 depicts the mechanism of TiO_2 activation and photocatalysis. When a photon of light having sufficient energy ($E > E_{bg}$) strikes a TiO_2 particle, electrons (e^-) are excited from the valence band and move to the conduction band. This movement of an electron leaves a hole (h^+) in the valence band. These species (h^+ and e^-) resulted from the absorption of light can either recombine (pathway A and B) or migrate to the surface (pathway C and D). The recombination of the separated electron and hole can occur in the volume of TiO_2 particle (pathway A) or on the surface (pathway B) with the release of heat.^[59] The hole and electrons that migrate to the surface can react with other species. The electrons can react with molecular oxygen to form the superoxide

radical-anion, $O_2^{\bullet-}$ which can be involved in further reactions. The holes can directly oxidize organic species adsorbed onto the TiO_2 particle or react with water or OH^- to produce hydroxyl radicals ($\cdot OH$). These highly reactive hydroxyl radicals can then attack organic compounds at or near the surface (pathway D).^[65]

Figure 2.2 Schematic photo-excitation in a solid followed by de-excitation events.^[61]

The photocatalysis mechanism can be described more clearly in the following equations.

1. Hydroxyl radical generation^[49]

2. Oxidation of electron donor (D: organic molecule) or reduction of electron acceptor (A: metal ion) reaction^[49]

2.4 TiO₂ Thin Film

TiO₂ can be applied in suspended form or immobilized on a substrate as thin film. The use of suspension is efficient due to the large surface area and the absence of mass transfer limitation. However, post-operation separation of the photocatalyst is required, which can be more expensive and difficult compared to the immobilized system and has the limitation on the depth of light. Besides that, the suspended powder TiO₂ tends to aggregate especially at high concentrations.^[66] All of these problems can be avoided if the immobilized system is utilized. It was hence suggested that the immobilized system is more superior to the suspension system.^[36]

TiO₂ thin film can be prepared by several physical and chemical methods such as sol-gel, sputtering, chemical vapor deposition (CVD) or light-induced CVD, spray pyrolysis, pulsed laser deposition, ion-assisted electron beam evaporation, and atomic layer deposition, etc.^[37] Among all of the methods mentioned above, the sol-gel

method is the most widely used, as it presents many advantages such as the use of very simple equipment and lower capital investment, the high homogeneity of thin films, the possibility of using different substrates, and the control of the microstructure and density of thin films.^[37-39]

Some of the preparation methods for TiO₂ thin film are described briefly as follow:

2.4.1 Physical Vapor Deposition (PVD)

PVD is a process of transferring growth species from a source or target and deposit them on a substrate to form a film, mostly without chemical reactions involved. In general, PVD can be divided into two groups: evaporation and sputtering.^[67]

Evaporation is the simplest deposition method which uses thermal means to transfer the growth species from the source, while sputtering uses energetic ions to knock atoms or molecules out from a target that acts as one electrode and subsequently deposit them on a substrate acting as another electrode.^[67]

2.4.2 Chemical Vapor Deposition (CVD)

In CVD, a volatile compound of a material to be deposited reacts with other gases to produce a non-volatile solid that deposits atomistically on a suitably placed substrate.^[67] The chemical reactions involved are pyrolysis, reduction, oxidation, compound formation, disproportionation and reversible transfer, depending on the precursors used and the deposition conditions applied.^[67] CVD has been modified to develop the growth of thin film on highly porous substrate or inside porous media, such as electrochemical vapor deposition (EVD) and chemical vapor infiltration (CVI).

^[67]

2.4.3. Atomic Layer Deposition (ALD)

Atomic layer deposition (ALD) can be considered as a special modification of the chemical vapor deposition (CVD), or a combination of vapor-phase self-assembly and surface reaction. ALD offers the best possibility of controlling the film thickness and surface smoothness in nanometer and sub-nanometer range, because only one atomic or molecular layer can grow each time.^[67]

2.4.4. Electrochemical Deposition (electrodeposition)

In electrochemical deposition, the growth species is transferred from the source and deposited on the substrate to form thin film by electrochemical reaction induced by potential difference. A careful control of over-potential is very important to avoid electrolysis of solvent or deposition of impurity phase. In addition, the interactions of the solute ion M^{m+} with the solvent, or with complex-forming ligands and the ionic strength of the solution must be controlled carefully. Besides these thermodynamics factors, kinetic factors must also be considered such as the rate of the electron transfer reaction, i.e. the oxidation-reduction kinetics, the nucleation rate of crystals, etc.^[67]

2.5 Sol-Gel Method

Sol-gel chemistry is considered a powerful technique for preparing inorganic materials such as glasses and ceramics. This method is also well known as one of the most appropriate technologies to produce oxide thin film and is used by most researchers to prepare TiO_2 coating. The sol-gel method presents many advantages such as the use of very simple equipment, low cost, the possibility of using different substrates, and the ability to control the microstructure, homogeneity and density of thin films.^[37-39, 68]

In sol-gel synthesis, a soluble precursor molecule is hydrolyzed to form a dispersion of colloidal particles, also known as the sol. Further reaction bonds the sol particles resulting in an infinite network of particles (the gel).^[61]

A typical sol-gel process consists of hydrolysis and condensation of precursors.^[67, 69]

Precursors can be either metal alkoxides or inorganic and organic salts. Organic or aqueous solvents may be used to dissolve precursors, and catalysts are often added to promote hydrolysis and condensation reactions^[67] as shown in the following reactions:

Hydrolysis:

Condensation:

There are many methods for sol-gel deposition, such as spin and dip-coating, spray and ultrasonically pulverized spray. Among these methods, dip and spin-coatings are the most commonly employed. In dip-coating, a substrate is immersed in a solution and withdrawn at a constant speed. The film thickness is determined by combination of viscous drag and gravitational forces as shown in the equation below:

$$H = c_1 (\eta U_0 / \rho g)^{1/2} \quad (\text{Eq. 2.1})$$

Where H is the film thickness, η is the viscosity, U_0 is the withdrawal speed, ρ is the density of the coating sol, and c_1 is a constant. The thickness of a dip-coated film is

normally in the range of 5 and 500nm.^[67] Dip-coating consists of three stages, namely immersion, deposition & drainage and evaporation as shown in Fig. 2.3.^[67]

Figure 2.3 Three stages of dip-coating.

In spin-coating, the centrifugal force is involved for forming the thin film. There are 4 stages involved in spin-coating, namely delivery of solution or sol onto the substrate centre, spin-up, spin-off and evaporation (overlap with all stages). After delivering the liquid to the substrate, centrifugal forces drive the liquid across the substrate (spin-up). The excess liquid leaves the substrate during spin-off. A uniform film can be obtained when the viscosity of the liquid is not dependent on the shear rate (i.e. Newtonian) and the evaporation rate is independent of position.^[67]

2. 5. 1 Peroxo Sol-Gel Method

As mentioned above, the sol-gel method offers many advantages. However, it suffers from several disadvantages such as the use of organometallic precursors that are expensive and easily hydrated in air.^[40] Besides, this method also requires acid or base to stabilize the prepared sol, rendering it difficult in the application on corrosive

substrate.^[41] A modified sol-gel technique known as the peroxo sol-gel method can overcome these issues in the preparation of TiO₂ thin film.^[42] In this technique, peroxo titanic acid (PTA) solution is prepared by adding ammonia solution to an aqueous titanium precursor solution, followed by the addition of H₂O₂ and heating to form TiO₂ nanocrystals.^[42] The formation mechanism of the titanium peroxo complex has been investigated by Muchlebach et al.^[70] while specific formation of TiO₂ using the PTA has been recently reported by Ichinose et al.^[71] The latter offers many advantages such as neutral pH^[41-42], low material cost^[42-43] and is environmentally friendly as it uses aqueous instead of organic solvents.^[43] Moreover, peroxo titanic acid (PTA) is stable in air^[42, 72] and its preparation is both simple and cost-efficient.^[72] PTA solution can be prepared from titanium alkoxide^[41, 71] or inorganic salt such as TiCl₄^[71] or TiCl₃.^[73]

The reactions involved are shown in the equations below.^[74]

When hydrogen peroxide (H₂O₂) is added, the hydroperoxide group can be formed easily according to the following reactions:

Peroxo tetra-phenylporphyrinato titanium, O₂Ti(TPP), is formed slowly from OTi(TPP) in the presence of alkyl hydroperoxide and oxo-peroxo exchange occurs in titanyl tetra-pyridylporphyrin in the presence of hydroperoxide^[71] which eventually leads to formation of Peroxo Titanic Acid (PTA).

The hydroxo complex, $= \text{Ti}(\text{OH})(\text{OOH})$, may be produced as an intermediate in the reaction, and the peroxo complex is formed later. Polymerization occurs due to the reaction between the peroxo group and the OH group, hence the viscosity of PTA solution increased with time.^[71]

All methods discussed above (with the exception of peroxo sol-gel method) are energy intensive and require expensive equipment to prepare good quality thin film. In contrast, peroxo sol-gel method involves not only simple equipment, the ease of preparation and low cost, but is also environmentally friendly.

2.6 Photo-induced Hydrophilicity

There are two distinct photo-induced phenomena of TiO_2 : the first is the photocatalytic phenomenon, which leads to the breakdown of organics, and the second is hydrophilicity phenomenon.^[2] The photocatalytic phenomenon has been studied extensively, and it is fairly well understood. The second phenomenon, hydrophilicity, has only been discovered recently.^[2] The hydrophilicity can be observed by measuring surface wettability that is generally evaluated by the water contact angle (CA). Water contact angle is defined as the angle between the solid surface and the tangent line of the liquid phase at the interface of the solid-liquid-gas phases.^[48]

When this surface is exposed to UV light, electrons and holes are induced. The electrons tend to reduce the Ti(IV) cations to the Ti(III) state, and the holes oxidize the O^{2-} anions. In this process, oxygen atoms are ejected, creating oxygen vacancies as

depicted in Fig. 2.4. Water molecules can then occupy these oxygen vacancies site, producing adsorbed OH groups, which tend to make the surface hydrophilic.^[2] The hydrophilicity is related to the density in surface OH groups. The longer the surface is illuminated with UV light, the more water molecules tend to be hydrogen-bound to the OH groups^[75], so the contact angle becomes smaller. If the contact angle approaches zero, it means that water has a tendency to spread uniformly across the surface and hence called superhydrophilic.^[2]

The hydrophilicity property has correlation with photocatalytic activity as it can enhance the photocatalytic activity (Fig. 2.5). If the surface is hydrophilic, the water molecules bounded on the surface increases which can then react with the holes (h^+) to produce hydroxyl radicals ($\cdot OH$). This $\cdot OH$ radical is responsible to decompose organic compound. So, the more water present on the surface, the more $\cdot OH$ radicals will be produced and hence better photocatalytic activity.

Furthermore, the superhydrophilic property of the surface results in anti fogging property and makes the surface easily washed as the water spreads completely across the surface rather than remain as droplets.^[76]

With these properties mentioned above, superhydrophilic self-cleaning TiO_2 coating glass can potentially be used for many applications including mirrors, windshields of automobiles, window glasses, etc.^[76]

Photoinduced oxygen vacancies are replaced by dissociated water molecules, resulting in a hydrophilic surface.

Figure 2.4 The mechanism of photo-induced hydrophilicity.^[2, 48]

Figure 2.5 The correlation of hydrophilicity with photocatalytic activity.

2.7 Visible Light-activated Photocatalyst

Since TiO₂ has a wide band gap, it can only be activated under the UV light which is only small part of solar energy (approximately 3-4%).^[77] Numerous efforts have been made to produce TiO₂ photocatalysts that are capable of effective utilization of visible light which constitutes a main part of the solar spectrum. So far, the effort developed to produce visible light responsive materials is either by depressing the band gap of photocatalyst material or coupling semiconductor with other semiconductor or molecules with narrower band gap (Fig. 2.6). There are two ways to narrow the band gap: the first is by doping TiO₂ with single atom and the second is by doping the TiO₂ with two kinds of atom, called codoping. Various kinds of cations (metal ions) such as

Cr, Fe, Ni, V, or Mn; and anions such as carbon, nitrogen, fluorine, phosphor or sulfur can be used as dopant. Among anion doping, nitrogen-doped material has received significant attention since Asahi et al. reported the activity of this material^[1] due to the superior photocatalytic activity under visible light irradiation.

Figure 2.6 Methods to develop visible light-activated TiO₂ photocatalysts.

2.7.1 Cation-doped TiO₂

As mentioned above, TiO₂ can be doped by cations (metals) to enable photocatalytic activity under visible light. The principle of doping with cation is the substitution of Ti⁴⁺ by other cations that have about the same size such as Cr, Fe, Ni, V, or Mn ions. Cation doping can decrease the band gap of TiO₂. Agrios et al. and Zhang reported that the mixture of the conduction band of Ti (d) of TiO₂ and the metal (d) orbital of the cation dopant was supposed to be the origin of the decrease in the band gap.^[66, 75] Thimsen et al. reported that the general consensus of dopant is that the doping introduces additional energy levels into TiO₂ band gap that lowers the energy required to excite electrons from the valence band to the conduction band.^[78] In other words,

cation doping can extend the spectral response of the TiO_2 to the visible light region.^[79-80] Besides that, metal ion dopant may act as electron or hole traps, so it can reduce photogenerated electron-hole pairs recombination rate.^[72, 80] Celik et al. reported the other role of metal ion dopant (Fe^{3+}), which is to increase the concentration of $\cdot\text{OH}$ in solutions which resulted in enhanced the decomposition rate.^[81] The roles of metal doping mentioned above improve the photocatalytic activity of TiO_2 . Metal doping also gives other route of the phase transformation which produces crystal defect and surface modifications, hence changes the activation energy of transformation.^[82]

The photocatalytic activity of cation-doped TiO_2 depends on many factors, such as the dopant concentrations, the location of energy levels of dopant in the lattice, d-electronic configurations and distribution of dopants.^[6]

2. 7. 2 Anion-doped TiO_2

Doping of non metals such as C, N, F, S, B into TiO_2 have been developed and considered as potentially effective method to extend the absorption of TiO_2 to the visible light region by substituting oxygen in the TiO_2 lattice.^[83]

Sulfur, despite having a larger ionic radius compared to N and C atoms, can be used to synthesize S-doped TiO_2 .^[84] For example, Ho et al. prepared S-doped TiO_2 by one step low-temperature hydrothermal method. They found that the oxygen atoms in TiO_2 lattice were replaced by sulfur atoms as shown by a peak at about 160-161 eV in XPS, corresponds to the Ti-S bond formation.^[18] In another study, Takeshita et al. prepared

S-doped TiO_2 in two methods: simple oxidation annealing of TiS_2 and mixing of titanium isopropoxide (TTIP) and thiourea, then study the effect of preparation method on the photocatalytic activity. The result showed that the photocatalytic activity of both samples were different which can be attributed to the different carrier behavior to the difference in the S atoms distributions or particle size. Doping of S will produce states in the band gap of TiO_2 that absorb visible light.^[19] On the contrary, Umebayashi et al. reported different band calculations. It indicated that the S 3p states mix with the valence band of TiO_2 increasing the width of the VB itself. This result is responsible for decreasing the band gap and consequently leads to the photon-to-carrier conversion in the visible light region.^[85-86]

Fluorine doped TiO_2 has been reported to promote photocatalytic activity.^[15] For example, Yu et al. prepared F- doped TiO_2 by hydrolysis of titanium isopropoxide (TTIP) in the $\text{NH}_4\text{F-H}_2\text{O}$ mixed solution. The prepared sample showed stronger absorption in the UV-visible range and red shift in the band gap transition. It was also found to improve the photocatalytic activity, three times higher than that of Degussa P25.^[15] Li et al. used spray pyrolysis of an aqueous solution of H_2TiF_6 to prepare F doped TiO_2 . They found that two kinds of oxygen vacancies were formed, confirmed by photoluminescence (PL) result, that were responsible for the photocatalytic activity in the visible light.^[16] These oxygen vacancies were proportional with the amount of O_2^- adsorbed on the surface of anatase TiO_2 . Here, F-doping was observed to significantly enhance the formation of those $\text{O}_2^{\bullet-}$ and Ti^{3+} ions which agreed with the calculated result.^[87]

Besides S and F, iodine doped TiO_2 has been reported as a visible light-activated photocatalyst as well. Iodine incorporation causes an absorption in the visible light range with a red shift in the band gap transition.^[88] Boron atoms can substitute oxygen atoms in the TiO_2 lattice as well to form B-doped TiO_2 . The p orbital of B is mixed with O $2p$ orbital, which results in band gap narrowing.^[17]

Among the anions dopant, C or N atoms has been found to attract more attention due to the superior photocatalytic activity under visible light irradiation.^[89] For example, Matos et al. prepared C-doped TiO_2 by a solvothermal method and evaluated the photocatalytic activity on methylene blue (MB) degradation. They found that C-doped TiO_2 exhibited first-order rate constant for degradation of MB which showed higher photocatalytic activity than un-doped one. This result was caused by direct optical charge transfer transition involving both the TiO_2 and carbon phase, keeping the high reactivity of the photogenerated electron and hole.^[11] In another study, Lin et al. prepared C-doped TiO_2 by sol-gel process combined with hydrothermal treatment. The photocatalytic activity results showed that the prepared samples exhibited the excellent photocatalytic activity under UV and visible light irradiation compared to un-doped TiO_2 and P25 film. In this case, O-Ti-C bond was formed indicating substitution of the oxygen sites in the TiO_2 lattice by carbon atoms.^[12]

2.7.2.1 N-doped TiO_2

Among the anions, N-doped TiO_2 was the most widely investigated since Asahi et al. reported the activity of this material.^[1] Based on the densities of anion doping states in the anatase TiO_2 crystal, N doping was found to be the most effective method for

inducing the visible light photocatalytic activity due to bandgap narrowing.^[13] Further explanation of the N-doped TiO₂ bandgap is provided in section 2.7.2.2. There are many ways to synthesize the N-doped TiO₂. Asahi et al. doped a small amount of N into TiO₂ crystal lattice by sputtering the TiO₂ target in a N₂/Ar gas atmosphere followed by a heat treatment at 600°C for 3 hours.^[90] Kobayakawa et al. prepared N-doped TiO₂ powder by heating titanium hydroxide with urea^[91] while Nosaka et al. doped nitrogen into TiO₂ using urea, guanidine, or chloride guanidine as the nitrogen source.^[13] Yang et al. prepared a white precursor which was synthesized from tetrabutoxytitanium, ethanol and thiourea and treated the precursor in NH₃ flow at a certain temperature.^[92] The increase in photocatalytic activity depends on the N content and the method of preparation. However, the challenge is the recombination rate of the charge carriers because of the possible creation of Ti-O-N bands or the introduction of interstitial N.

2.7.2.2 Study of the band gap of N-doped TiO₂

The visible light photocatalysis of N-doped TiO₂ has been confirmed by many studies. However, two vital issues are unresolved. One of them is the mechanism for exhibiting visible activity in this system. Asahi et al. claimed that the doped N atoms narrow the band-gap of TiO₂ and thus makes it capable of absorbing visible light and demonstrating visible activity.^[90] The narrowing of the band gap is due to a mixing of the N2*p* and O2*p* states, being identified as the dominant transitions at the absorption edge from N2*p*_π to Ti*d*_{xy}, instead of from O2*p*_π as occurred in TiO₂ (by quantum chemical calculations). Irie et al. suggested that the N2*p* levels are separated from the valence band (formed by O2*p* states) forming an isolated narrow band^[87] located above

the valence band that is responsible for the visible response. In addition, Ihara et al. attributed oxygen vacancies caused by N-doping as the main contributor towards visible activity.^[87] Other authors pointed out that N-doping of TiO_2 is rather similar in properties to impurity sensitization, inducing the formation of localized states in the band gap. In this sense, the doped nitrogen may exist as NO-related species which may be present alone or together with Ti-N bondings; the former (NO-type) created by a N-O interaction where N is close to tetrahedral-like interstitial positions and the latter (Ti-N) bond form by substitutional replacement of O anions by N anions.^[93]

Figure 2.7 The mechanism of doped N atoms in narrowing the band-gap of TiO_2 : (a) Asahi et al. model (b) Irie et al. model.

2.7.3 Codoping TiO_2

At present, doping TiO_2 with two kinds of atom, called codoping, has gained considerable attention due to the higher photocatalytic activity compared to single-element doping.^[89] Codoping TiO_2 with N and other anions was reported to show favorable photocatalytic properties including synergetic effect, high surface area, well-crystallized anatase phase, red-shift in adsorption edge, strong absorbance of light with longer wavelength, etc.^[83]

The mechanism of codoping TiO_2 system for visible light activation is different, depends on the element used. For example, in N-F-codoped TiO_2 , Valentin et al. reported that the situation was more complex. The process involved superposition of two single doped materials with the simultaneous presence of both shallow and deep localized state into the band gap. Smaller oxygen defects were expected to be present in N-F-codoped TiO_2 bulk samples which probably became a reason for the larger photostability and photocatalytic activity for that codoped sample.^[94] In the case of N-P-codoped TiO_2 , Long et al. mentioned that N and P could act as substitutional dopants and adsorptive dopants.^[95] When both N and P acted as substitutional dopants, the bandgap narrowed slightly. However, upon N and P adsorption on the surface, the bandgap narrowing can be significantly induced even at low dopant concentrations. In another study, Jia et al. reported on the N-Fe-codoped system. They showed that codoping with N and Fe leads to lattice distortion which changes the dipole moments and makes the easier separation of photo-excited electron-hole pairs. Then, a significant red shift occurs resulting the efficient enhancing of photocatalytic activity.^[96]

2.7.4 Composite Semiconductor

Coupling of semiconductor with other semiconductor or molecules with narrower band gap have been reported as a promising method to improve visible light photocatalytic activity. The principle for improving the photocatalytic activity in the visible light region is due to increasing efficiency of charge separation and extending the energy range of photoexcitation for the system.^[59] For coupling with TiO_2 , many Aurivillius based compounds have gained remarkable interest because of their promising and

excellent photocatalytic activity under visible light irradiation.^[97-98] Aurivillius oxide family has general formula $\text{Bi}_2\text{A}_{n-1}\text{B}_n\text{O}_{3n+3}$ ($\text{A}=\text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}, \text{Bi}, \text{Na}, \text{K}$ and $\text{B}=\text{Ti}, \text{Nb}, \text{Ta}, \text{Mo}, \text{W}, \text{Fe}$).^[99] Bi_2WO_6 is the simplest member of the family and the most studied example so far.^[35] Bi^{3+} with 6s2 configuration is a candidate for valence band control element. The valence band can be controlled by the Bi 6s or hybrid Bi 6s-O 2p orbitals. The hybridization of the Bi 6s and O 2p levels will push up the position of the valence band, giving even smaller band gap compared to compounds that do not contain Bi in their structures. This hybridization also makes the valence band largely dispersing, which favors the mobility of holes in the valence band and hence beneficial for photocatalytic reactions.^[100] The structure of bismuth tungstate is perovskite-like structure that is defined by WO_6 units forming a layer perpendicular to the 100 direction and sandwiched the $(\text{Bi}_2\text{O}_2)^{2+}$ unit^[35] as shown in Fig. 2.8.

Figure 2.8 The structure of Bi_2WO_6 .^[101]

The idea of coupling is that the semiconductors must have matching band potential. For example, Bi-based oxide couples with TiO_2 to form heterojunction interfaces.^[97] As a result, they will be bonded tightly to form efficient heterostructure^[102] and this structure can extend the lifetime of the photon-induced electron-hole pairs.^[97, 102]

CHAPTER 3

Research Methodology

3.1 Methodology

A modified sol-gel method called peroxo sol-gel method was applied to synthesize nanosize un-doped and doped TiO_2 materials. Sol-gel processing is a wet chemical method for synthesis of colloidal dispersion of inorganic and organic-inorganic hybrid materials, particularly oxides and oxide-based hybrids.^[38] In this modified sol-gel method, an aqueous ammonia solution is added to an aqueous solution of Ti precursor to form $(\text{Ti}(\text{OH})_4)$, followed by the addition of H_2O_2 to form Peroxo Titanic Acid (PTA) solution. Then, heat treatment is applied to obtain pure anatase crystal.^[42] The peroxo sol-gel method also offers other advantages such as neutral pH condition,^[41-43] low material cost^[42-43] and is environmentally friendly as it uses aqueous solution instead of organic solvents.^[43] Moreover, PTA is stable in air^[42, 72] and its preparation is both simple and cost-efficient.^[72] For the thin film preparation, commercially available soda lime glass slides are used as the substrate and will be heated first to render it hydrophilic, then coated with the solution. This hydrophilic-assisted method is an easy and effective way to produce thin film with uniform coating result.

3.2 Experimental Method

This project consists of 4 main parts involving: (1) Synthesis of photocatalysts, namely N-doped TiO_2 , C-N-codoped TiO_2 , Fe-doped TiO_2 , and $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ composite. As

mentioned above, peroxo sol-gel method is used to prepare the precursor solution. The main novelty involved is that no additional stabilizer is added to the main precursors, making this a “greener” and cheaper process. (2) A simple hydrophilicity-assisted deposition of photocatalysts on substrates. The glass substrate is heated first before coating it with photocatalyst’s solution. The obtained hydrophilic glass substrate enables the solution to spread evenly over the surface, resulted in high quality, crack-free thin film. (3) Sample characterizations, and (4) Evaluation of the photocatalytic activity and/or photoelectrochemical properties of the synthesized materials.

3.2.1 N-doped TiO₂

3.2.1.1 Chemicals

All chemicals were used directly without further purification. Titanium (IV) chloride (TiCl₄) as TiO₂ source and ammonia solution (NH₃.H₂O, 25%) as pH adjuster and source of Nitrogen were purchased from Merck. Hydrogen peroxide (H₂O₂, 30%) was purchased from AnalaR.

3.2.1.2 Preparation of N-doped TiO₂ precursor^[103]

A 3.6 mL aliquot of TiCl₄ was added drop-wise into 300 mL distilled water in an ice-water bath and stirred with a magnetic stirrer. The water was adjusted to ~4 °C before TiCl₄ was added. After 30 min, the pH of the solution was adjusted to 7, 8, 9, 10 and 10.5 by drop-wise addition of ammonia solution. After stirring for 24 h, the obtained white precipitates were filtered and washed thoroughly with distilled water repeatedly until Cl⁻ was no longer detected. Then, the precipitates were dispersed in 80 mL distilled water. After that, 28 mL H₂O₂ was added drop-wise into

the mixture under continuously stirring for 4 h until a transparent and yellow Peroxo Titanic Acid (PTA) solution was obtained. The concentration of TiO_2 in that solution was adjusted to 2.0 wt.% by distilled water.

3.2.1.3 Preparation of N-doped TiO_2 films

Glass substrates were first cleaned by ultrasonication in a bath with distilled water for 30 min and then washed with isopropanol, ethanol and acetone sequentially. The glass slides were then heated in a furnace at 500 °C for 1 h with a heating rate of 10 °C per min. The glass slides were then cooled down to room temperature within one hour and the contact angles of the glass slides were around 2.9°, indicating the glass slides were hydrophilic. The prepared glass slide was dip-coated with the PTA solution using the KSV Dip Coater at a withdrawing speed of 0.2 cm/s. After drying in vacuum at room temperature for 10 min, the coated glass slide was then heated in the furnace at a heating rate of 10 °C per min to 500 °C for 1 h. All the prepared films were labeled based on the pH used as N- TiO_2 -7, N- TiO_2 -8, N- TiO_2 -9, N- TiO_2 -10 and N- TiO_2 -10.5.

The schematic of N-doped TiO_2 preparation is depicted in Fig. 3.1.

Figure 3.1 Scheme for the preparation of N-doped TiO_2 films from Peroxo Titanic Acid (PTA) Solution.

3.2.2 C- N-codoped TiO₂

3.2.2.1 Chemicals

All chemicals were used directly without further purification. Titanium (IV) chloride (TiCl₄) as TiO₂ source and ammonia solution (NH₃·H₂O, 25%) as pH adjuster and source of nitrogen were purchased from Merck. Carbon black and sodium hydroxide were purchased from Sigma. Hydrogen peroxide (H₂O₂, 30%) was purchased from AnalaR.

3.2.2.2 Preparation of C-N-codoped TiO₂ precursor

Peroxo Titanic Acid (PTA) solution was prepared using the same method described in part 3.2.1.2 with the following modification. A 3.6 mL aliquot of TiCl₄ was added drop-wise into carbon solution suspension in an ice-water bath and stirred with a magnetic stirrer and the pH of the solution was adjusted to 10 by drop-wise addition of ammonia solution. Carbon solution was prepared first by dispersing carbon black (5.0, 10 and 20 wt.% with respect to TiO₂) in 300 mL distilled water and ultrasonically treated for 1 h. The samples were named as CN5-PTA, CN10-PTA and CN20-PTA, according to the concentration of carbon black. In every solution, the theoretical TiO₂ concentration was adjusted to 2.0 wt.% by distilled water. Different solutions of nitrogen-PTA (N-PTA, without carbon), carbon-PTA (CPTA, 10 wt.% of carbon black with respect to TiO₂, ammonia solution was replaced by NaOH solution) and PTA (without carbon black and ammonia solution was replaced by NaOH solution) were also prepared for comparison.

3.2.2.3 Preparation of C-N-codoped TiO_2 films

The glass substrate was first cleaned and heated as explained in part 3.2.1.3. The prepared glass slide was dip-coated with the CN10-PTA solution using the KSV Dip Coater at a withdrawing speed of 0.2 cm/s. After drying in vacuum at room temperature for 10 min, the coated glass slide was then heated in the furnace at a heating speed of 10 °C per min and kept at 450 °C, 500 °C and 550 °C for 1 h respectively. The obtained films were labeled according to the calcination temperatures: CNT10-450, CNT10-500 and CNT10-550 respectively.

The effect of carbon black concentration was evaluated by preparing the samples at the same calcination temperature with various concentration of carbon black. CN5-PTA, CN10-PTA and CN20-PTA were used as the dip-coating solution. Then, the coated glass slide was heated in the furnace at a heating speed of 10 °C per min at 500 °C. The obtained films were labeled as CNT5-500, CNT10-500 and CNT20-500 respectively in accordance to the original concentration of carbon black. The scheme of C-N-codoped TiO_2 preparation is shown in Fig. 3.2. N- TiO_2 film (NT-500), C- TiO_2 film (CT-500) and pure TiO_2 film (T-500) were also prepared by using the coating solution respectively.

Figure 3.2 Scheme for the preparation of C-N-codoped TiO_2 films from Peroxo Titanic Acid (PTA) Solution.

3.2.3 Fe-doped TiO₂

3.2.3.1 Chemicals

All chemicals were used directly without further purification. Titanium (IV) chloride (TiCl₄) was used as TiO₂ source, purchased from Merck. Iron (III) chloride hexahydrate (FeCl₃·6H₂O) used as the source of Fe³⁺ dopant was obtained from Alfa Aesar. Ammonia solution (NH₃·H₂O, 25%) used as pH adjuster and source of nitrogen was purchased from Sigma-Aldrich. Hydrogen peroxide (H₂O₂, 30%) was purchased from VWR BDH Prolabo.

3.2.3.2 Preparation of Fe-doped TiO₂ precursor

Peroxo Titanic Acid (PTA) solution was prepared using the same method described in part 3.2.1.2 with the following modification. A 3.6 mL aliquot of TiCl₄ was added drop wise into 300 mL Fe³⁺ solution containing 0.5 wt.% of Fe³⁺ to TiO₂ in an ice-water bath and stirred with a magnetic stirrer and the pH of the solution was adjusted to 7 by drop-wise addition of ammonia solution. A 86 mL volume of distilled water was added to disperse the precipitate and then 20 mL H₂O₂ was added drop-wise into the mixture under continuous magnetic stirring for 4 h until a transparent and yellow Peroxo Titanic Acid (PTA) solution was obtained. This was used as the coating solution. The preparation of Fe-doped TiO₂ precursor solution was repeated using 300 mL of Fe³⁺ solution containing 1.0, 1.5 and 5.0 wt.% of Fe³⁺.

3.2.3.3 Preparation of Fe-doped TiO₂ thin films

The glass substrate was cleaned first and heated as explained in part 3.2.1.3. Then, the prepared glass slide was dip-coated with the PTA solution using the KSV Dip Coater

at a withdrawing speed of 0.2 cm/s. The coated glass slide was then heated in the furnace at 550 °C for 1 h. The films obtained were labeled according to the concentration of Fe^{3+} as FeTiO_2 -0.5, FeTiO_2 -1.0, FeTiO_2 -1.5 and FeTiO_2 -5.0 respectively. Fig. 3.3 illustrates the preparation of Fe-doped TiO_2 film.

Figure 3.3 Scheme for the preparation of Fe-doped TiO_2 films from Peroxo Titanic Acid (PTA) Solution.

3.2.4 $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ Composite Film

3.2.4.1 Chemicals

All chemicals were used directly without further purification. Diethylenetriaminepenta-acetic acid (H_5DTPA), Bi_2O_3 , $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$, titanium (IV) isopropoxide (purity 97%), stearic acid (purity 95%) and acetyl acetone (purity 99%) were purchased from Sigma-Aldrich. Isopropanol and ammonia solution (25%) were purchased from Merck.

3.2.4.2 Preparation of the precursors

1. Preparation of Bi_2WO_6 precursor^[104]

A 6.3 g Diethylenetriaminepenta-acetic acid (H_5DTPA) and 6 mL ammonia solution were added to hot de-ionised water (80 °C). After that, 1.86 g of Bi_2O_3 powder and 1.02 g of $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$ powder were added. The solution was stirred and maintained at 80 °C in an oil bath to promote dissolution and complexation of Bi^{3+} and W^{6+} with DTPA, until the mixture became a colorless transparent solution. The concentrations of the theoretical Bi_2WO_6 in the precursor solution were adjusted to 1.5 wt%, 3.0 wt% and 5.0 wt% using deionized water.

2. Preparation of TiO_2 solution (3.0 wt.%)

Typically, a mixture of 0.1 mL of distilled water and 10 mL of isopropanol was added drop-wise to the mixture of 2.5 g of TTIP and 10 mL of isopropanol. The solution was stirred in an oil bath at 80 °C for 18 h. 6 mL of acetyl acetone (AcAc) was then added to the TiO_2 sol. Finally, the concentration of the TiO_2 sol was adjusted to 3.0 wt.% by isopropanol.

3.2.4.3 Preparation of the composite $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ film

To make the $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ heterojunction film, a Bi_2WO_6 film was first prepared. The FTO (fluorine doped tin oxide) glass substrate, purchased from Xin Yan Technology Ltd, China, was cleaned first and heated as explained in part 3.2.1.3. Then, the prepared glass slide was dip-coated with the Bi_2WO_6 coating solution using the KSV Dip Coater at a withdrawing speed of 0.2 cm/s for 1 min. After drying in vacuum at room temperature for 2 min to remove volatile solvents, the coated glass slide was then calcined in the furnace at 300 °C for 0.5 h. The obtained Bi_2WO_6 films were labeled as BWO-1.5, BWO-3 and BWO-5 for Bi_2WO_6 concentration of 1.5 wt.%, 3.0 wt.% and 5

wt.%, respectively. Single-layered Bi_2WO_6 film calcined at 500 °C was prepared as well for comparison.

The composite $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ heterojunction bi-layer films were prepared by dip-coating the obtained Bi_2WO_6 film into TiO_2 sol for 1 min. The dipped glass slides were then calcined in furnace at 500 °C. According to the concentration of Bi_2WO_6 , the obtained $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ heterojunction bi-layer films were labeled as BWO-1.5/ TiO_2 , BWO-3/ TiO_2 and BWO-5/ TiO_2 respectively. Single-layer TiO_2 film was prepared by dipping the FTO glass substrate into TiO_2 sol and calcined at 500 °C.

3.2.5 Synthesis of TiO_2 Photocatalyst in Powder Form

To prepare the powder form of the photocatalyst, 30 mL of the yellow solution was put into a tube flask in a water evaporator for 1 h followed by oven drying at 70 °C for 12 h. The powder was then calcined at high temperature.

3.3 Characterization Method

3.3.1 Powder X-Ray Diffraction (XRD) Analysis

X-ray diffraction is an important technique to determine the structure of materials.^[105]

Samples in powder form constitute a large collection of very small crystals at random orientation. Therefore, the different pattern is resultant from all sets of crystal planes.

The sample is finely ground and shaped into a thin layer in a sample holder and is then inserted in the path of X-ray. The relationship between the wavelength of X-ray beam, diffraction angle, and the distance between each set of atomic planes of the crystal lattice is derived by Bragg formulation : $\lambda = 2d \sin \theta$, which λ is the wavelength of X-

ray radiation, d is the crystal plane distance, and θ is the diffraction angle. The XRD patterns are collected using LabX-Shimadzu XRD6000 diffractometer with Cu $K\alpha$ as the X-ray source ($\lambda = 1.54060 \text{ \AA}$).

3.3.2 UV-Vis Spectroscopy

Optical spectroscopy is widely used to determine the optical properties of materials. Absorption & emission spectroscopy and vibrational spectroscopy are two of such technique.^[67] UV-visible spectroscopy can be used to measure absorption due to the excitation of electrons from ground state to excited states of atoms, ions, molecules or crystal. Then, the absorption spectrum is used to determine band gap energy by the equation

$$E_{bg} = (h \cdot c) / (\lambda \cdot e) \cdot 1239.8 / \lambda \quad (\text{Eq. 3.1})$$

Where E_{bg} is the band gap, h is Planck's constant, c is the light speed, e is the elementary charge, and λ is the wave length of the absorption edges that is taken from the peak position of the differential plots in the spectrum.^[106, 107]

UV-visible spectra of the thin films were obtained using a UV-visible spectrophotometer (Shimadzu 2450).

3.3.3 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy is a non-destructive analysis that can provide information about the chemical bonding, particularly in solids or thin films material. The goal of the FTIR spectroscopy is to determine the transmittance of the sample as a function of

wavelength or frequency. The transmittance is defined as the fraction of incident light at a specified wavelength that passes through a sample, that is

$$T_w = (I_t/I_0)_w \quad (\text{Eq. 3.2})$$

where T_w is the transmittance of the sample at frequency w , and I_0 and I_t are the incident and transmitted light, respectively, at frequency w . A plot of this ratio versus frequency produce the infrared spectrum.^[108] If absorbance is measured, the equation can be defined as below.

$$A = ((I_0 - I_t)/I_0)_w \quad (\text{Eq. 3.3})$$

The Beer-Lambert Law gives a simple foundation for quantitative application of FTIR.^[108] In this work, a Digilab FTS3100 FTIR is used.

3.3.4 Field Emission Scanning Electron Microscopy (FESEM)

SEM provides a highly magnified image of the surface of a material that is very similar to the actual object.^[108] FESEM is adapted from SEM and combines the system of a field emission electron source smallest scanning probe to produce an ultra high resolution of 0.7 nm.^[109] The sample must be conducting; if the sample is an insulator, the sample must be coated with a thin (10 nm) conducting film of carbon, gold, or some other metal to make it conductive.^[108]

In this project, FESEM JEOL JSM-6700F SEM is used. Prior to testing, the samples were coated with an ultrathin coating of platinum as electrically conductive material by a JFC-1600 Auto Fine Coater.

3.3.5 Energy-dispersive X-ray Spectroscopy (EDX/EDS)

Wavelength-dispersive X-ray spectroscopy (WDX) and energy-dispersive X-ray spectroscopy (EDX) are two main X-ray spectroscopic techniques depending on the physical property measured (the wavelength or energy of the emitted X-rays). EDX is a highly sensitive method of detecting elements of medium and high atomic number. EDX can give qualitative and quantitative spectral information. In qualitative EDX spectra, the X-ray intensity is usually plotted against energy. They consist of several approximately Gaussian-shaped peaks which are characteristic of the elements present in the transmitted volume. Most of the chemical elements can be identified by EDX. For quantitative purpose, EDX analysis involves the determination of the background contribution, background subtraction, and the net intensities of the characteristic X-ray peaks. For investigating bulk materials and thin films, the procedure from Castaing and Cliff-Lorimer is commonly used, respectively.^[110]

EDX equipment can be combined with Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM) equipment. An imaging of element distribution either along a line or two-dimensionally in a rectangular field of view is obtained.^[110] In this work, JED-2300F EDX is used, coupled with JEOL JSM-6700F FESEM.

3.3.6 Atomic Force Microscopy (AFM)

Nanoscale texture (surface roughness) and morphology of coated glass surface can be investigated by AFM. This technique is based on the measurement of different forces (e.g. attractive, repulsive, magnetic, electrostatic, van der Waals) between a sharp tip

and the sample surface. Imaging is accomplished by measuring the interaction force via deflection of a soft cantilever while raster-scanning the tip across the surface. Although various types of forces are encountered when a tip approaches the sample surface, signal generation in AFM is essentially based on interatomic repulsive forces, which are of extreme short-range nature. Since the interatomic repulsive force is influenced by the total electron density around an atom, this force can be used to map the topography of the surface down to atomic dimension.^[115] In this project, AFM MFP 3D is used.

3.3.7 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is one of the most widely used surface analysis techniques because it provides exceptional combination of compositional and chemical information, easy operation, and the commercial equipment is readily available. XPS can be used for analysis of all elements in the periodic table except hydrogen and helium. XPS is concerned principally with photoelectron and their kinetic energies. When the surface is irradiated with soft X-ray photons, an energy $h\nu$ interacts with an electron in a level X with the binding energy E_B . Then, the entire photon energy is transferred to the electron, with the result of a photoelectron ejected with the kinetic energy:

$$E_{\text{kin}}(h\nu, X) = h\nu - E_B - \Phi_s \quad (\text{Eq. 3.4})$$

where Φ_s is small, almost constant, work function term.

The ejected electron can come from the occupied portion of the valence band or from a core level that being a focus in XPS. Because no two elements share the same set of

electronic binding energies, measurement of the photoelectron kinetic energies enable elemental analysis. The instrument of XPS consists of vacuum equipments, X-ray sources, synchrotron radiation, electron-energy analyzer, and spatial resolution.^[110]

In this project, a PHI Quantum 2000 Scanning ESCA Micro-probe equipment physical electronics, MN, USA) using monochromatic Al-K α radiation was used. The X-ray beam diameter was 100 μm , and the pass energy was 29.35 eV for the sample. The binding energy was calibrated with respect to C (1s) at 284.6 eV.

3.3.8 Differential Thermal and Thermogravimetric Analysis (DT-TGA)

DT-TGA (Differential Thermal and Thermogravimetric Analysis) consists of two kind of analyses. They are Different thermal analysis (DTA) and Thermogravimetric Analysis (TGA). DTA can be used to measure the absorption or liberation of heat caused by physical or chemical change in a material, while TGA measures the change of material weight as a function of temperature and/or as a function of time at desired temperature. Any sample in solid and liquid form can be studied by DT-TGA. The principle of DT-TGA is measuring the differential temperature between an inert reference and the sample upon heating or cooling at a particular rate or under isothermal condition and the weight loss or gain is recorded as a function of time.^[111]

In this work, a PerkinElmer Pyris Diamond TG/DTA is used in the temperature ranges from room temperature to 800 °C with air flow rate of 20 mL min⁻¹ and heating rate of 10 °C min⁻¹.

3.3.9 Nitrogen Sorption

Nitrogen sorption is a measurement technique based on physical adsorption or physisorption phenomenon. The equilibrium and saturation pressure of the nitrogen gas, as well as the amount of gas adsorbed at constant temperature was measured, from which the surface area can then be determined using the Brunauer-Emmet-Teller (BET) model. That model is the most widely used theory in this method, which assumes that the adsorbate molecules settle on two types of specific local sites, either on the adsorbent surface or on top of another adsorbate molecule.^[112] The BET equation is shown in Eq. 3.5.

$$n_{ad}/n_m = CP / (P_s - P)[1 + (C - 1)(P/P_s)] \quad (\text{Eq. 3.5})$$

and normally rearranged to Eq. 3.6.

$$P / [n_{ad}(P_s - P)] = 1/(n_m C) + (C - 1)/(n_m C) (P/P_s) \quad (\text{Eq. 3.6})$$

where n_{ad} is the amount of adsorbate, n_m is the number of moles of adsorbate in a monolayer, C is BET constant, P is adsorptive pressure, and P_s is saturated vapor pressure over the bulk liquid.^[112] Then, obtained n_m can be used to calculate surface area, A_s :

$$A_s = n_m N_A a \quad (\text{Eq. 3.7})$$

Where N_A is Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$), and a is the cross sectional area of the adsorbate molecule which is calculated by Eq. 3.8.^[112]

$$a = (M/\rho)^{2/3} (N_A)^{1/3} \quad (\text{Eq. 3.8})$$

In this work, nitrogen adsorption–desorption isotherms were measured at -196°C on a Quantachrome AUTOSORB-6B static volumetric instrument. Prior to measurements, the samples were degassed at 250°C for 5 h under high vacuum.

3.3.10 Photoluminescence

Photoluminescence is a nondestructive, high-sensitivity and effective technique to investigate the photophysical and photochemical properties of excited states generated by adsorption in the aggregate states in solid semiconductors. Photoluminescence techniques can supply information such as surface oxygen vacancies and defect, surface states and charge separation and/or recombination.^[113-114] The application of photoluminescence as a technique for the characterization of solid surface is in relation to adsorption, catalysis and photocatalysis.^[113] The photoluminescence (PL) spectra of the samples were recorded with Fluoromax-4 Spectrophotometer (Horiba Jobin Yvon) at room temperature. The excitation wavelength was 300 nm and the emission slit was 1.0 nm.

3.3.11 Contact Angle Measurement

The hydrophilicity of the surface is interpreted by measuring water contact angle. The contact angle (CA) is defined as the angle between the solid surface and the tangent line of the liquid phase at the interface of the solid-liquid-gas phases.^[48] Water contact angles of coated glasses are measured on a commercial contact angle meter (goniometer by FIBRO system AB, SWEDEN, model PG-2) at ambient temperature.

3.4 Photocatalytic Activity Test

The visible light photocatalytic activities of the prepared samples were investigated using stearic acid as a model organic compound. Stearic acid has been widely used as model of organic compound for determination of photocatalytic activity because it is easy to prepare stearic acid film. Stearic acid films are very easily laid down from a

methanol or chloroform solution, the reaction kinetics of stearic acid photodegradation follow a simple zero-order reaction and so the film thickness is not a critical factor in photocatalytic activity test, and the mineralization process can be monitored easily using FTIR.^[115-117]

Stearic acid was dissolved in methanol (0.035 moles in 100 mL methanol). A 300 μ l aliquot of this solution was spun-coated by WS-400B-6NPPL/LITE for 2 min at 2000 rpm onto the TiO₂ thin films and dried in an oven at 70 °C. Prior to stearic acid coating, the samples were UV irradiated for 2 h to clean the surface from any organic contaminants that might have been adsorbed from atmosphere. The visible light source used was a 300 W halogen lamp held at 15 cm from the sample with 420 nm UV filter (JB420) placed 5 cm above the sample. UV intensity below 420 was measured and it was confirmed that no significant irradiance < 420 nm was detected. The degradation of stearic acid was determined by monitoring the concentration of stearic acid using FTIR (Digilab FTS3100). The absorbance at 2917 cm⁻¹ of the samples at 0 and 24 hrs (named A_i and A_f, respectively), and the time taken visible light irradiation was recorded. The stearic acid degradation was calculated using equation 3.9.

$$\% \text{ degraded} = [(A_i - A_f)/A_i] \times 100\% \quad (\text{Eq. 3.9})$$

In this experiment, a negative control (stearic acid deposited onto unmodified glass only) was evaluated and it was found that no obvious change of stearic acid layer, which was monitored from FTIR absorbance at 2917 cm⁻¹.

3.5 Photoelectrochemical Study

Semiconductors have been used as electrode material in photoelectrochemical system. Semiconductor can take the energy of photon and converts it into electrochemical energy.^[118] In photoelectrochemical cells (PEC), semiconductor is dipped into electrolyte solution and the liquid junction potential barrier can be easily established.^[119] This semiconductor electrolyte-interface can be used not only for PEC cell, but also for photoelectrolysis, photocatalysis, and photoelectrochemical power generation.^[120] The properties of such system are mainly dependent on the microstructure of the photoelectrode surface which then affect the interfacial property formed between the semiconductor electrode and electrolyte.^[121]

Photoelectrochemical measurements were carried out in a standard three compartment cell consisting of a working electrode, a Pt wire counter electrode, and a saturated Ag/AgCl reference electrode. N₂-saturated 0.5 M Na₂SO₄ in water was used as an electrolyte. A 300 W Xe lamp (Oriel) equipped with a 420 nm cut-off filter was used for excitation. A Newport integrated monochromator was used to generate selected wavelengths for incident-photon-to-current efficiency (IPCE) measurement. An Autolab PGSTAT302N model potentiostat and its GPES program were employed for recording the current and voltage signals.

CHAPTER 4

N-doped TiO₂ Film

4.1 Introduction

Numerous efforts have been made to produce a photocatalyst that is capable of effective utilization of visible light. Doping TiO₂ with nitrogen is one of the promising ways and has gained more attention due to significant enhancement in photocatalytic activity in visible light region.

N-doped TiO₂ was first reported by Sato in 1986. He reported that impurity NH₄Cl shifted the absorption threshold of TiO₂ into the visible light region upon calcinations. This sample showed higher photocatalytic activity for oxidation of carbon monoxide and ethane than un-doped TiO₂ in the visible light region. The sample was assigned to NO_x-doped TiO₂^[122] and became an important first step towards the development in N-doped TiO₂. Asahi's work published in 2001 is considered a major milestone in visible light photocatalysis. They found that the N-doped TiO₂ exhibited good photocatalytic activity under visible light irradiation.^[90] The enhancement in visible light photocatalytic activity is due to its ability to increase the amount of photon absorbed in the visible range.^[48] They also calculated densities of states (DOSs) of several anion dopant such as C, N, F, P, S for substitute O in the anatase crystal and found that N doping was the most effective because its p states contribute to band gap narrowing by mixing with O 2p states.^[90]

Many methods have reported the preparation of N-doped TiO₂ photocatalyst. For example, Asahi et al. prepared N-doped TiO₂ by sputtering TiO₂ target in an N₂ (40%)/Ar gas mixture followed by annealing at 550 °C in N₂ gas.^[90] Ihara et.al prepared the same photocatalyst by calcinations of the hydrolysis products of Ti(SO₄)₂ treated with NH₃ aqua solution.^[123] Chi et al. reported a mixture of tetrabutoxytitanium, HCl, ethanol and urea by a template-free solvothermal method to prepare N-doped TiO₂,^[124] while Yang et al. synthesized N-doped TiO₂ from tetrabutoxytitanium, ethanol, and thiourea and then treated the precursor in NH₃ flow at a certain temperature.^[125] However, to the best of our knowledge, there is no report in the open literature on transparent N-doped TiO₂ films prepared by aqueous peroxo titanic acid (PTA) solution as a Ti source.

In this work, we principally aim to study the effect of pH on nitrogen doping concentration in TiO₂ films and evaluate their photocatalytic activities. The precursor of N-doped TiO₂ was prepared using peroxo sol-gel method. This method is environmentally friendly because no organic solvent and organic Ti precursor is involved. A subsequent hydrophilicity-assisted method was used to prepare transparent, uniform, crack free and visible light-activated N-doped TiO₂ thin film. The crystal structure, surface morphology and photocatalytic activity were evaluated. It was observed that all of N-doped TiO₂ films showed an excellent visible light absorption and enhanced photocatalytic activity compared to that of un-doped TiO₂ and commercial self-cleaning glass. The N-TiO₂-10 film was found to be optimal for visible light photocatalytic photodegradation of stearic acid in this study.

4.2 Hydrophilicity-assisted Coating Method

In this work, silica glass was used as a substrate for N-doped TiO₂ thin films. During heat treatment, the structural changes in the silica glass occur.^[126] Surface hydroxyl groups (OH⁻) are generated when silica reacts with water molecules at high temperature.^[127] The wettability property has positive correlation with absorbed hydroxyl groups;^[128] in other words, if the absorbed hydroxyl groups increase, the contact angle will decrease. Fig. 4.1a shows that the contact angle of pure glass decreases if the annealing temperature increases, i.e. CA decreases to ~2.5° after being heated at 500 °C and almost 0° after being heated at 650 °C. This happens because at higher temperature, the amount of hydroxyl groups generated increase and the surface contaminants decrease, resulting in the small of contact angle. This hydrophilic property is temporal. From Fig. 4.1b, it can be seen that after being left in ambient condition, the contact angle increases and becomes 52° after 24 h. When silica reacts with molecular water at high temperature, hydroxyl group generation is usually observed. The reaction is:^[127]

The reaction above is reversible. If the heated glass is left under ambient temperature, the glass temperature decreases and the reverse reaction occurs. Therefore, the amount of hydroxyl groups decrease, resulting in an increase of water contact angle. In addition, the absorption of contaminant on the silica glass surface also increases after 24 h and contributes to the increase in contact angle.

Figure 4.1 (a) Contact angle of pure glass after being heated at different temperatures, (b) Variation of contact angle of heated glass (500 °C) with time after being left in ambient conditions.

Fig. 4.2 shows the images of pure glass substrate without and with heat treatment after dipping into PTA aqueous solution. In Fig. 4.2a, only certain parts of the glass surface are deposited with PTA solution and droplets are found on the glass surface. This results in a non-uniform coating. For the freshly heat-treated glass substrate (Fig. 4.2b), PTA solution is coated uniformly on the glass substrate. The glass substrate appears slightly opaque due to a thin film of PTA solution coated on the surface. The thin films obtained after heat treatment on pure glass with and without heat treatment are shown in Fig. 4.2c&d, respectively. It is obvious that the coating result in Fig. 4.2d is not uniform while the coated glass in Fig. 4.2c is uniform, transparent, and a little yellow due to the doping of N atoms in the TiO₂ film.

Figure 4.2 Images of pure glass substrate (a) without and (b) with heat treatment after being dipped into PTA aqueous solution; (c) coated with transparent N-TiO₂-10 film on temporary superhydrophilic glass; (d) coated with N-doped TiO₂ film on glass without heat treatment.

4.3 XRD, FTIR and XPS Characterizations

Figure 4.3 XRD pattern of N-doped TiO₂ prepared at different pH conditions: (a) N-TiO₂-7, (b) N-TiO₂-8, (c) N-TiO₂-9, (d) N-TiO₂-10, (e) N-TiO₂-10.5.

Fig. 4.3 shows the XRD patterns of N-doped TiO₂ samples prepared at different pH after calcination at 500 °C for 1 h. The XRD spectra show the presence of only anatase phase for all samples. The crystal sizes of N-TiO₂-7, N-TiO₂-8, N-TiO₂-9, N-TiO₂-10 and N-TiO₂-10.5 are approximately 17.0 nm as determined by Scherrer's equation using the (101) diffraction peak of anatase.

The FTIR spectra of the yellow peroxo titanic acid (PTA) of all samples before and after heat treatment are presented in Fig. 4.4a and b respectively. In Fig. 4.4a, a peak at 900 cm⁻¹ corresponding to the stretching vibration of the O-O bond (peroxo group) in the Ti-O-O-H bond of the peroxo titanic acid is observed. The wide bands at 3100 - 3700 cm⁻¹ are attributed to the stretching vibration of the hydrogen-bonded OH groups of the adsorbed water. The absorption around 1620 cm⁻¹ is assigned to the bending vibration of adsorbed H₂O molecules. The peaks around 1400 cm⁻¹ are assigned to the stretching vibrations of the N-H bonds in NH₃, which provides evidence of the presence of NH₃ in Ti complex.^[27] The NH₃ in the Ti complex is regarded as a nitrogen source for the N-doped TiO₂. PTA has unstable chained atoms of hydrogen, which will decompose and release oxygen molecules to form stable N-doped TiO₂ during heating. In this process, NH₃ also decomposes. The disappearance of 900 cm⁻¹ and 1400 cm⁻¹ bands in Fig. 4.4b evidences the decomposition of PTA and NH₃ respectively.^[40, 129] A new peak found at 1387 cm⁻¹ is attributed to hyponitrite peak.^[130]

Figure 4.4 FTIR spectra (a) before calcinations, (b) after calcinations, of N-doped TiO₂ samples at different pH values after calcination at 500 °C for 1 hour.

The hydrolysis of TiCl₄ involves a series of complex reactions because many compounds and ions are involved such as H₂O, Cl⁻, Ti⁴⁺, NH₃, NH₄⁺, OH⁻, etc. Sun et al.^[131] suggested a modified term of Ti complex formation with the formula [Ti(H₂O)_a(NH₃)_b(OH)_cCl_d]^(4-c-d) (where a+b+c+d = 6) to represent an overview of that hydrolysis process with the addition of ammonia solution. The precipitate from hydrolysis could include NH₄Cl and NH₃ in Ti complex.^[14] In our work, FTIR spectra in Fig. 4.4a shows that the intensity of peak at 1400 cm⁻¹, which is assigned to the stretching vibrations of the N-H bonds in NH₄⁺, is almost similar for all samples. This suggests that the amount of NH₄⁺ does not depend on pH, so we can reduce the effect of NH₄⁺ in the system and focus on the effect of NH₃. In our work, when pH increases, OH⁻ and NH₃ concentration increase as well (the values of b and c increases, d decreases). Sun et al. reported that NH₃ is located closer to the Ti atoms in the Ti complex, making the nitrogen atoms easier to be incorporated into the TiO₂ lattice.^[131] Here, we can see that NH₃ plays the most important role in nitrogen doping.

To investigate nitrogen doping states and to determine the degree of x in the TiO_{2-x}N_x thin films, N 1s core levels were measured by XPS. Fig. 4.5 shows N 1s spectra for all N-doped TiO₂ samples calibrated with respect to the C 1s peak at 284.6 eV. The concentration of nitrogen in the samples N-TiO₂-7, N-TiO₂-8, N-TiO₂-8, N-TiO₂-10, and N-TiO₂-10.5 are obtained 0.08 at%, 0.20 at%, 0.26 at%, 0.78 at% and 0.96 at%, respectively. The results support that nitrogen concentration increases with pH. From Fig. 4.5, one strong peak is found centered at 400 eV. The intensity of the peak increases with pH and no obvious peak is found in sample N-TiO₂-7.

Figure 4.5 N 1s XPS spectra of N-doped TiO₂ films.

Many studies have suggested that this peak is responsible for a visible light response which means the intensity of the peak at 400 eV correlates with the intensity of optical absorbance^[13, 131] as shown in Fig. 4.7 in this work. The XPS signal at around 400 eV has been a subject of controversy in the identification of nitrogen species in the study of nitrogen-doping materials. Saha et al. assigned this peak as molecularly chemisorbed γ -N₂.^[132] Asahi et al. reported that this peak corresponded to N₂ molecules incorporated into the TiO₂ lattice.^[90] Similar to Asahi, Horikawa et al. assigned this peak to the presence of N atoms from molecularly adsorbed nitrogen containing compound onto the surface of samples.^[106] In another study, Valentin et al. reported that the peak at 400 eV was attributed to a lower valence state of nitrogen.^[133] Gole et al. and Chen et al. considered this peak as N-Ti-O linkage in the lattice.^[134-135] Yamada et al. reported the peaks in the range of 399-400 eV are associated with N-N and N-O bonds which presumed that oxygen atoms in TiO₂ lattice were substituted by

nitrogen atoms to form Ti-N bond or they were introduced in TiO₂ to form N-N and N-O bonds.^[136] In another publication, Navio et al. assigned this peak to hyponitrite.^[137] Therefore, sample N-TiO₂-7 can be considered as un-doped TiO₂ because the nitrogen concentration is so low that it can not be detected by XPS, and thus should display minimal effect in visible light absorption and photocatalytic activity.

4. 4 Surface Characterization

A typical N-doped TiO₂ coated glass is shown in Fig. 4.6a. The coated glass is visually transparent and uniform with a yellow tint due to N doping. FESEM (Fig. 4.6b and c) reveals that the N-TiO₂-10 thin films have no cracks, which are attributed to uniform adsorption of PTA on the hydrophilic pure glass resulting in uniform coating. The particle size shown in Fig. 4.6c is around 17-20 nm, which is consistent with that obtained from XRD. The morphology of N-TiO₂-7, N-TiO₂-8 N-TiO₂-9 and N-TiO₂-10.5 films, which are not shown here, are similar to that of the N-TiO₂-10 film, indicating that N-doping has a little effect on the shape and size of the particles.^[138]

(a)

(b)

(c)

Figure 4.6 (a) Image of transparent N-TiO₂-10 coated glass, FESEM images for N-TiO₂-10 film (b) at low and (c) high magnifications.

4.5 Optical Property

The color of the transparent thin films is yellowish, as shown at Fig. 4.6a, indicates that the absorption of visible light is enhanced.^[139] Fig. 4.7 shows the UV-visible diffuses reflectance spectra of the un-doped and N-doped TiO₂ thin films. Compared to un-doped TiO₂, enhanced absorption in the visible range of 400-550 nm is observed, which is attributed to N atoms doping.^[138] It is also observed that the optical absorption in the visible region increases with pH due to the increase of nitrogen doping concentration in the TiO₂, as supported by XPS results. The shape of the absorption edge indicates that nitrogen atom is primarily substitutional, with an insignificant concentration of oxygen vacancies.^[140] A slightly increment of absorption in N-TiO₂-7 (un-doped TiO₂) sample may be attributed to quantum size effect of TiO₂ film and the thermal stress in the films due to the difference in the thermal expansion coefficients between the fused substrate and coating material.^[141]

Figure 4.7 UV-visible diffuse reflectance spectra of N-doped TiO₂ films prepared at different pH conditions.

4. 6 Photocatalytic Activity Evaluation

Fig. 4.8a shows the photocatalytic activities of all samples. The photocatalytic activity of the N-doped TiO₂ films is evaluated by photodegradation study of stearic acid (SA) under visible light irradiation for 24 h. Stearic acid is chosen as the model organic pollutant to evaluate the photocatalytic activity on TiO₂ film structure.^[14]

The enhancement of visible light photocatalytic activity of N-doped TiO₂ is mainly attributed to the improvement visible light absorption by N doping, so the number of photons taking part in the photocatalytic reaction increases and results in the improvement of photocatalytic activity.^[138] Fig. 4.8a shows that the photocatalytic

activity increases with pH until pH = 10. As explained above, this can be attributed to the increase of N doping concentration, which also results in the increase of visible light absorption as shown in Fig. 4.7. Sample N-TiO₂-10 shows the highest photocatalytic activity with 12.5% stearic acid degraded compared to initial concentration. This result is 9.5 and 13.6 times higher than that of N-TiO₂-7 (un-doped TiO₂) film and commercial self-cleaning glass (PILKINGTON ActiveTM Self-cleaning Glass), respectively. However, at the highest ammonia concentration (pH = 10.5), the percentage of stearic acid degraded decreases to 8.7%. Higher dopant concentrations may lead to greater recombination rate and lower photocatalytic activity.^[142-143]

Figure 4.8 (a) Photocatalytic activities of N-doped TiO₂ prepared at different pH under visible light illumination for 24 h, (b) Evolution of the IR absorbance spectra of N-TiO₂-10.

4.7 Conclusions

In summary, a “green” and simple method has been developed to prepare N-doped TiO₂ precursor by peroxo sol-gel method without using any organic compound. The hydrophilicity of freshly heated pure glass slides is exploited for the preparation of the thin films. The prepared thin films are transparent, uniform, crack free and visible light-activated photocatalytic activity. The photocatalytic activity increases with the increase of pH until pH = 10, which is attributed to the increase of N-doping concentration. The photocatalytic activity of N-TiO₂-10 is about 9.5 and 13.6 times higher than that of un-doped TiO₂ film and commercial self-cleaning glass,

respectively. Beyond optimal N-doping concentration, reduced photocatalytic activity for the N-TiO₂-10.5 film is attributed to higher number of charge recombination sites.

CHAPTER 5

C-N-codoped TiO₂ Film

5.1 Introduction

Recently, nonmetal codoping presents a more promising strategy to enhance the photocatalytic activity of TiO₂ in the visible light region than single atom doping.^[22, 27] C-N-codoped TiO₂ has been reported to exhibit superior photocatalytic activity under visible light irradiation as both carbon or nitrogen can effectively narrow the band gap of TiO₂.^[144-147] For example, Lin et al. reported that the C-doped TiO₂ thin film exhibited a significant red shift to the visible region and a significant improvement in the photocatalytic activity under visible light irradiation.^[12] They prepared C-doped TiO₂ thin film by sol-gel method combined with hydrothermal treatment. In another study, Matos et al. prepared the C-doped TiO₂ thin film by solvothermal synthesis and calcinations.^[11] They showed a similar result with Lin et al. whereas the prepared C-doped TiO₂ thin film exhibited very strong photoactivity for methylene blue degradation under visible light irradiation. Using a different preparation method, Wong et al. developed C-doped TiO₂ by ion-assisted electron-beam evaporation and found that the photocatalytic activity for methylene blue degradation was enhanced and the carbon doping concentration was an important factor for that.^[148] Many studies have reported the excellent performance of N-doped TiO₂ in the photodegradation of organic compound^[149-150], including our work reported in chapter 4.

In another study on C-N-codoped TiO₂, Chen et al. prepared C-N codoped TiO₂ using a sol-gel method and found that the photocatalytic activity under visible light irradiation of the samples were the highest compared to C-doped and N-doped TiO₂.^[142] The same codoping TiO₂ was prepared by Zhang et al. by a hydrolysis-polymerization-calcination method and showed that photocatalytic activity of C-N codoped TiO₂ was greatly improved.^[89]

In this work, we extend our quest of fabricating visible light-activated thin films by preparing C-N-codoped TiO₂ using a similar technique for the preparation of N-doped TiO₂ thin film. Calcination temperature and carbon doping concentrations were varied to find the optimal conditions for the preparation of photocatalysts with the highest visible light photocatalytic activity. It is observed that all C-N-codoped TiO₂ films showed excellent visible light absorption and enhanced photocatalytic activity compared to that of un-doped TiO₂, C-doped TiO₂ and N-doped TiO₂. The CNT10-500 film was found to be the optimal for visible light photocatalytic photodegradation of stearic acid in this study.

5.2 The Effect of Calcination Temperature

5.2.1 XRD and XPS Characterizations

The crystalline phase and particle size of the C-N-codoped TiO₂ prepared at different calcination temperatures were determined by XRD as shown in Fig. 5.1. The XRD spectra show the presence of only anatase phase for all samples. It is obvious that the intensity of CNT10-450 is lower compared to that of CNT10-500 and CNT10-550, which is due to lower amount of crystalline phase formed at lower temperature. The

crystallite size can be estimated using the Scherrer formula using the (101) diffraction peak of anatase and is summarized in Table 5.1. The crystal sizes increase with the increase of calcination temperatures, which is due to the aggregation of TiO₂ particles at high temperature.

Table 5.1 Crystal size of the samples at different calcination temperatures obtained from Scherrer formula.

No	Sample's name	Temperature of calcination (°C)	Carbon concentration (wt.%)	Crystallite size (nm)
1	CNT10-450	450	10	16.5
2	CNT10-500	500	10	17.2
3	CNT10-550	550	10	20.5

Figure 5.1 XRD pattern of C-N-codoped TiO₂ prepared at different calcination temperatures.

Surface chemical compositions and bonding states of the thin films were carried out by XPS (Fig. 5.2). The atomic concentration of the elements (C, N, Ti) present in the surface were calculated and summarized in Table 5.2.

Table 5.2 The atomic concentrations of elements (C, N, Ti) present on the surface of prepared thin films.

No	Sample	Atomic percentage of carbon (at%)	Atomic percentage of nitrogen (at%)	Ti ³⁺ /Ti ⁴⁺
1	CNT10-450	42.51	0.41	4
2	CNT10-500	28.59	0.32	10.5
3	CNT10-550	26.27	0.26	11.3
4	NT-500	-	-	0.1

Two peaks at the binding energies of 284.6 and 288.5 eV are observed for C 1s state of C-N-codoped TiO₂ sample. The peak at 284.6 eV corresponds to C-C bond came from the adventitious elemental carbon^[146, 151] and the peak at 288.5 eV is assigned to the presence of C-O bonds.^[147] These data indicate that carbon may substitute some of the Ti atoms lattice and form a Ti-O-C structure.^[152] The peak at around 281.0 eV of Ti-C bond is not observed in these samples, which suggests that carbon does not substitute for oxygen atom in the lattice of TiO₂ in the current system. It has been reported that the carbon doping states and species cannot be directly confirmed by only analyzing the XPS C 1s spectra.^[153-154] Further analysis of the XPS Ti 2p spectra can help to investigate the carbon doping state, because carbon-doping can lead to the formation of oxygen vacancies and Ti³⁺ defects and result in a slight shift of the Ti 2p peaks toward the lower binding energy.^[153-154] Fig. 5.2c shows a comparison of the Ti 2p peaks of the N-doped TiO₂ film (NTO-500) and C-N-codoped TiO₂ films. For the NTO-500

film, two XPS signals are observed at binding energies at around 458.7 eV and 464.5 eV, which are in good agreement with that of pure TiO₂.^[146] By comparing the Ti 2p peaks for all samples, the obvious red shift of C-N-codoped TiO₂ films toward lower binding energy reveals the successful carbon-doping in these C-N-codoped TiO₂ films.^[153] Moreover, the Ti 2p peaks of the CNT10-550 film are red shifted to the binding energies slightly lower than that of CNT10-450 and CNT10-500 films, which is probably due to the enhancement in carbon doping in TiO₂ at a higher temperature. The Ti³⁺ to Ti⁴⁺ ratios for the NT-500, CNT10-450, CNT10-500 and CNT10-550 films estimated from XPS curve fitting program are 0.1%, 4.0%, 10.5%, 11.3%, respectively. In Fig. 5.2a, the intensities of the peaks attributed to elemental carbon in the C-N-codoped TiO₂ films decrease with the increase of calcination temperature, which is due to the combustion of carbon black in the presence of air at higher temperature. The atomic percentages of carbon in the CNT10-450, CNT10-500 and CNT10-550 films are determined to be 42.51 at%, 28.59 at% and 26.27 at%, respectively. It should be noted that some of the carbon atoms in the C-N-codoped TiO₂ films are originated from the equipment itself.

So far, the carbon states and species in carbon-doped TiO₂ which are responsible for visible light photocatalytic activity have remained controversial. Khan et al.^[155] and Irie et al.^[156] reported that the band-gap narrowing of C-doped TiO₂ was caused by the shift of valence band edge to higher energy as a result of the substitutional carbon atoms in the lattice of TiO₂. Lee et al.^[153] and Ren et al.^[146] reported that the formation of Ti-O-C led to the enhancements of visible light absorption and photocatalytic activities. Yang et al.^[157] and Lettmann et al.^[158] reported that the elemental carbon

incorporated interstitially in C-doped TiO₂ was responsible for visible light absorption up to 600 nm. Sakthivel et al.^[159] and Ohno et al.^[160] found that the absorption edge of TiO₂ was largely shifted to 700 nm by carbonate species absorbed on the TiO₂ surface. In the current work, our XPS data strongly suggest the presence of carbon doped into the TiO₂ material, and hence resulting in enhanced absorption and hence visible light photocatalytic activity.

For the N 1s spectrum, two peaks appear at 400.0 eV and 406.8 eV. The peak at 406.8 eV is generally considered as the evidence for the presence of nitrate species.^[106] The XPS signal of nitrogen at around 400.0 eV has also been a subject of controversy in the identification of nitrogen species in the study of N-doped TiO₂. Many reports had suggested that the signal at 400.0 eV was attributed to NO_x species adsorbed on crystallite surface.^[106] Sakthivel et al.^[130] and Navio et al.^[137] reported that the signal at around 400.0 eV was attributed to the presence of hyponitrite. Qiu et al. assigned the signal at 400.0 eV to the nitrogen incorporated into the TiO₂ lattice.^[161] However, they unanimously reported that the peak at 400.0 eV was critical for a visible light response. As shown in Table 5.2, the atomic percentages of nitrogen in the CNT10-450, CNT10-500 and CNT10-550 films were determined to 0.41 at%, 0.32 at% and 0.26 at%, respectively. The atomic percentages of nitrogen decreased with the increase of calcination temperature. According to previous reports, a higher temperature resulted in lower atomic percentage of nitrogen doped in TiO₂, which may be attributed to desorption of nitrogen species on TiO₂ at high temperature.^[122, 142, 162-163] The accuracy of nitrogen quantification can vary from 5% to about 30% depending on parameters such as signal to noise ratio and peak intensities.^[108] In the current work, the major

peaks are reported and thus it is reasonable to assume the accuracy to be around 90-95%. We estimate the error to be ± 0.04 at.%, ± 0.03 at.% and ± 0.03 at.% for the CNT10-450, CNT10-500 and CNT10-550 films, respectively.

Figure 5.2 XPS spectra of the C-N-codoped TiO₂ films (a) C spectra; (b) N spectra; (c) Ti spectra at different temperature.

5.2.2 Photocatalytic Activity Evaluation

In order to investigate the optimal calcination temperature, the photocatalytic activities of CNT10-450, CNT10-500 and CNT10-550 films were evaluated by monitoring the degradation of stearic acid under visible light illumination and the results are shown in Fig. 5.3. The photocatalytic activity depends on several factors such as dopant concentration, crystallinity that is affected by calcination temperature, and surface area. CNT10-500 film exhibits the highest photocatalytic activity, with 38.6% of stearic acid degraded. The relative lower photocatalytic activity of the CNT10-450 film probably can be attributed to its lower crystallinity. For the CNT10-550 film, the increase of nanoparticle size and the decrease of carbon and nitrogen concentrations could be responsible for the lower photocatalytic activity, compared with that of the CNT10-500 film. Based on the above results, 500 °C is considered to be the optimal calcination temperature for the preparation of C-N-codoped TiO₂ films.

Figure 5.3 Photocatalytic activities of C-N-codoped TiO₂ films prepared at different calcination temperatures.

5.3 The Effect of Carbon Concentration

To further optimize the photocatalytic film, different concentrations of carbon black were used to prepare C-N-codoped TiO₂ films.

5.3.1 XRD, FTIR, TG-DTA and XPS Characterizations

The crystalline phase and particle size of T-500, NT-500, CNT5-500, CNT10-500 and CNT20-500 were determined by XRD (Fig. 5.4). The distinctive peaks at $2\theta = 25.3^\circ$, 38.0° , 48.1° , 53.8° , 54.8° and 62.8° are attributed to anatase TiO₂. Compared to pure TiO₂ (T-500), no shift of the peak position is observed for NT-500, CNT5-500, CNT10-500 and CNT20-500, which probably because C/N do not substitute the atoms in TiO₂ lattice or the concentration of C/N substituted in TiO₂ lattice is low. The crystal sizes of CNT5-500, CNT10-500 and CNT20-500 were determined to be 17.5 nm, 17.2 nm and 17.0 nm respectively using Scherrer's equation as shown in Table 5.3. Wang et al. prepared nanocrystalline TiO₂/activated-carbon composite catalysts for the degradation of chromotrope 2R.^[164] They found that the combustion of carbon during calcinations resulted in a higher temperature inside the composite catalysts and the increase of TiO₂ particle size.^[164] However, Yu et al. reported that carbon doped into TiO₂ increased steric hindrance for grain growth and decreased TiO₂ particle size.^[33] In our case, the particle sizes of C-N-codoped TiO₂ films were not significantly affected by the concentration of carbon black.

Table 5.3 Crystal size of the samples at different carbon black concentrations obtained from Scherrer formula.

No	Sample's name	Temperature of calcination (°C)	Carbon concentration (wt.%)	Crystallite size (nm)
1	CNT5-500	500	5	17.5
2	CNT10-500	500	10	17.2
3	CNT20-500	500	20	17

Figure 5.4 XRD pattern of C-N-codoped TiO₂ prepared at different carbon black concentrations.

The FTIR spectra of the CN5-PTA, CN10-PTA, CN20-PTA, N-PTA and PTA films before and after heat treatment are presented in Fig. 5.5a and b respectively. In Fig. 5.5a, a peak at 900 cm^{-1} corresponding to the stretching vibration of the O-O bond (peroxo group) in the Ti-O-O-H bond of the peroxo titanate acid is observed. The wide bands at $3100 - 3700\text{ cm}^{-1}$ are attributed to the stretching vibration of the hydrogen-bonded OH groups of the adsorbed water. The absorption around 1620 cm^{-1} is assigned

to the bending vibration of adsorbed H₂O molecules. The peaks around 1400 cm⁻¹ are assigned to the stretching vibrations of the N-H bonds in NH₃, which evidences the presence of NH₃ in Ti complex.^[27] The NH₃ in the Ti complex is regarded as a nitrogen source for the N-doped TiO₂.^[27, 106] The band at 1400 cm⁻¹ is not observed for PTA. PTA has unstable chained atoms of hydrogen, which will decompose and release oxygen molecules to form stable visible light-activated photocatalyst TiO₂, N-doped TiO₂ and C-N-codoped TiO₂ with various carbon concentration during heating. In this process, NH₃ also decomposes. The disappearance of 900 cm⁻¹ and 1400 cm⁻¹ bands in Fig. 5.5b evidences the decomposition of peroxotitanate and NH₃ respectively.^[40, 129] The new peak found at 400-1250 cm⁻¹ is characteristic of an O-Ti-O lattice formation.^[165] There are no obvious stretching bands attributed to the NO_x species, which is probably due to the low atomic percentage of nitrogen doping in TiO₂. No peaks corresponding to -CH₃, -CH₂ or -CH bonds are found, confirming that the C-doped TiO₂ are free of organic species on the surface.

Figure 5.5 FTIR spectra of the CN5-PTA, CN10-PTA, CN20-PTA, N-PTA and PTA (a) before and (b) after calcination at 500 °C.

To elucidate the effect of carbon on CN-PTA, N-PTA was used for photocatalytic performance comparison. Fig. 5.6 shows a typical TG-DTA profile that exhibits weight loss of the N-PTA and CN-PTA (10 wt.% C) powders. An endothermic minimum at 100 °C in Fig. 5.6a is assigned to the evaporation of adsorbed water. The second peak at around 270 °C is attributed to the decomposition of peroxo group in PTA.^[71] A broad peak at about 350-370 °C is attributed to the crystallization of amorphous TiO₂ to anatase,^[166] after which no further weight loss is observed. The weight loss at the temperature lower than 350 °C is mainly attributed to the removal of adsorbed water and the decomposition of peroxo group. The same endothermic minimum at 100 °C, exothermic peak maximum at 250 °C and a broad peak at about 350-370 °C are found in Fig. 5.6b. But in the CN-TiO₂ sample, about 6% weight loss can be found in the range 400-550 °C and another broad peak at 500 °C which is attributed to the combustion of carbon. The combustion of carbon during calcinations results in a higher temperature inside the catalysts, which is consistent with the result reported by Wang et al.^[164]

Figure 5.6 TG-DTA patterns in air of the (a) N-PTA and (b) C-N-PTA (10 wt.% C).

The presences of carbon, nitrogen and Ti atoms in the CNT5-500, CNT10-500 and CNT20-500 films were also revealed by XPS (Fig. 5.7a, b and c). Similarly, the C 1s spectrum shows a single strong peak at 284.6 eV and a weak shoulder at around 288.5 eV, and the N 1s spectrum shows two peaks at 400.0 eV and 406.8 eV. The atomic percentages of nitrogen in the CNT5-500, CNT10-500 and CNT20-500 films are determined to be 0.39 at%, 0.32 at% and 0.15 at% respectively. The atomic percentages of nitrogen decrease with the increase of the concentration of carbon black. This could be due to the combustion of carbon black, which releases high heat energy and increases the temperature of the C-N-codoped TiO₂ films.^[164] Higher initial carbon content implies a greater amount of carbon to be burnt at 500 °C, which should result in a higher temperature inside the composite catalysts, and thus, a decrease in the atomic percentage of doped nitrogen.^[122, 142, 162-163] A comparison of the Ti 2p peaks of the NTO-500 film and CNT5-500, CNT10-500 and CNT20-500 films is shown in Fig. 5.7c. An obvious red shift of the CNT5-500, CNT10-500 and CNT20-500 films toward the lower binding energy is observed, which may suggest successful carbon-doping in these C-N-codoped TiO₂ films.^[153] The Ti³⁺ to Ti⁴⁺ ratios for the NT-500, CNT5-500, CNT10-500 and CNT20-550 films estimated from XPS curve fitting are 0.1%, 10.3%, 10.5%, 9.2%, respectively.

5. 3. 2 Surface Characterization

The surface morphology of the samples was observed by FESEM. Fig. 5.8 shows FESEM images of N-doped TiO₂ and C-N-codoped TiO₂ films at different carbon concentrations. FESEM images reveal that all samples have no cracks, which are attributed to uniform adsorption of PTA on the hydrophilic pure glass resulting in

uniform coating. N-doped TiO₂ thin film is very flat compared to C-N-codoped TiO₂ thin films. When the concentration of carbon increases, the surface becomes rougher.

Figure 5.7 XPS spectra of the C-N-codoped TiO₂ films (a) C spectra; (b) N spectra; (c) Ti spectra at different carbon black concentrations.

Figure 5.8 FESEM images of (a) NT-500 film; (b) CNT5-500 film; (c) CNT10-500 film; (d) CNT20-500 film.

Fig. 5.9 displays the AFM 3D images of the NT-500, CNT5-500, CNT10-500 and CNT20-500 films. They further confirm that the addition of carbon black and calcination at 500 °C leads to the increases of surface roughness. The surface roughness of the NT-500, CNT5-500, CNT10-500 and CNT20-500 films are 3.2 nm, 35.6 nm, 48.8 nm and 61.8 nm, respectively, as determined by AFM. BET analysis of the NT-500, CNT5-500, CNT10-500 and CNT20-500 powder samples are determined to be 45.3, 53.6, 58.8 and 61.5 m²/g respectively, indicating an increase in surface area and surface roughness with the increase of carbon black concentration. Yang et al.^[167] reported that organic compounds were pre-adsorbed on the surface of the semiconductor particles to effectively utilize the photogenerated charge carriers, thus

higher surface area can provide more surface active sites for the adsorption of organic compound and exhibit higher photocatalytic efficiency. Along with the function as a dopant, the carbon also increases the surface area, which provides more accessible active sites, thus enhancing the photocatalytic activity.

Figure 5.9 AFM images of (a) NT-500 film; (b) CNT5-500 film; (c) CNT10-500 film; (d) CNT20-500 film.

5.3.3 Optical Property

The color of the transparent thin films is yellowish which could indicate enhancement in visible light absorption.^[139] Fig. 5.10 shows the UV-visible diffuse reflectance

spectra of the un-doped, N-doped and C-N-codoped TiO₂ (with different carbon concentration) thin films. For this experiment, it was found that most samples have high reproducibility and negligible errors

Figure 5.10 UV-visible diffuse reflectance spectra of C-N-codoped TiO₂ films prepared at different carbon black concentration.

The absorption intensities of C-N-codoped TiO₂ films in the visible region are higher than that of the NT-500 and T-500 films, attributed to linear contributions (discussed later) of carbon and nitrogen doping.^[167] From the XPS results, it is understood that the doping of carbon and nitrogen could be responsible for the visible light response. Fig. 5.10 shows the absorption edges of these C-N-codoped films slightly shift toward longer wavelengths of 390-393 nm, which further confirms successful carbon-doping in these C-N-codoped films. The presence of both nitrogen and carbon species in TiO₂ have evidently enhanced visible light absorption. A study has proposed that the visible light absorption enhancement in C-N-codoped TiO₂ was caused by a narrowing band

gap due to mixed C or N 2p states with O 2p state in the valence band,^[133] while others have suggested the appearance of intra-band gap localized states of dopants.^[133, 168] The absorption intensities of C-N-codoped TiO₂ films in the visible region increase with the increase of the concentration of carbon black. However, the absorption intensity of CNT20-500 showed no obvious difference in the visible light region compared with that of CNT10-500, even though the concentration of carbon doping in CNT20-500 is higher than that of CNT10-500.

5.3.4 Photocatalytic Activity Evaluation

Fig. 5.11 shows the photocatalytic activities of the NT-500, CNT5-500, CNT10-500 and CNT20-500 films under visible light illumination. With an increase in carbon dopant concentration and surface roughness, it is found that the photocatalytic activities of C-N-codoped TiO₂ films is optimal at 10.0 wt.% C. The photocatalytic activity of CNT20-500 film is lower than that of CNT10-500 film, which may due to lower amount of nitrogen dopant. It is found that 38.6% of stearic acid is degraded on the CNT10-500 film, which is more than double to that of NT-500 film. To identify the linear contributions of carbon and nitrogen dopants, the photocatalytic activities of CT-500 and T-500 films were measured for comparison. As shown in Fig. 5.11, the photocatalytic activities of CT-500 and T-500 films are 16.4% and 1.3% in percentage of stearic acid layer degraded respectively, which are much lower than that of the CNT10-500 film. It should also be mentioned that no obvious decrease in stearic acid amount was observed for uncoated glass slides under visible light illumination. Herein, the high photocatalytic activities of C-N-codoped TiO₂ films are attributed to high surface area and linear contributions of carbon and nitrogen dopants.^[167]

Figure 5.11 Photocatalytic activities of C-N-codoped TiO₂ films prepared at different carbon black concentrations.

The excellent photocatalytic activity of C-N-codoped TiO₂ in the visible light region correlates with band gap narrowing due to nitrogen and carbon codoping in TiO₂. A mechanism of photogenerated charge transfer attributed to the linear contributions of carbon and nitrogen dopants in TiO₂ under visible light illumination is proposed (Fig. 5.12). Carbon-doping in TiO₂ may lead to the formation of impurity level above the valence band of TiO₂. Nakano et al. reported three deep levels located at about 0.86, 1.30, and 2.34 eV below the conduction band of TiO₂.^[169] The first level was attributed to the intrinsic nature of TiO₂, while the second and third levels were introduced by carbon doping. Upon visible light irradiation, an electron is promoted from the isolated C2p states above the valence band of TiO₂ to conduction band, leaving a hole behind.^[157] Electrons can also be excited from surface states energy level (due to the

nitrogen surface species) to the conduction band of anatase TiO₂ under visible light irradiation.^[170] Subsequently, the photogenerated electrons are directly captured by the adsorbed O₂ molecules on the surface of C-N-codoped TiO₂ to form O₂^{•-}, which is capable of degrading organic compounds.^[157-158] In addition, the photogenerated holes at both the impurity level and surface states can directly oxidize organic compounds, or be trapped by surface hydroxyl groups to form active hydroxyl radicals (•OH). For the current C-N-codoped TiO₂ films, electron-hole pairs can be generated simultaneously by both routes. Hence, co-doping the current TiO₂ films with C (forming Ti-O-C band) and nitrogen surface species may lead to an increase of photogenerated electrons and holes, compared with pure TiO₂ and single N-doped TiO₂ films, thus leading to an increase of visible light photocatalytic activity as observed in the current work.

Figure 5.12 Mechanism of stearic acid degradation by C-N-codoped TiO₂ under visible light irradiation. N represents the nitrogen surface species, N* represents surface states energy level of nitrogen surface species.

5.4 Conclusions

A transparent, uniform and crack free C-N-codoped TiO₂ thin films have been successfully prepared using a “green” aqueous PTA solution approach. XRD results confirm the presence of only anatase phase for all samples after calcination at 500 °C for 1 h. All C-N-codoped thin films have excellent absorption in visible region compared to N-doped TiO₂ and un-doped TiO₂. With the increase of carbon dopant concentration and surface roughness, the photocatalytic activity of stearic acid (SA) degradation is optimal for CNT10-500, which is 29, 2.4 and 2.2 times higher than that of un-doped TiO₂, C-doped TiO₂ and N-doped TiO₂, respectively. Beyond optimal carbon concentration, reduced photocatalytic activity is attributed to the decrease of nitrogen dopant. The linear contributions of carbon and nitrogen dopants and increased surface roughness are the main factors for high visible light photocatalytic activity of the C-N-codoped TiO₂ films.

CHAPTER 6

Fe-doped TiO₂ Film

6.1 Introduction

As revealed in chapter 2, doping TiO₂ with transition metal ions can enhance photocatalytic activity in the visible light region by extending the light absorption into that region.^[84, 171-172] Among the transition metals, iron (Fe) deserves special attention due to the fact that Fe³⁺ radius (78.5 pm) is similar to that of Ti⁴⁺ (74.5 pm),^[173] therefore rendering easier insertion of Fe³⁺ into the crystal structure of TiO₂.^[80] Many groups have reported the benefits of Fe-doped TiO₂ in enhancing the life time of electron-hole pairs to minutes or even hours^[174-175] and improving absorption in the visible range due to band gap narrowing.^[66, 174] Most reported applications of Fe-doped TiO₂ include water splitting,^[84] antibacterial,^[176] N₂ photoreduction to ammonia,^[84] or other oxidation reactions.^[66, 80, 175, 177]

In this chapter, the synthesis of Fe-doped TiO₂ is discussed using the same approach as that of N-doped TiO₂ and C-N doped TiO₂ described in chapter 4 and 5, and without the addition of a stabilizer. The light absorption of the synthesized Fe-doped TiO₂ and its photocatalytic activity was studied and reported in subsequent sections. This peroxo sol-gel method has also been investigated by Yan et al. for preparing Cr-doped TiO₂. In contrast to Fe-doped TiO₂, the photocatalytic activity of the prepared Cr-doped TiO₂

didn't show much improvement compared to un-doped TiO₂ due to the smaller diffusion length of the minority carriers.^[179]

6.2 Setting Experimental Condition

The isoelectric point of TiO₂ is in the range of pH 4.5-6.8. When the pH is far from the isoelectric point, the TiO₂ particles will bear an electric charge and hence need to be stabilized in the form of sol. Sasirekha et al. reported that at neutral and basic pH, the TiO₂ particles are stabilized by the mutual repulsion of the negative charges present at the surface of the TiO₂ particle and maintain their particle size.^[103] Our results on N-doped TiO₂ indicated that it was formed at alkaline pH. Therefore, in this work, pH 7 was chosen to avoid the presence of nitrogen in the Fe-doped TiO₂ photocatalyst.

In this study, Fe ion was added as the dopant together with other precursors at the first stage to obtain stable PTA coating solution. It was noted that if the Fe ions were added into the PTA at a final stage, the viscosity of solution immediately increased with Fe ion being precipitated out. The precipitate did not revert to the original transparent PTA solution even if ammonia solution or hydrogen peroxide solution was added. This was probably due to the formation of TiO(OH)(OOH) immediate species when Fe³⁺ polyvalent ion was added, resulting in the precipitation.^[129]

6.3 FTIR, TG-DTA and XRD Characterizations

FTIR spectra of the yellow peroxo titanic acid (PTA) before and after heat treatment were investigated and presented in Fig. 6.1a and b respectively. In Fig. 6.1a, a peak at 900 cm⁻¹ corresponding to the stretching vibration of the O-O bond (peroxo group) in

the Ti-O-O-H bond of the peroxo titanate acid are observed. The wide bands at 3100 - 3700 cm⁻¹ are attributed to the stretching vibration of the hydrogen-bonded OH groups of the adsorbed water. The absorption around 1630 cm⁻¹ is assigned to the bending vibration of adsorbed H₂O molecules. The peaks around 1400 cm⁻¹ are assigned to the stretching vibrations of the N-H bonds in NH₃. PTA has unstable chained atoms of hydrogen, which will decompose and release oxygen molecules to form stable Fe-doped TiO₂ during heating. In this process, NH₃ also decomposes. The disappearance of 900 cm⁻¹ and 1400 cm⁻¹ bands in Fig. 6.1b evidences the decomposition of PTA and NH₃ respectively.^[40, 129]

Figure 6.1 FTIR spectra (a) before calcinations, (b) after calcinations, of Fe-doped TiO₂ samples with different concentration of Fe³⁺ after calcination at 550 °C for 1 hour: (a) 0 wt%, (b) 0.5 wt%, (c) 1.0 wt%, (d) 1.5 wt%, and (e) 5.0 wt%.

TG-DTA profile (Fig. 6.2) of the Fe-doped TiO₂ shows an endothermic minimum at 100°C and exothermic peak maximum at 260°C. The first stage of weight loss (endothermic) is attributed to the removal of physically adsorbed water. The second stage (exothermic) is attributed to the decomposition of peroxo group.^[180] Other broad exothermic peak at about 320°C is probably due to the decomposition of remaining NH₄Cl.^[129] There is no further weight loss in the range of 400-420°C, but a broad exothermic peak is observed which is attributed to the slow conversion of amorphous phase to anatase.^[180] Our observation is consistent with the 3 distinct stages reported during the annealing process: (1) removal of water, (2) decomposition of a peroxo group, and (3) amorphous-anatase phase transformation.^[180]

Figure 6.2 TG-DTA of Fe-doped TiO₂ with 1.0 wt% Fe³⁺.

Fig. 6.3 shows the XRD patterns of Fe-doped TiO₂ samples at different concentration of Fe³⁺ after calcination at 550 °C for 1 hour. The XRD spectra show the presence of only anatase phase. No peaks due to haematite (Fe₂O₃) are observed in any of the samples. This may be due to Fe³⁺ ions substituting Ti⁴⁺ ions in the TiO₂ lattice since the radii of Ti⁴⁺ and Fe³⁺ ions are similar (78.5 pm and 74.5 pm for Ti⁴⁺ and Fe³⁺ radii^[173] respectively) and the electronegativity of both ions are reasonably close (Fe³⁺ : 1.96,^[181] Ti⁴⁺ : 1.5^[181]). Based on Hume-Rothery rule, if the % difference of atomic radii is less than 15% and the electronegativity of the elements are similar, a substitutional solid solution is most likely to be formed. The phenomenon of Fe³⁺ ion doping to TiO₂ crystal satisfies the third of Hume-Rothery rule as well which states that a lower-valent metal is soluble in a higher-valent host.^[182] Hence the Fe ions may be inserted into the lattice site of Ti⁴⁺.^[80]

Figure 6.3 XRD patterns of Fe-doped TiO₂ samples with different concentration of Fe³⁺ after calcination at 550 °C for 1 hour: (a) 0 wt%, (b) 0.5 wt%, (c) 1.0 wt%, (d) 1.5 wt%, and (e) 5.0 wt%.

To detect possible segregated iron oxide phase in the Fe-doped TiO₂, the samples were calcined at 800 °C for 1 hour. The XRD spectra (Fig. 6.4) show the presence of rutile for all samples. For Fe-doped TiO₂ samples with 0.5, 1.0 and 1.5 wt% Fe³⁺, no other peak is observed. However, for the sample with 5.0 wt% Fe³⁺, two peaks at $2\theta = 33^\circ$ and 60.5° are identified as perovskite structure of iron titanium oxide (Fe₂TiO₅).^[80] Analysis using Bruker AXS TOPAS v.3 shows that 0.5, 1.0 and 1.5 wt% Fe³⁺ samples contain 100% rutile, while 5.0 wt% Fe³⁺ sample contain 0.84% Fe₂TiO₅ in addition to TiO₂ rutile phase. These data suggest that almost all of the Fe³⁺ in 0.5, 1.0 and 1.5 wt% Fe³⁺ samples are trapped in the crystal lattice of TiO₂, whereas the 5.0 wt% Fe³⁺ sample contains segregated iron oxide in addition to Fe³⁺ doped TiO₂.

Figure 6.4 XRD patterns of samples after calcination at 800 °C for 1 hour with different concentration of Fe³⁺: (a) 0.5 wt%, (b) 1.0 wt%, (c) 1.5 wt%, and (d) 5.0 wt% (r = rutile, o = iron titanium oxide peak)].

6.4 Surface Characterization

A prepared Fe-doped TiO₂ coated glass is shown in Fig. 6.5a. The coated glass is visually transparent and uniform with a yellow tint due to Fe doping. FESEM image (Fig. 6.5b) reveals that the Fe-doped TiO₂ thin films have no cracks, attributed to uniform dispersion of PTA on the hydrophilic pure glass. EDX measurement (Fig. 6.5c and d) further confirms the presence and amount of iron present in the Fe-doped TiO₂ samples. Fe element is observed in the EDX pattern in the Fe-doped TiO₂ (Fig. 6.5c), while no trace of Fe element is found in the EDX pattern of the un-doped TiO₂ (Fig. 6.5d). The amounts of Fe element in un-doped TiO₂, Fe-doped TiO₂ (0.5 wt.% Fe³⁺),

Fe-doped TiO₂ (1.0 wt.% Fe³⁺), Fe-doped TiO₂ (1.5 wt.% Fe³⁺) and Fe-doped TiO₂ (5.0 wt.% Fe³⁺) were determined to be 0, 0.60, 0.96, 1.74 and 4.96 wt.%, respectively.

The results are consistent with the original amounts of Fe in the samples.

Figure 6.5 (a) Image of transparent Fe-doped TiO₂ coated glass; (b) FESEM image of Fe-doped TiO₂ thin films (1.0 wt.% Fe³⁺); (c) EDX pattern of the un-doped TiO₂ and (d) Fe-doped TiO₂ (1.0 wt.% Fe³⁺).

6.5 Optical Property

In the doping process of Fe³⁺ into TiO₂, wherein Fe³⁺ ions replace Ti⁴⁺, Fe³⁺ will act as an electron donor and form donor level close to the conduction band, resulting in a smaller energy transition, which may lead to visible light photoactivation.^[182-183] In Fig. 6.6, the UV-visible absorption spectra of the Fe-doped TiO₂ films show obvious enhanced absorption in the visible light region (400-600 nm) compared to that of the

un-doped TiO₂ film, indicating their potential to absorb visible light and improve photocatalytic activities under visible light illumination, even though no significant shift of the absorption edge to visible light region is observed.^[184] The absorption edges of un-doped TiO₂, Fe-doped TiO₂ (1.0 wt.%) and Fe-doped TiO₂ (5.0 wt.%) films are 340, 350 and 362 nm, respectively. According to the empirical formula, $E_{bg} = 1239/\lambda$ (λ = the wavelength of the optical absorption edge),^[66] the bandgap energies of the un-doped TiO₂, Fe-doped TiO₂ (1.0 wt.%) and Fe-doped TiO₂ (5.0 wt.%) films are 3.64, 3.54 and 3.42 eV, respectively. The bandgap energies of the un-doped TiO₂, Fe-doped TiO₂ (1.0 wt.%) and Fe-doped TiO₂ (5.0 wt.%) films are higher than those reported in the literature (3.2 eV for anatase TiO₂), which may be attributed to quantum size effect of TiO₂ film and the thermal stress in the films due to the difference in the thermal expansion coefficients between the fused substrate and coating material.^[141]

Figure 6.6 Absorbance spectra of Fe-doped TiO₂ with different concentration of Fe³⁺: (a) 0 wt% (un-doped TiO₂), (b) 0.5 wt%, (c) 1.0 wt%, (d) 1.5 wt% and (e) 5.0 wt%.

6.6 Photocatalytic Activity Evaluation

Fig. 6.7 shows the photocatalytic activity of the Fe-doped TiO₂ coated glass in the photodegradation study of stearic acid (SA) under visible light irradiation. 1.0 wt% Fe³⁺ is found to be the optimal dopant concentration and the associated photocatalytic activity is 4 times higher than that of un-doped TiO₂ coated glass. The increased in photocatalytic activity is due to the ability of Fe ions doping in extending light absorption into the visible light region, as supported by other studies^[79-80] and our current results as shown in Fig. 6.6. However, higher Fe ions concentration at 1.5 wt% may increase the number of trap sites,^[6, 185] resulting in higher recombination rate and lower photocatalytic activity. At 5.0 wt% Fe ions concentration, the existence of segregated iron oxide phase further decreases the photoactivity.^[185-188]

Figure 6.7 (a) Photocatalytic activities of un-doped TiO₂ and Fe-doped TiO₂ films under visible light illumination for 24 h; (b) Evolution of IR absorbance spectra of Fe-doped TiO₂ (1.0 wt.%).

6.7 Conclusions

Visible light active Fe-doped TiO₂ coated glass slides have been successfully prepared using a “green” aqueous PTA solution approach. The prepared thin films are transparent, uniform and crack free. The visible light photocatalytic activity of the Fe-doped TiO₂ films is attributed to bandgap narrowing as observed from absorption red-shift. The photocatalytic activity of optimal 1.0% wt Fe³⁺ doped TiO₂ is about 4 times higher than that of un-doped TiO₂ coated glass. At higher dopant concentration, the photocatalytic activity is reduced and its stability may be lowered due the presence of segregated iron oxide phase.

CHAPTER 7

Bi₂WO₆/TiO₂ Heterojunction Film

7.1 Introduction

Coupling TiO₂ with narrower band gap semiconductors, such as CdS,^[31] WO₃,^[32-33] and Bi₂WO₆,^[34-35] has become another promising method to activate TiO₂ in the visible light region. Biswas et al. prepared annealed CdS-TiO₂ thin film on glass slide and indium tin oxide (ITO) substrate by chemical bath deposition technique.^[31] They found that the photocatalytic activity of CdS-TiO₂ thin film for methanol degradation was enhanced due to the improvement of crystallinity in CdS and TiO₂ layers and the increase of roughness of CdS surface after high-vacuum annealing.^[31] They also reported that the higher photocatalytic activity might be attributed to the fact that the photogenerated electrons and holes can be well separated under UV–visible irradiation due to their suitable valence band and conduction band potentials.^[31] In another study, Resta et al. found CdS-TiO₂ thin film having higher absorption efficiency in visible light region with respect to TiO₂.^[189] They prepared the thin film by a novel in situ approach based on an unimolecular precursor for CdS, [Cd(SBz)₂]-1-methylimidazole.^[189] They also reported that CdS was used as a sensitizer to TiO₂ film leading to improved photocatalytic activity. For WO₃-TiO₂ system, Somasundaram et al. prepared a WO₃-TiO₂ thin film by pulse electrodeposition method and found an

optimal condition for minimizing electron-hole recombination.^[32] An excellent photocatalytic activity in the photodecomposition of 2-propanol of WO₃-TiO₂ was reported by Pan et al. which was prepared via an evaporation-induced self-assembly (EISA) process.^[33]

Among various semiconductors, Bi₂WO₆ was the most studied because it is the simplest member of Aurivillius^[34-35] and it offers the important physical and chemical properties, such as ferroelectricity, oxide anion conductivity and non-linear dielectric susceptibility^[190-191] Shang et al. created a 3D Bi₂WO₆/TiO₂ multi-component oxide mat by depositing Bi₂WO₆ on TiO₂ nanofibres via a electrospinning-assisted route.^[102] The Bi₂WO₆/TiO₂ mat exhibited significant enhancement in photocatalytic activity both in air and water compared to pure TiO₂ sample. Recognizing the potential application of Bi₂WO₆/TiO₂ composite, Zhou et al. developed a novel process of impregnating TiO₂ on Bi₂WO₆ microspheres and their preliminary results indicated significant improvement of photocatalytic activity under visible light illumination.^[190] Most recently, Colón et al. reported a highly photoactive Bi₂WO₆/TiO₂ heterostructures for degradation of rhodamine B under sunlight, which was attributed to the efficient charge separation between TiO₂ and Bi₂WO₆.^[34] Although these composites of TiO₂ and Bi₂WO₆ have exhibited enhanced activities in powdered photocatalytic reaction, similar positive effect of combining the two components is not necessarily reflected in the thin film condition, especially when external bias is involved in the photoelectrochemical system. However, to the best of our knowledge, the preparation of Bi₂WO₆/TiO₂ heterojunction bi-layer film has not been reported yet.

In this chapter, we present a simple technique to prepare porous $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ composite thin films at various Bi_2WO_6 concentrations (1.5, 30 and 5.0 wt.%). Single layer of Bi_2WO_6 was prepared as under layer on hydrophilic FTO (fluorine doped tin oxide) glass slides. Then, the bi-layer $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ films were prepared by dip-coating the Bi_2WO_6 under-layer film into TiO_2 sol followed by calcination. The films were characterized and photocatalytic degradation of stearic acid was evaluated. The visible light photocatalytic activity and photoelectrochemical properties of $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ films were significantly improved compared to those of Bi_2WO_6 and TiO_2 thin films.

7.2 XRD Characterization

Figure 7.1 XRD patterns of Bi_2WO_6 and $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ heterojunction bi-layer films. (A = anatase; O = orthorhombic)

The Bi₂WO₆/TiO₂ bi-layer film was formed via a two-step deposition process. A Bi₂WO₆ under-layer was first deposited on the glass substrates and calcined at 300 °C, followed by the deposition of the TiO₂ over-layer and calcination at 500 °C. The crystal structure and composition of Bi₂WO₆ and Bi₂WO₆/TiO₂ composite samples were characterized by X-ray diffraction (XRD), as shown in Fig. 7.1. The Bi₂WO₆ films demonstrate the presence of orthorhombic crystalline structure^[35, 97, 102] and anatase TiO₂, indicating the successful formation of Bi₂WO₆/TiO₂ films.

7.3 Surface Characterization

Fig. 7.2a, c and e show the 3D AFM images of the Bi₂WO₆ under-layers prepared at different concentrations and calcined at 300 °C. The surface roughness increases from 4.1 nm to 8.8 nm with the increase of Bi₂WO₆ concentration from 1.5 wt.% to 3.0 wt.%. However, further increase to 5.0 wt% leads to the decrease of surface roughness to 2.0 nm. Similar results are observed for the Bi₂WO₆ under-layers prepared at different concentration and calcined at 500 °C. Fig. 7.2b, d and f show the AFM images (3D) of the Bi₂WO₆ films calcined at 500 °C, the surface roughness of BWO-1.5, BWO-3 and BWO-5 films are 13.1 nm, 16.1 nm and 7.3 nm, respectively. The high and increasing surface roughness with increasing Bi₂WO₆ concentration is attributed to the formation of gaseous byproducts and particles aggregation (as explained in the next paragraph) at higher temperature. During the calcination process, gaseous byproducts (CO₂, CO and H₂O vapor) were formed due to the thermal decomposition of the organics components in the precursors. The gaseous byproducts induced surface roughness in the Bi₂WO₆ films. It is reasonable to suggest that with

the increase of the amount of H_5DTPA , the amount of gaseous byproducts is expected to increase, which leads to the increase of surface roughness.

Figure 7.2 AFM images of Bi_2WO_6 under-layers calcined at 300 °C (a) 1.5, (c) 3.0, (e) 5.0 wt% of Bi_2WO_6 and 500 °C (b) 1.5, (d) 3.0, (f) 5.0 wt% of Bi_2WO_6 , respectively.

However, the surface roughness of Bi₂WO₆ films decreased from 8.8 nm to 2.0 nm and 16.1 nm to 7.3 nm, when the concentration of Bi₂WO₆ was increased from 3.0 wt% to 5.0 wt% at calcination temperatures of 300 °C and 500 °C, respectively. In other words, there is an optimal surface roughness for the Bi₂WO₆ under-layer. This can be explained by the formation of uneven thin films due to the agglomeration of Bi₂WO₆ particles after calcination. Fig. 7.3 shows the FESEM images of the as-prepared Bi₂WO₆ thin films at various Bi₂WO₆ concentrations. The magnified images are shown as insets. As the insets display, the Bi₂WO₆ particles form agglomeration of size greater than 100 nm. For the BWO-1.5 film (Fig. 7.3a), after the film was calcined, some Bi₂WO₆ particles on the glass substrate aggregated to form bigger particles, exposing the glass surface and resulting in non-uniformity surface deposition. The BWO-1.5 film, due to uneven coating, displayed relatively higher surface roughness even at low H₅DTPA concentration. For the BWO-5 film (Fig. 7.3c), the increase of surface roughness created by the aggregation and uneven film are counter-acted by a greater amount of Bi₂WO₆ particles. Because the BWO-5 film is compact, the surface of the film is more flat compared to the BWO-1.5 and BWO-3 films. Herein, the BWO-3 film (Fig. 7.3b) shows the highest surface roughness and lowest glass surface exposed. It was thus chosen as the under-layer for TiO₂ deposition as it would provide the maximum surface contact at the interface between Bi₂WO₆ film and TiO₂ film.

Figure 7.3 FESEM images of (a) BWO-1.5; (b) BWO-3; (c) BWO-5 films. Insets are high magnification images (50, 000 $\times$)

Fig. 7.4 shows the AFM images of TiO_2 film and $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ heterojunction bi-layer films. The single-layered TiO_2 film (Fig. 7.4a) has a relatively flat surface morphology with lower surface roughness (0.5 nm) compared with that of the BWO-1.5/ TiO_2 , BWO-3/ TiO_2 and BWO-5/ TiO_2 films (Fig. 7.4b, c, d). The surface roughness of the $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ heterojunction bi-layer films is around 2.0 nm, which is lower than that of the unmodified Bi_2WO_6 films (Fig. 7.2). This is because the deposited TiO_2 overlayer fills up the gaps to form a flat surface.

Fig. 7.5 shows the FESEM images of the TiO_2 film, BWO-1.5/ TiO_2 , BWO-3/ TiO_2 and BWO-5/ TiO_2 films. All these films are uniform and crack-free. The $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ heterojunction bi-layer films have fine porous structure, constructed from nanoparticles with average size of 7-15 nm. By contrast, the single-layered TiO_2 film

displays flat surface without porous structure. The porous structure of $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ film is resulted from the evolution of gaseous by-products from the Bi_2WO_6 under-layer, which was first calcined at 300 °C after the first deposition so that not all the organic precursors were completely burnt-off. When the bi-layer films were calcined at 500 °C after TiO_2 deposition, gaseous byproducts generated in the Bi_2WO_6 under-layer evolved through the TiO_2 over-layer, thus forming the porous structure. This demonstrates that further decomposition of organic compounds at 500 °C can generate $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ heterojunction bi-layer films of higher porosity. Other works have also reported that the addition of organic template in TiO_2 film can induce rough surface with porous structure due to the formation of gaseous byproducts.^[76, 128, 192]

Figure 7.4 AFM images of (a) TiO_2 ; and $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ heterojunction bi-layer films (b) BWO-1.5/ TiO_2 ; (c) BWO-3/ TiO_2 ; (d) BWO-5/ TiO_2 .

Figure 7.5 SEM images of (a) TiO_2 ; (b) BWO-1.5/TiO_2 ; (c) BWO-3/TiO_2 ; (d) BWO-5/TiO_2

The cross-sectional SEM images of the BWO-3/TiO_2 and BWO-3 (inset) films are shown in Fig. 7.6a. Two different shades of gray, indicating two different layers, with thicknesses of 300 nm and 115 nm for Bi_2WO_6 under-layer and TiO_2 over-layer, respectively, can be observed. The thickness of single-layered Bi_2WO_6 film is around 325 nm (inset), which is consistent with that of the Bi_2WO_6 under-layer in the BWO-3/TiO_2 bi-layer film. To investigate the surface composition and chemical state of as-prepared $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ bi-layer film, XPS was carried out. The results are shown in Fig. 7.6b. The binding energies obtained in the XPS analysis are attributed to Ti, O and C. No peak of Bi 4f binding energy is found. This indicated that the Bi_2WO_6 under layer is covered with TiO_2 . A weak C signal is originated from the equipment itself.

Figure 7.6 (a) Cross-sectional SEM images of the BWO-3/ TiO_2 and BWO-3 films (inset); (b) XPS survey spectra of the BWO-3/ TiO_2 film.

Graphical illustration of the morphological evolution of $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ heterojunction bi-layer films is depicted in Fig. 7.7 to highlight the formation of porous and high interface area nanostructures. Under normal conditions, a bi-layer film (Fig. 7.7a) has a flat under-layer with low surface area. After being covered with an over-layer, the interface area between two layers is low. However, for the current BWO-3/ TiO_2 film (Fig. 7.7c), the Bi_2WO_6 under-layer has high surface area as depicted by AFM images (Fig. 7.2c, d). When the rough surface is covered with the TiO_2 over-layer, the uneven surface is filled up, which leads to the formation of a relative flat surface and high interface area between Bi_2WO_6 film (under-layer) and TiO_2 film (over-layer). Because the surface roughness of the Bi_2WO_6 under-layers of BWO-1.5/ TiO_2 and BWO-5/ TiO_2 films are lower than that of BWO-3/ TiO_2 film, it is reasonable to suggest that the interface areas of the BWO-1.5/ TiO_2 and BWO-5/ TiO_2 films are also lower than that of BWO-3/ TiO_2 .

Figure 7.7 Graphical illustration of the morphology of (a) common bi-layer film; (b) BWO-1.5/ TiO_2 ; (c) BWO-3/ TiO_2 ; (d) BWO-5/ TiO_2 heterojunction bi-layer films

7.4 Optical Property

The ability of the samples to absorb visible light was measured by UV-visible spectrophotometer. Fig. 7.8 shows absorbance spectra of all samples. Compared to TiO_2 spectrum, BWO-3 and all BWO/ TiO_2 samples shows absorption in visible light region. The capability to absorb visible light implies the possibility of its high photocatalytic activity under visible light irradiation. For Bi_2WO_6 , the intense absorption in visible light region (see BWO-3 spectrum) is not due to the transition from impurity levels but due to the band gap transition.^[193] The visible light response of BWO was due to the transition from the valence band formed by the hybrid orbitals of Bi 6s and O 2p to the conduction band of W 5d.^[194] The inset in Fig. 7.8 shows that the intensity of visible light absorbance increases with increasing concentration of Bi_2WO_6 . UV-visible absorption spectra (Fig. 7.8a) of BWO-1.5/ TiO_2 , BWO-3/ TiO_2 and BWO-5/ TiO_2 bi-layer films show obvious enhanced absorption in the visible light region (400-600 nm) compared to that of

the TiO₂ film, indicating their potential to absorb visible light and improve photocatalytic and photoelectrochemical performances under visible light irradiation, even though no significant shift of the absorption edge to visible light region is observed.^[184] The UV-visible absorption spectra of the bi-layer films may be interpreted as comprising of overlapping absorption spectra of Bi₂WO₆ and anatase TiO₂ films.^[195-196] The UV-visible absorption spectra (Fig. 7.8a) also shows an additive absorption of TiO₂ and BWO-3 (TiO₂ + BWO-3), that the visible light absorption of TiO₂+BWO-3 is similar to that of BWO-3/TiO₂. Optical band gap of the films are demonstrated in Tauc plots (Fig. 7.8b). Bi₂WO₆ and TiO₂ films reveal band gaps of 2.9 (direct) and 3.6 eV (indirect), respectively. It is obvious that the optical band gaps for the TiO₂ and Bi₂WO₆ thin films annealed at 773 K were larger than that of usually reported in the literature (3.2 eV for anatase TiO₂ and 2.8 eV for Bi₂WO₆). This may be attributed to quantum size effect of TiO₂ and Bi₂WO₆ thin films and the thermal stress in the films due to the difference in the thermal expansion coefficients between the fused substrate and coating materials (TiO₂ and Bi₂WO₆).^[141] As the bi-layer BWO-3/TiO₂ film consisted of components with different band gap nature (indirect band gap for anatase TiO₂ and direct band gap for Bi₂WO₆), optical band gap of the bi-layer films was not determined. However, based on the absorption edge as shown in the UV-visible absorption spectra, the band gap of the films should lie in between those of the pure TiO₂ and Bi₂WO₆ films. Herein, it is reasonable to suggest that the Bi₂WO₆/TiO₂ bi-layer films slightly shift the absorption edge of TiO₂ to longer wavelength and also greatly enhance the light absorption in the visible light region.

Figure 7.8 (a) UV-visible diffuse reflectance spectra of $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ heterojunction bi-layer films, additive of TiO_2 and BWO-3 films ($\text{TiO}_2+\text{BWO-3}$), and (inset) Bi_2WO_6 films; (b) Tauc plots of the BWO-3 and TiO_2 films.

Fig. 7.9 presents typical photoluminescence (PL) spectra of Bi_2WO_6 and $\text{Bi}_2\text{WO}_6\text{-TiO}_2$. PL emission is the result of the recombination of excited electrons and holes, and therefore PL emission spectra can be used to investigate the efficiency of charge carrier trapping, migration and transfer of electron-hole pairs in semiconductor.^[167] Higher PL intensity indicates an increase in the number of the emitted photons resulting from the electron-hole recombination^[167, 197], hence lower charge separation efficiency and reduces photocatalytic activity.^[190] Therefore, there is a strong relationship between PL intensity and photocatalytic activity. From Fig. 7.9, it can be

seen that the BWO-3 film has a broad emission and a strong emission peak at around 450 nm, which is attributed to the intrinsic luminescence of Bi_2WO_6 and is consistent with the UV-visible diffuse reflectance spectra. An obvious fluorescence decrease (or quenching) of BWO-3/ TiO_2 is observed compared to that of BWO-3, suggesting that the coupling of Bi_2WO_6 and TiO_2 increases the charge separation efficiency, which is attributed to interfacial photogenerated holes transfer from Bi_2WO_6 to TiO_2 .^[34, 102, 190]

A proposed charge mechanism is illustrated in Fig. 7.13.

Figure 7.9 PL spectra of the BWO-3 and BWO-3/ TiO_2 films

Based on the UV-visible absorption and PL spectra, Bi_2WO_6 particles should undergo charge separation upon excitation with visible light. When employed as a

photoanode in a standard three-electrode photoelectrochemical cell, all films exhibited anodic photocurrent generation, indicating their n-type semiconductor behaviors. Fig. 7.10a shows photocurrent generated from Bi₂WO₆, Bi₂WO₆/TiO₂, and TiO₂ films upon visible light excitation (>420 nm). All electrodes were prompt in generating photocurrent with a reproducible response to ON-OFF cycles. The magnitude of photocurrent represents charge collection efficiency of the electrode surface. It is interesting to note that the Bi₂WO₆/TiO₂ heterojunction film exhibits a high photocurrent generation of 14.0 $\mu\text{A cm}^{-2}$, which is greatly enhanced compared with that of the unmodified Bi₂WO₆ (8.0 $\mu\text{A cm}^{-2}$) and TiO₂ films (1.0 $\mu\text{A cm}^{-2}$). It is noted that the photoresponse of TiO₂ film should be resulted from the remnant UV that passes through the 420 nm cut-off filter. Although in general, the photocurrent generated is not high as compared to other well studied semiconductor films such as WO₃ photoelectrode, the value of 14.0 $\mu\text{A cm}^{-2}$ photocurrent density achieved in this work is an evident improvement in comparison with the literature.^[104, 198] This enhancement in visible photocurrent generation signifies the suppression of charges recombination process in the BWO-3/TiO₂ heterojunction bi-layer film, as proven by the PL analysis. Incident photon conversion to charge carrier conversion efficiencies (IPCE) of the bare Bi₂WO₆, Bi₂WO₆/TiO₂ and pure TiO₂ films were further evaluated by analyzing the photocurrent generated at monochromatic wavelengths. The photocurrent action spectra of the three electrodes at 1V vs Ag/AgCl are shown in Fig. 7.10b. In the absence of TiO₂, a maximum IPCE of 8% was observed at 320 nm and the efficiency gradually diminished upon subject to wavelength >420 nm. The IPCE response shows an encouraging enhancement to 16 % when TiO₂ is incorporated. In visible region ($\lambda =$

440–500 nm), though the efficiency is in general considerably small, the photon energy conversion efficiency of $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ film [(0.26 % (440 nm); 0.36 % (480 nm)] is much higher than that of bare TiO_2 film [0.04 % (440 nm); 0.11 % (480 nm)]. The efficiency enhancement level in visible light region is in between 3- and 7-fold compare with bare TiO_2 and this is in good agreement with the visible light activities observed in the photocurrent generation and the photodegradation of stearic acid which is discussed later.

Figure 7.10 (a) Photocurrent response vs time profiles of Bi_2WO_6 (BWO-3), $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ (BWO-3/ TiO_2) and TiO_2 thin films and (b) IPCE of Bi_2WO_6 , $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ and TiO_2 at 1V vs Ag/AgCl.

7.5 Photocatalytic Activity Evaluation

The constructive effect of efficient charge separation in the current composite films is also probed by photocatalytic efficiency study. The photocatalytic activity of the TiO_2 , Bi_2WO_6 and $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ heterojunction bi-layer films were evaluated by photodegradation study of stearic acid (SA) under visible light irradiation for 24 h. All the results are shown in Fig. 7.11. The $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ heterojunction bi-layer films exhibit much higher photocatalytic activities than that of single-layer TiO_2 and

Bi_2WO_6 (BWO-1.5, BWO-3 and BWO-5) films. The result suggests that the enhanced photocatalytic activities under visible light illumination are attributed by the synergistic combination of the two semiconductors. Fig. 7.11 also shows that the BWO-3/ TiO_2 heterojunction bi-layer film exhibits the highest photocatalytic activity compared to BWO-1.5/ TiO_2 and BWO-5/ TiO_2 films. This is attributed to its high interface area between Bi_2WO_6 and TiO_2 semiconductors. With an increase of interface area, the electron-hole pair separation efficiency and photocatalytic activity should be improved.

Figure 7.11 Photocatalytic activities of different thin films under visible light illumination for 24 hours.

7.6 Photoelectrochemical Study

In order to verify the origin of these improvements in both photoelectrochemical and photocatalytic properties of $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ film, charge transfer interactions between excited TiO_2 and Bi_2WO_6 were determined based on their current-voltage (I-V) characteristics (Fig. 7.12).

Figure 7.12 Current-voltage functions of TiO_2 and Bi_2WO_6 (BWO-3) films under repeating on-off UV illumination cycles.

Since both Bi₂WO₆ and TiO₂ are n-type semiconductors, the potentials corresponding to the onset photocurrent, often referred to as flat band potential, could be employed to study the comparative Fermi level of these semiconductors. The flat band potentials recorded on excited TiO₂ and Bi₂WO₆ were -0.70 and -0.05 V vs Ag/AgCl, respectively. Employing the Nernst equation to recalculate the flat band of TiO₂ at pH 0 resulted in a flat band potential of -0.09 V vs NHE. This value is in good agreement with literature that anatase has a flat band potential of ~-0.1 V vs NHE (pH 0),^[199] suggesting that a significant discrepancy between photocurrent onset and flat band potential did not occur in this work. Considering the Fermi levels of these materials are close to their conduction bands, their relative valence band positions can be estimated by subtracting the band gap energy difference from the difference in Fermi levels. The I-V measurement reveals that Bi₂WO₆ possesses a valence band of ~0.2 eV more positive than that of TiO₂. This value is reasonably consistent with the estimation reported by Shang et al.^[102] When made into bi-layer films, only Bi₂WO₆ is excited under visible light illumination, and the holes generated in the valence band of Bi₂WO₆ migrate to the valence band of TiO₂, thus leading to a more efficient charge separation process.

A mechanism depicting the dynamics of photogenerated charge transfers is shown in Fig. 7.13. The TiO₂ over-layer functions as a hole-accepting semiconductor. A higher conduction band (CB) edge of TiO₂, compared to that of Bi₂WO₆, inhibits the interfacial electrons transfer from Bi₂WO₆ to TiO₂, resulting in the enhancement of the separation efficiency of the electron-hole pairs. This is consistent with the results from PL experiments (Fig. 7.9).^[34, 102, 190] As a result, visible light-generated electrons on

Bi_2WO_6 can be efficiently transported to the FTO electrode leading to higher photocurrent generation. For the photocatalytic activity measurement, a larger number of holes migrated to TiO_2 (due to valance bands interaction between the two semiconductors) for the degradation of adsorbed stearic acid. The high interface area between the TiO_2 over-layer and Bi_2WO_6 under-layer can also facilitate electron-hole pair separation. Furthermore, the nanoporous structure and higher surface roughness (2.1 nm) found in the $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ heterojunction bi-layer films can increase the adsorption of stearic acid and therefore improving the photodegradation efficiency.^[200]

Figure 7.13 Mechanism of the photocatalytic induction process in the $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ bi-layer film under visible light irradiation.

7.7 Conclusions

The Bi₂WO₆/TiO₂ bi-layer films have been successfully prepared using a hydrophilicity-assisted method. The films were uniform, crack free, porous and had good visible light absorption. The Bi₂WO₆ film as under layer had high surface roughness resulting in the greatly increase of the interface area of the Bi₂WO₆/TiO₂ bi-layer film, which led to the improvement of electron-hole pair separation efficiency and photoelectrochemical/photocatalytic performance under visible light illumination. Photocurrent generation of the bi-layer films was also increased by a factor of two compared with that of the unmodified Bi₂WO₆ film. The optimal visible light photocatalytic activity of the Bi₂WO₆/TiO₂ film was 20.6% of stearic acid degraded in 24 hrs, which was 15.7 and 7.4 times higher than that of TiO₂ film and BWO-3 film under the same reaction conditions, respectively. The improvement in photoelectrochemical and photocatalytic performances was attributed to the porous film structure and facilitation of higher charge separation efficiency, the latter evidenced by PL and I-V analyses.

CHAPTER 8

Conclusions and Recommendations

8.1 Conclusions

The work presented in the preceding chapters of this dissertation demonstrates efforts towards the development of visible light-activated TiO_2 photocatalyst thin film for self-cleaning and potentially other solar energy harvesting applications. Most of the photocatalysts were prepared via a peroxo sol-gel method, which is “green” as it uses aqueous instead of organic solvents. The thin films were prepared simply by a hydrophilicity-assisted coating method, which is by dip-coating hydrophilic uncoated glass into the coating solution. Detail characterizations and performance analysis were undertaken to study the property of the thin film such as structural, optical and surface properties. Photocatalytic activity was evaluated by measuring stearic acid degradation under visible light illumination for 24 hours. For the $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ composite nanostructure film, the photoelectrochemical properties were also reported. The important results of this study are summarized as follow:

- (1) N-doped TiO_2 precursor have been successfully synthesized by a “green” and simple peroxo sol-gel method and then coated onto pure glass substrates via a hydrophilicity-assisted method, forming anatase N-doped TiO_2 thin films upon calcination. The prepared thin films were transparent, uniform, crack free and visible light-activated photocatalytic activity. The photocatalytic activity

increased with increase pH attributed to the higher N-doping concentration. The photocatalytic activity of N-TiO₂-10 with optimal N-doping was 9.5 and 13.6 times higher than that of un-doped TiO₂ coated glass and commercial self-cleaning glass, respectively. Beyond optimal N-doping concentration, reduced photocatalytic activity was attributed to higher number of charge recombination sites.

(2) Extending the strategy for visible light-activated photocatalyst preparation, carbon and nitrogen codoped TiO₂ films were synthesized. The precursor of C-N-codoped TiO₂ was prepared using a “green” peroxo sol-gel and hydrophilicity-assisted method that have been used for preparing N-doped TiO₂ (as mentioned above). The thin films were uniform, crack-free and have high surface roughness. All the C-N-codoped samples showed absorption in the visible light region and exhibited enhanced visible light photocatalytic activities. The photocatalytic activity of CNT10-500 film (10 wt.% C) was found to be optimal and more than double that of single doped NT-500 (N-doped TiO₂ film calcined at 500 °C). The high photocatalytic activities of C-N-codoped TiO₂ were attributed to the high surface area and the linear contributions of carbon and nitrogen dopants.

(3) The same PTA solution approach was used to prepare visible light active Fe-doped TiO₂ precursor. The obtained thin films were transparent, uniform and crack free. The visible light photocatalytic activity of the Fe-doped TiO₂ films was attributed to bandgap narrowing as observed from absorption red-shift.

The photocatalytic activity of optimal 1.0% wt Fe^{3+} doped TiO_2 was about 4 times higher than that of un-doped TiO_2 coated glass. Fe^{3+} was doped into the TiO_2 crystal lattice but at higher dopant concentration, its stability was lowered due the presence of segregated iron oxide phase.

(4) Porous $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ composite nanostructure thin-films, prepared by combining a narrower band gap Bi_2WO_6 semiconductor with TiO_2 , were evaluated for their photocatalytic and photoelectrochemical properties. Bi_2WO_6 was prepared as an under layer of this bi-layer film. The $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ films were porous and visible light active. The optimal photocatalytic activity under visible light irradiation was 15.7 and 7.4 times higher than that of TiO_2 film and BWO-3 film under the same reaction conditions, respectively. The improvement in photoelectrochemical and photocatalytic performances was attributed to the porous film structure and higher charge separation efficiency, the latter supported by photoluminescence (PL) and current-voltage (I-V) analyses.

(5) The property of all visible light active titanium dioxide films prepared can be summarized and compared in Table 8.1 below.

Table 8.1 Comparison among all prepared visible light active titanium dioxide films

No	Property		The optimal photocatalyst			
			N-TiO ₂ -10	CNT-10-500	Fe-TiO ₂ with 1.0% wt Fe^{3+}	BWO-3/TiO ₂
1	Thin	film	Transparent, uniform, crack free	Transparent, uniform, crack free, high surface roughness	Transparent, uniform, crack free	Transparent, uniform, crack free, porous
2	Crystal phase		Anatase	Anatase	Anatase	Anatase

No	Property	The optimal photocatalyst			
		N-TiO ₂ -10	CNT-10-500	Fe-TiO ₂ with 1.0% wt Fe ³⁺	BWO-3/TiO ₂
3	Visible light absorption (compared to un-doped TiO ₂)	Enhanced	Enhanced significantly	Enhanced not significantly	Enhanced obviously
4	Photocatalytic activity (times higher compared to un-doped TiO ₂)	9.5	29	4	15.7

From all prepared visible light active titanium dioxide films, the optimized C-N-codoped TiO₂ (CNT-10-500) was the best performed photocatalyst.

8.2 Recommendations

In recent years, the development of modified TiO₂ nanomaterials for visible light-activated photocatalyst has attracted significant attention. In order to exploit their full potential for indoor self-cleaning application, the author proposes the following recommendations for of the visible light active TiO₂ thin films investigated in this dissertation, and the future development of visible light-activated photocatalyst in general.

- (1) *Antibacterial study*: The current work has demonstrated successful synthesis of various visible light-activated photocatalysts based on TiO₂ semiconductor: N-doped TiO₂, C-N-codoped TiO₂, Fe-doped TiO₂ and composite Bi₂WO₆/TiO₂ thin films which showed significant improvement in stearic acid photodegradation under visible light illumination. Many studies have shown that various bacteria, *E. coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa*, etc., were killed rapidly on TiO₂ surfaces under UVA illumination.^[201] Sunada et al. showed that not only bacteria were killed, but the toxic ingredient of bacteria could also be decomposed on the TiO₂ surface.^[202]

The investigation of antibacterial properties under indoor lighting is important and useful because of the increasing incidents of bacterial infection and continued evolution of bacteria towards antibiotic resistance. In a recent work, Azad et al. prepared photoactive TiO₂ on the surface of Ti implants in order to impede infection, achieving accelerated wound healing in post-orthopedic

surgery patients.^[203] It was observed that level of *Escherichia coli* necrosis was reduced about 60-70%.

Hence, future work should include antibacterial studies using codoped C-N-TiO₂, which was shown to have the highest visible light photoactivity.

(2) *Modifying the obtained photocatalysts for solar harvesting applications such as solar fuel production (production of hydrogen via solar water splitting):* The demand for energy is rising due to increasing world population.^[200-201] Besides, the consumption of fossil fuels has an impact on climate change or other environmental problems.^[200-201] Therefore, the use of renewable energy is paramount. Hydrogen production from solar water splitting may be a potential solution due to the abundance of water and solar energy.^[202] Fujishima and Honda were the first to report the application of TiO₂ on hydrogen production using solar energy via photoelectrochemical decomposition of water. They used n-type TiO₂ single crystals as the electrode materials and UV light to split water.^[203] Since then, many researchers have tried to modify TiO₂ to improve the rate of hydrogen production. For example, Ikuma et al. prepared Pt-deposited TiO₂ and study the effect of Pt deposition method and Pt concentration on the hydrogen production rate. They found that the highest rate of production was obtained from the Pt-deposited TiO₂ that was formed by the formaldehyde method.^[204] In another study, Seger et al. prepared TiO₂-based membrane electrode assembly as anode in a photoelectrolysis cell for hydrogen generation. They observed that the photoelectrolysis cell could continuously

generate hydrogen at the cathode.^[205] Patsoura et al. have reported photocatalytic degradation of organic pollutants accompanied by evolution of hydrogen with the use of Pt/TiO₂ photocatalyst and UV irradiation.^[206]

In the present work, most of the modified TiO₂ thin films were applied only for stearic acid photodegradation, mainly for demonstration as self-cleaning materials. For the next phase of studies, the obtained photocatalysts could be investigated for hydrogen production under solar irradiation. Visible light irradiation should be investigated since all of the photocatalysts showed excellent absorption in visible light region.

(3) *Evaluating the photocatalytic activity for real pollutants, such as formaldehyde, toluene, NO_x etc.* We have demonstrated successful degradation of stearic acid on visible light active photocatalyst-coated glass. Stearic acid was used as a model organic compound for determination of photocatalytic activity.^[207-209] However, there are many other pollutants that are present in real life such as formaldehyde (common indoor air pollutant^[210]) and toluene, which are emitted from interior furnishings and construction materials. The presence of these volatile organic pollutants may lead to the “sick building syndrome” and other diseases.^[211] Other common pollutants includes nitrogen oxides (NO_x) which is emitted from automobiles exhaust and is known to be air pollutant responsible for the ground level ozone built up in urban areas.^[211]

Therefore, for the next phase of studies, photocatalytic activity evaluation of the obtained visible light active photocatalyst films can be extended to the real pollutants under UV and visible light irradiation. I believe that the results will be useful for pollutant abatement studies.

(4) *Fundamental studies of metal-doped TiO₂ nanomaterials:* In the current work on Fe-doped TiO₂ synthesis, the sequence of Fe ion added affected the coating solution obtained. Herein, Fe ions were added as the dopant together with other precursors at the first stage to obtain stable PTA coating solution. If the Fe ions were added into the PTA at a final stage, the viscosity of solution immediately increased with Fe ions being precipitated out. The precipitate did not revert to the original transparent PTA solution even if ammonia solution or hydrogen peroxide solution was added. As mentioned in part 6.2, this was probably due to the formation of TiO(OH)(OOH) immediate species when Fe³⁺ polyvalent ion was added, resulting in the precipitation.^[129] However, a fundamental study is recommended to observe the phenomena more clearly and deeply. Speciation studies using computer software such as STABCAL, CHEMIX or MINTEQA is therefore recommended as it can show the chemical species including their phases at different pH and concentrations and hence can provide better understanding of Fe precipitation.

(5) *Evaluating other type of carbon material as C sources for preparing C-N-codoped TiO₂:* In the current work, carbon black was used as carbon source for preparing C-N-codoped TiO₂. Beside carbon black, many other types of

carbon materials have been reported carbon source, such as graphite, carbon black, activated carbon, activated carbon fibres, carbon-covered alumina, graphite intercalation compound, fullerenes, nanotubes, polymer-derived carbon, etc.^[212] Many factors such as porous structure, surface area, particle size and amount of carbon doped, amongst others, can be examined to determine the best carbon source for C-N-codoped TiO₂ photocatalyst.

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