DEVELOPMENT OF NEW CHARACTERISATION METHODS TO STUDY THE PHOTOCATALYSIS PROCESSES AT NANOPARTICULATE TiO$_2$ FILM ELECTRODES

William Wen

November 2010
DEVELOPMENT OF NEW CHARACTERISATION METHODS TO STUDY THE PHOTOCATALYSIS PROCESSES AT NANOPARTICULATE TiO₂ FILM ELECTRODES

William Y. Wen (MSc, BSc)

Submitted in fulfilment of the requirements of the degree of

Doctor of Philosophy.

Griffith School of Environment

Science, Environment, Engineering and Technology

Griffith University

November 2010
Declaration

This work has not previously been submitted for a degree or diploma in any university. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made in the thesis itself.

William Wen

1 November 2010
Abstract

Titanium dioxide, TiO$_2$, has a wide range of applications as a photocatalyst in the field of solar energy conversion and environmental remediation including water purification and wastewater treatment. In general, a TiO$_2$ photocatalytic process consists of three major steps, namely, the mass transfer process in solution, the interfacial step, and the photoelectron transport inside the catalyst. This work explores the characterisation of TiO$_2$ photocatalysis using a photoelectrochemical method to focus on each fundamental reaction steps. Each of these steps will be used to gain an accurate understanding of processes and identify possible improvements of the overall performance of TiO$_2$ semiconductor photocatalysts.

In this work, nano-sized TiO$_2$ semiconductor photocatalysts were prepared by the sol-gel method, and immobilised onto a conducting ITO glass substrate to form a photoanode. Photocatalytic studies utilising immobilised TiO$_2$ thin films have many advantages over the suspension/slurry system, including the elimination of the separation process. Most importantly however, photocatalysis by immobilised TiO$_2$ photocatalyst can be manipulated by applying an external potential bias to focus on understanding certain aspects of the photocatalytic process (e.g. the rate determining steps).

The mass transfer process is one of the important steps that has a great influence on the overall efficiency of a photocatalytic system involving immobilised TiO$_2$ photocatalysts. In many cases, the mass transfer process can be the rate-limiting step in the removal of organic compounds from an aqueous system for environment application. This thesis proposed and validated an *in-situ* photoelectrochemical method to determine the effective diffusion coefficients of various organic
compounds. As the obtained diffusion coefficients were measured in identical photocatalytic conditions, this method can provide a fast, simple and useful tool for studying mass transfer processes involved in photocatalytic processes.

By definition, interfacial processes are comprised of multiple processes that occur at the solid-liquid phase boundary, including the interaction of light with the TiO$_2$ photocatalyst, photohole and electron generation and recombination. Particularly important is the surface adsorption of the reactant at the surface of the TiO$_2$ photocatalyst.

In this work, the adsorption of organic compounds was studied by an *in-situ* method based on photoelectrochemical principles. Phthalic acid was selected to represent organic compounds with strong adsorption at TiO$_2$ surface. The adsorption equilibrium constant was determined by measuring the phthalic acid adsorption amount at the TiO$_2$ photoanode surface.

Methanol is known to be a weak adsorbate at the TiO$_2$ surface. Adsorption of methanol at the TiO$_2$ thin film photocatalyst was investigated by a simple and convenient *in-situ* method.

The characteristics of interactions between water and TiO$_2$ photocatalysts have been the subject of intensive research for many years. Surface speciation of the TiO$_2$ photocatalyst is affected by solution pH, and has a strong influence on the water adsorption at the TiO$_2$ thin film surface. This study demonstrated evidence of two types of adsorption complexes with different binding strength due to the heterogeneity of the TiO$_2$ surface. Investigation of adsorption kinetics also revealed how solution pH affected the adsorption rate. Based on the oxidation of adsorbed water at the TiO$_2$
surface, the behaviour of water adsorption under the given conditions was explained by an adsorption model.

Finally, the electron transport properties within the thin film photocatalyst were investigated. Electron transport properties were characterised and expressed by the reaction resistance and the invariable resistance component. This was calculated by the photocurrent response of photocatalytic oxidation of glucose under varying light intensities and in the presence of different concentrations of photohole scavenger. The effect of thin film thickness was also studied in relation to the overall resistance.
# Table of Contents

## CHAPTER 1  GENERAL INTRODUCTION

1.1  Introduction .......................................................................................................................... 3

1.2  Applications of TiO$_2$ Photocatalysts ........................................................................... 5
   1.2.1. Solar energy conversion .............................................................................................. 6
   1.2.2. Environmental remediation ......................................................................................... 8
   1.2.3. Other applications ...................................................................................................... 11

1.3  Semiconductor Photocatalysts ....................................................................................... 11
   1.3.1. Energy levels and the band theory .............................................................................. 11
   1.3.2. Photoelectron-hole generation and recombination ...................................................... 14
   1.3.3. Band energy ............................................................................................................... 17

1.4  TiO$_2$ Photocatalysts ...................................................................................................... 19
   1.4.1. Bulk and nano-sized TiO$_2$ ..................................................................................... 20
   1.4.2. Surface structure and morphology ............................................................................. 22
   1.4.3. Photocatalytic degradation ....................................................................................... 23
   1.4.4. Slurry and immobilised TiO$_2$ photocatalytic systems ............................................. 24
   1.4.5. Study of photocatalysis by photoelectrochemical approach ..................................... 28

1.5  Photoelectrocatalysis ...................................................................................................... 29
   1.5.1. Mass transfer process ............................................................................................... 30
   1.5.2. Interfacial steps ......................................................................................................... 34
   1.5.3. Photoelectrons transport ......................................................................................... 41
1.6 Scope of Thesis................................................................. 44

1.7 References ........................................................................... 47

CHAPTER 2 EXPERIMENTAL...................................................... 61

2.1 Introduction ........................................................................ 61

2.2 TiO$_2$ photocatalyst preparation ....................................... 61
   2.2.1. TiO$_2$ colloid synthesis ................................................. 61

2.3 Fabrication of TiO$_2$ thin film electrode .............................. 63

2.4 Physical characterisation of TiO$_2$ photocatalyst .................. 64
   2.4.1. XRD ........................................................................... 64
   2.4.2. FESEM ........................................................................ 65

2.5 Photoelectrochemical characterisation .................................. 66
   2.5.1. Apparatus and experimental setup ................................. 66
   2.5.2. LSV and CV ................................................................. 67
   2.5.3. Photocurrent from photocatalytic oxidation ..................... 70

2.6 Conclusions ....................................................................... 72

2.7 Reference ........................................................................... 72

CHAPTER 3 STUDY OF MASS TRANSFER PROCESS: A RAPID
PHOTOELECTROCHEMICAL METHOD FOR IN-SITU DETERMINATION
OF EFFECTIVE DIFFUSION COEFFICIENT OF ORGANIC
COMPOUNDS ........................................................................... 77
3.1 Introduction .................................................................................................................. 77

3.2 Experimental ............................................................................................................... 80
  3.2.1. Materials .............................................................................................................. 80
  3.2.2. Preparation of TiO₂ thin-film electrodes ............................................................. 80
  3.2.3. Apparatus .......................................................................................................... 80

3.3 Results and Discussion ............................................................................................... 81
  3.3.1. Measurement principle ......................................................................................... 81
  3.3.2. Optimisation of experimental conditions ............................................................ 85
  3.3.3. Experimental validation ....................................................................................... 87
  3.3.4. Determination of diffusion coefficient ................................................................. 93

3.4 Conclusions ................................................................................................................ 98

3.5 Reference .................................................................................................................. 98

CHAPTER 4 STUDY OF STRONG ADSORBATE: IN-SITU
PHOTOELECTROCHEMICAL MEASUREMENT OF PHTHALIC ACID ON TITANIA........... 103

4.1 Introduction ................................................................................................................ 103

4.2 Experimental ............................................................................................................. 105
  4.2.1. Materials ............................................................................................................ 105
  4.2.2. Preparation of the nanoporous TiO₂ film electrode ........................................... 105

4.3 Results and Discussion ............................................................................................. 106
  4.3.1. The photoelectrochemical property of the TiO₂ electrode .................................. 107
4.3.2. *In-situ* transient photocurrent response ................................................. 110

4.3.3. The Principle of *in-situ* adsorption measurement ................................. 115

4.3.4. Effect of PA Concentration ....................................................................... 117

4.4 Adsorption Thermodynamics .......................................................................... 122

4.5 Conclusions ....................................................................................................... 125

4.6 References .......................................................................................................... 125

CHAPTER 5 *IN-SITU* PHOTOELECTROCHEMICAL
CHARACTERISATION OF WEAK ADSORPTION BEHAVIOUR ON TiO$_2$
SURFACE............................................................................................................. 129

5.1 Introduction ......................................................................................................... 129

5.2 Experimental ....................................................................................................... 131

5.2.1. Materials ...................................................................................................... 131

5.2.2. TiO$_2$ photoanode preparation .................................................................... 131

5.3 Results and Discussion ..................................................................................... 133

5.3.1. Effect of potential bias in photocatalytic oxidation of methanol ............... 133

5.3.2. Photocatalytic oxidation of methanol at TiO$_2$ thin film photoanode ....... 134

5.3.3. The *in-situ* measuring principle .............................................................. 136

5.3.4. Adsorption thermodynamics ...................................................................... 139

5.4 Conclusions ....................................................................................................... 146

5.5 References ......................................................................................................... 146
CHAPTER 6  PHOTOELECTROCHEMICAL STUDY OF WATER

ADSORPTION BEHAVIOUR ON TIO₂ SURFACES ................................................. 151

6.1 Introduction ............................................................................................... 151

6.2 Experimental ............................................................................................. 153
   6.2.1. Materials .............................................................................................. 153
   6.2.2. Preparation of the TiO₂ thin film photoanode ........................................ 153
   6.2.3. Apparatus and methods ...................................................................... 154

6.3 Results and Discussion .............................................................................. 155
   6.3.1. Photoelectrochemical properties of the TiO₂ photoanode ...................... 155
   6.3.2. Transient photocurrent response ......................................................... 157
   6.3.3. Quantification of charge from the photocurrent .................................... 158
   6.3.4. Kinetics of photocatalytic oxidation of water ...................................... 162
   6.3.5. iₓ and water adsorption under UV illumination ..................................... 166
   6.3.6. Adsorption rate of water at TiO₂ surface .............................................. 170
   6.3.7. Influence of pH on the adsorption rate ................................................. 172

6.4 Conclusions ............................................................................................... 174

6.5 Reference .................................................................................................. 175

CHAPTER 7  PHOTOELECTROCHEMICAL QUANTIFICATION OF
PHOTOELECTRON TRANSPORT INSIDE NANOPARTICULATE TIO₂
THIN FILM PHOTOANODES ............................................................................ 181

7.1 Introduction ............................................................................................... 181
7.2 Experimental........................................................................................................ 184
7.2.1. Materials........................................................................................................ 184
7.2.2. Fabrication of TiO₂ thin film photoanodes...................................................... 184
7.2.3. Photoelectrochemical measurement................................................................. 185

7.3 Results and Discussion ....................................................................................... 186
7.3.1. Structural and phase compositional characteristics of the photoanodes .. 186
7.3.2. Effect of potential bias, light intensity and glucose concentration.......... 188
7.3.3. Effect of film thickness and the saturated photocurrent............................ 194
7.3.4. Quantification of resistance .......................................................................... 198

7.4 Conclusions ........................................................................................................ 203

7.5 Reference............................................................................................................ 203

CHAPTER 8  GENERAL CONCLUSIONS .............................................................. 209

8.1 Summary.............................................................................................................. 209

8.2 Conclusions........................................................................................................ 209

8.3 Suggestions for future work ............................................................................. 212
Acknowledgements

I would like to thank all the people who have helped and supported me in any respect during completion of this project.

First of all, I am heartily thankful to my supervisor, Professor Huijun Zhao, whose guidance and encouragement enabled me to develop an understanding of the subject. As a result, research life has become smooth and rewarding for me.

My thanks also go to Associate Professor Richard John for his support through the years of my doctoral study. I would like to thank Dr Eddie Zhang for his time and effort in helping me through different stages of this project. I thank the Griffith School of Environment for its generous support.

My appreciation extends to my colleagues at school and in the laboratory, especially to Clare for her time and effort in proof reading the manuscript, to Dianlu, Weijia, Haiming, Yun Wang, Yanhe, Robert and Lydia, Guiying and Taicheng, Fisher, Hongzhong, Kris, Seanan, Shane and Sally for friendship.

I want to express my heartfelt thanks to members of my family: my parents Aifang and Zhi Wen, my children Sophie and Hayden, and foremost, my wife Jennifer for their loving support and understanding of this long journey. I shall be forever grateful.

This thesis is dedicated to the memory of my father Zhi Wen who would have been pleased to know of the completion of my project. Although he is no longer with us, he is forever remembered.
Publications Resulting from this Thesis

Lihong Li, Min Yang, Shanqing Zhang, Porun Liu, Guiying Li, William Wen, Haimin Zhang and Huijun Zhao. The fabrication of CNTs/TiO$_2$ photoanodes for sensitive determination of organic compounds. Nanotechnology 21 (2010) 485503


List of Figures

Figure 1.1: Schematic demonstration of the double layers at the solid/liquid interface.\textsuperscript{119} .................................................................................................................. 14

Figure 1.2: Schematic illustration for photo-excitation in a solid......................... 15

Figure 1.3: Band edge position of semiconductors in contact with aqueous electrolyte at pH 1.\textsuperscript{10} .................................................................................................................. 19

Figure 1.4: Band bending at solution and bulk or nanoparticles semiconductor interface.\textsuperscript{10} .................................................................................................................. 21

Figure 1.5: Bulk structure of rutile and anatase.\textsuperscript{15} ................................................................. 23

Figure 1.6: Electrochemical approach in the study of photocatalytic processes...... 29

Figure 1.7: The three major steps for photocatalysis .............................................. 30

Figure 2.1: Schematic illustration of the reaction setup for TiO\textsubscript{2} colloid synthesis... 62

Figure 2.2: An X-ray diffraction pattern ........................................................................ 65

Figure 2.3: SEM images of TiO\textsubscript{2} thin film................................................................. 66

Figure 2.4: System setup for the photoelectrochemical experiments...................... 68

Figure 2.5: The E-t and i-t in a CV experiment ............................................................. 69

Figure 2.6: Photocurrent response to the applied potential bias ......................... 70

Figure 2.7: A typical photocurrent-time profile obtained under UV illumination... 71

Figure 3.1 Voltammograms and saturation photocurrent...................................... 86
Figure 3.2: Photocurrent-time profiles ................................................................. 88

Figure 3.3: Photocurrent – Light intensity relationship ................................. 90

Figure 3.4: The net limiting photocurrent ............................................................ 91

Figure 3.5: Limiting photocurrent and AFDNe.................................................. 93

Figure 3.6: Determination of diffusion coefficients for strong and weak adsorbates 95

Figure 4.1: Linear sweeping voltammetry (LSV) in PA solution ..................... 108

Figure 4.2: Photocurrent–time profile ................................................................. 111

Figure 4.3: Limiting current and PA concentration ............................................ 114

Figure 4.4: The determination of adsorbed organic compound ......................... 117

Figure 4.5: Q_{net} - time.................................................................................. 119

Figure 4.6: Adsorption rate and PA concentrations .......................................... 122

Figure 4.7: The fitting of the isotherm to Langmuir adsorption model ............ 124

Figure 5.1: Voltammograms of TiO\textsubscript{2} thin film photoanode .................. 134

Figure 5.2: Effect of on-off illumination on photocurrent .............................. 135

Figure 5.3: Photocurrent from photocatalytic oxidation of water (i_{0,w}) and from photocatalytic oxidation of methanol (i_{0,total}) .................................... 137

Figure 5.4: The net initial photocurrent of oxidation of phthalic acid after 20 minutes of pre-adsorption ................................................................. 141
Figure 5.5: The fitting of Langmuir isotherm for adsorption of phthalic acid........ 142

Figure 5.6: The dependence of net on the pre-adsorption time....................... 143

Figure 5.7: $i_{ph}$ and time............................................................................. 144

Figure 5.8: Net initial photocurrent and methanol concentration ................... 145

Figure 5.9: Plot of the Langmuir adsorption isotherm for methanol adsorption at the TiO$_2$ thin film surface. ................................................................. 145

Figure 6.1: Voltammograms of the TiO$_2$ photoanode.................................. 156

Figure 6.2: Photocurrent-time profile............................................................ 158

Figure 6.3: Photocurrent - time ................................................................. 159

Figure 6.4: Relationship between $Q^0_s/Q^0_f$ and solution pH..................... 163

Figure 6.5: $Q^0_{fit}$ and $Q^0_m$....................................................................... 164

Figure 6.6: Relationship between steady photocurrent and pH condition....... 167

Figure 6.7: Relationship between steady state photocurrent and light intensity...... 170

Figure 6.8: Charge $Q^0_{fit}$ vs adsorption time ........................................... 171

Figure 6.9: The relationship between adsorption rate and pH...................... 173

Figure 6.10: Surface speciation distribution ............................................... 174

Figure 7.1: SEM cross-session image of photoanode $T_{0.4}$ ............................ 187

Figure 7.2: SEM cross-session image of photoanode $T_{1.0}$ ............................ 187
Figure 7.3: XRD analysis patterns. .......................................................... 188

Figure 7.4: Linear increase of photocurrent with the applied potential. ............... 190

Figure 7.5: Voltammograms of TiO$_2$ thin film photoanode $T_{0.4}$. .................. 192

Figure 7.6: Relationship between saturated photocurrent and glucose concentration for photoanode $T_{0.4}$ and $T_{1.5}$ under UV light intensity of 5mW/cm$^2$. ... 193

Figure 7.7: Relationship between saturated photocurrent and light intensity in photoanodes $T_{0.4}$ and $T_{1.5}$ with glucose concentration of 1.0 mM. ....... 194

Figure 7.8: Relationship between saturated photocurrent and film thickness. ....... 195

Figure 7.9: Relationship between total resistance and film thickness at a light intensity of 5.0 mW/cm$^2$. .............................................................. 195

Figure 7.10: A model of charge transport in TiO$_2$ thin film photoanodes with different film thicknesses......................................................... 197

Figure 7.11: Resistance and inversed saturated photocurrent ............................ 199

Figure 7.12: Resistance and inversed saturated photocurrent ............................ 200

Figure 7.13: Relationship between k values and film thickness. ......................... 202

Figure 7.14: Relationship between $R_0$ and film thickness............................... 202
List of Tables

Table 1.1: Examples of organic compounds mineralised by TiO$_2$ photocatalysts (from Mills 1997.\textsuperscript{4}) ........................................................................................................................................................................... 10

Table 1.2: Characteristic times for primary processes in TiO$_2$ photocatalysis\textsuperscript{7} .......... 16

Table 2.1: Effect of calcination temperature and duration on the crystalline phase composition ........................................................................................................................................................................................................... 65

Table 3.1: $\delta$ values of individual organic compounds ................................................................................. 93

Table 3.2: Diffusion coefficients of individual organic compound ......................................................... 94

Table 4.1: List of slopes and intercepts in Figure 4.5(b). ............................................................................. 121

Table 6.1: Equations for charge vs time in Figure 6.8, and adsorption rate. .......... 171

Table 7.1: Film thickness for each photoanode ............................................................................................. 186

Table 7.2: Film thickness and values of $k$ and $R_0$ for the four photoanodes tested.. 198
Chapter 1

General Introduction
Chapter 1 General Introduction

1.1 Introduction

Nanostructured titanium dioxide (TiO\textsubscript{2}) has been the dominant metal oxide photocatalyst for the past two decades, due to its widespread application, especially for environmental remediation and solar energy conversion.\textsuperscript{1-9} Its popularity can also be attributed to its superior photoactivity, high resistance to photo-corrosion, non-toxic nature, abundance, low production costs, and more importantly, the vast variety of forms and structures that can be produced to suit different applications.\textsuperscript{1,2,10-12}

The discovery of TiO\textsubscript{2} photoassisted water splitting for hydrogen production in 1972 by Fujishima and Honda\textsuperscript{13} has stimulated great interest in the scientific community to explore the full potential of this class of materials and has led to tremendous research activity as evidenced by over 8000 papers being published.\textsuperscript{1,14,2,7} The reported research activities to date have focused on developing new synthetic methods to obtain different forms/structures of TiO\textsubscript{2}, exploring their application potentials and related mechanistic studies.\textsuperscript{2,15-17} In this regard, a large body of work has been dedicated to environmental remediation (e.g., photocatalytic degradation/removal of organic and biological contaminants)\textsuperscript{17-26} and solar energy conversion (e.g., water splitting and dye sensitised solar cells),\textsuperscript{13,27-31} both of which are based on the photocatalytic properties of TiO\textsubscript{2}.\textsuperscript{1,3,7,10,32,33} TiO\textsubscript{2} photocatalysis processes are essentially photoelectron/hole generation, separation, transportation and consumption processes,\textsuperscript{1,10,32,34} involving mass transfer from reaction media\textsuperscript{14,35-38}, interfacial reactions and charge transport/separation inside photocatalysts.\textsuperscript{1,39-41} A complete understanding of these fundamental processes is therefore paramount and extensive studies have been conducted to gain knowledge of
these fundamental processes.\textsuperscript{3,7,10,11,32,34} To this end, the development of suitable methodologies to enable the fundamental studies is critically important.\textsuperscript{40-42}

This study aims to develop a suite of facile yet effective photoelectrochemical characterisation techniques. Mass transfer in reaction media is an important process and the effective diffusion coefficient of the reactant can be used to present the inherent properties of such a process. A \textit{in-situ} photoelectrochemical method was therefore developed to determine the effective diffusion coefficient of organics in a simple, rapid and effective manner. Adsorption is an essential step of interfacial reactions in any photocatalytic process. Consequently, an \textit{in-situ} photoelectrochemical method was developed to quantify the kinetic and thermodynamic processes of strong and weak organic adsorbents and water. These methods are also capable of rapidly determining adsorbability, adsorption capacity and the adsorption constant. The photoelectron transport inside photocatalysts is a decisive factor for photoactivity and photoefficiency. A photoelectrochemical method was therefore developed to enable the direct quantification of the inherent resistance of a photocatalyst. These new characterisation methods can be used for rapid screening studies of new photocatalysts, to extract useful information to guide their applications and for system optimisation of a particular application. It is envisaged that these new characterisation methods could become useful tools for researchers in the field.

Although extensive research has been conducted on the photocatalytic oxidation of various inorganic and organic compounds, leading to substantial progress in understanding the fundamentals of photocatalysis, the low quantum efficiency of utilising light energy is a major limitation that has hindered large scale applications from being economically sustainable.\textsuperscript{1,43}
Despite the great achievement in the development of semiconductor photocatalysis over the past three decades, the lack of efficient methodologies to characterise TiO₂ photocatalysts has resulted in the delay of large-scale applications. Current research methods, in particular the study of reaction kinetics of TiO₂ photocatalytic systems, cannot provide sufficiently accurate knowledge about the photocatalytic reaction under the given experimental conditions. Furthermore, in studies of different photocatalytic systems under different conditions, the resulting data are often highly related to experimental conditions. As a result, the data are rarely comparable. Therefore, the development of a systematic methodology that can evaluate the performance of a photocatalytic system is a necessity.

This study aims to develop a series of photoelectrochemical characterisation methods useful for the evaluation of photocatalysts in a simple and effective manner. The developed methods will also be used to study the kinetic and thermodynamic properties of the photocatalysis processes.

This chapter reviews the literature directly relevant to this study.

1.2 Applications of TiO₂ Photocatalysts

Due to its chemical stability and non-toxic properties, powdered TiO₂ has been widely used as white pigments in the paint industry due to the fact that the material does not absorb visible light. Scientific studies on the photo activity of TiO₂ have been reported since the early 20th century due to flaking paints and degradation of fabrics incorporating TiO₂. However, it was not until 1972 after Fujishima and Honda’s discovery of water splitting by illumination of a TiO₂ electrode that photo-induced semiconductor catalysis has become a subject of immense interest for scientists from often divergent areas. The number of yearly citations of this 1972 Nature paper on water photolysis has been
steadily rising over the past ten years. Due to its optical and electrochemical properties, TiO$_2$ has been used in a wide range of applications among which the most significant and noticeable achievements are in the area of searching for new energy as alternatives to fossil fuels, and in the fields of environmental cleaning and remediation.

1.2.1. Solar energy conversion

The development of alternative energy sources has been motivated by economical and political interests, as well as those related to health and environmental concerns. The 1970’s were known as the time of “oil crisis” featured by the sudden increase in oil prices due to views that the future crude oil stocks were a serious concern. Solar energy has been considered one of the most important energy sources that could realise the dream of generations of scientific researchers and engineers by converting a freely available energy source into electric power or chemical fuels. Investigations focused on two types of cells: photosynthetic and regenerative cells. The two types of cells follow the same principle of generating electron-hole pairs by absorbing photons of energy exceeding that of the band gap (see Section 1.3). The photosynthetic cells generate chemical fuels such as hydrogen via water cleavage by sunlight. Regenerative cells convert solar energy into electric power leaving no net chemical change behind.

**Hydrogen production:** Fujishima and Honda’s demonstration of water photolysis with TiO$_2$ is based on the principle that when the surface of the rutile TiO$_2$ electrode was irradiated with light whose wavelength is shorter than its band gap, photocurrent flowed from the platinum counter electrode to the TiO$_2$ electrode through the external circuit demonstrating oxygen and hydrogen evolution.

This observation was recognized as an important and attractive target of chemical conversion and storage of solar energy by means of producing hydrogen ($H_2$) as a
clean, renewable fuel to reduce reliance on fossil fuels. Even though the efficiency of the process was low, this research field of photocatalysis and photoelectrochemistry has flourished and demonstrated a great potential for realising this goal. More importantly, research and development of semiconductor photoelectrochemistry since the 1970’s have greatly sped up the development of photocatalysis.

However, due to some drawbacks of the TiO\(_2\) semiconductor, especially the wide optical gap of 3.2 eV that limits the full use of the solar spectrum, TiO\(_2\) can only absorb the UV light component contained in the solar spectrum. Therefore, TiO\(_2\) photocatalysis has not been very attractive from the viewpoint of H\(_2\) production technology. Various other semiconductors with a small band gap, such as CdS and CdSe, have been investigated, but their efficiency and stability were much lower than that of TiO\(_2\).

**Dye sensitised solar cells:** The efficient utilisation of solar energy is one of the major goals of modern science and engineering, particularly in relation to global warming and fossil fuel depletion. Of the semiconductor materials being developed for photocatalytic applications, TiO\(_2\) remains the most promising because of its high efficiency, low cost and chemical inertness. Because UV light accounts for only a small fraction (8%) of the sun’s energy compared to visible light (45%), any shift in the optical response of titania from UV towards full spectrum light will have a positive impact on the photocatalytic and photoelectrochemical utility of the material. Historically, doping of titania has been the approach taken for band-gap engineering of the semiconductor material in attempt to improve its efficiency. However, due to some very large drawbacks of the TiO\(_2\) as a semiconductor photocatalyst, especially the wide band gap preventing its full use of the solar spectrum, recombination of photo-excited electron-hole
pairs and thermal instability, commercial use of this material has not been realised. Also, the photoactivity of TiO₂ has shown a noticeable decrease.⁶¹

Developed as an alternative to overcome the spectral sensitivity limitation that restricts TiO₂ semiconductors from efficiently using solar light, the dye-sensitised solar cell (DSSC) has attracted much attention since it was first invented in 1990’s by O’Regan and Graztel.⁸,⁶⁴,⁶⁵

This new type of solar cell technology using the dye sensitisation of mesoporous nanocrystalline TiO₂ film remarkably improved the energy conversion efficiency by covering the TiO₂ surface with a monolayer of a dye. Photo-induced electron injection from the sensitisier dye into the metal oxide conduction band initiates charge separation after absorbing high radiation. Subsequently, the injected electrons are transported through the metal oxide film to one device electrode, while a redox-active electrolyte is employed to reduce the dye cation and transport the resulting positive charge to a platinum counter electrode.⁴⁸,⁶⁶

The overall efficiency of the DSSC in energy conversion depends on the performance of each cell component. Efficiencies of DSSC devices employing nanocrystalline TiO₂ films have been reported up to 10.4%.¹⁰,⁶⁷-⁷⁰

1.2.2. Environmental remediation

Soon after the discovery of the conversion of solar energy to hydrogen as a combustible fuel by a TiO₂ semiconductor, the strong photo oxidation power of TiO₂ has found its potential utilisation in environmental remediation and wastewater treatment. It became apparent that many organic compounds, commonly found as major components of wastewater contaminant and pollutants, could be decomposed by either partial or complete oxidation in a photocatalytic process induced by surface UV irradiation.²,⁵,⁷¹-⁷⁸
Since Frank and Bard’s attempts in 1977 to explore the possibility of using TiO$_2$ to decompose cyanide in water, and to propose that illuminated TiO$_2$ could be used for the purification of water by photocatalytic decomposition of pollutants\textsuperscript{2,79,80} extensive research effort has been focused on the application of TiO$_2$ photocatalysts in environmental remediation\textsuperscript{26}.

The work done by Ollis and others\textsuperscript{81,82} on photocatalytic mineralisation of halogenated hydro-carbons in 1983 was the first recognition and implementation of semiconductor sensitizer TiO$_2$ for organic pollutants.\textsuperscript{83} The TiO$_2$ was initially believed to be limited to non-aromatic compounds, but the list of compounds extended to a wide range from aliphatic to aromatic compounds that commonly existed as pollutants in environmental water resources.\textsuperscript{4,23,84-87} Table 1.1 lists examples of organic compounds that can be mineralised by TiO$_2$ photocatalysts.\textsuperscript{4}

Photocatalysis applied to water purification and treatment has provided a great opportunity for the treatment of toxic material in waste water to meet the ever-increasing demands of handling serious environmental pollution problems.\textsuperscript{1} One of the advantages of TiO$_2$ photocatalysis for water decontamination is that only the TiO$_2$ photocatalyst and UV light are needed and thus the cost is expected to be lower than for other advanced oxidation techniques. This makes it very attractive as a means of water purification.\textsuperscript{43,81,82,88-93}

The ability to decontaminate low concentration pollutant from water is another attractive feature of environmental cleaning by TiO$_2$ photocatalysis. One interesting application is to remove endocrine disruptor chemicals (EDC) in the aqueous environment.\textsuperscript{94,95}
Table 1.1: Examples of organic compounds mineralised by TiO$_2$ photocatalysts (from Mills 1997, 4)

<table>
<thead>
<tr>
<th>Class</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes</td>
<td>Methane, isobutane, pentane, heptane, cyclohexane, paraffin</td>
</tr>
<tr>
<td>Haloalkanes</td>
<td>Mono-, di- tri- and tetrachloromethane, tribromoethane, 1,1,1-trifluoro-2,2,2-trichloroethane</td>
</tr>
<tr>
<td>Aliphatic alcohols</td>
<td>Methanol, ethanol, isopropyl alcohol, glucose, sucrose</td>
</tr>
<tr>
<td>Aliphatic carboxylic acids</td>
<td>Formic, ethanoic, dimethylethanoic, propanoic, oxalic acids</td>
</tr>
<tr>
<td>Alkenes</td>
<td>Propene, cyclohexene</td>
</tr>
<tr>
<td>Haloalkenes</td>
<td>Perchloroethene, 1,2-dichloethene, 1,1,2-trichloroethene</td>
</tr>
<tr>
<td>Aromatics</td>
<td>Benzene, naphthalene</td>
</tr>
<tr>
<td>Haloaromatics</td>
<td>Chlorobenzene, 1,2-dechlorobenzene, bromobenzene</td>
</tr>
<tr>
<td>Nitrohaloaromatics</td>
<td>3,4-Dichloronitrobenzene, dichloronitrobenzene</td>
</tr>
<tr>
<td>Phenols</td>
<td>Phenol, hydroquinone, catechol, 4-methylcatechol, resorcinol, o-m-p-cresol</td>
</tr>
<tr>
<td>Halophenols</td>
<td>2,3,4-Chlorophenol, pentachlorophenol, 4-fluorophenol, 3,4-difluorophenol</td>
</tr>
<tr>
<td>Aromatic carboxylic acids</td>
<td>Benzoic, 4-aminobenzoic, phthalic, salicylic, m- and p- hydroxybenzoic, chlorohydroxybenzoic acids</td>
</tr>
<tr>
<td>Polymers</td>
<td>Polyethylene, poly(vinyl chloride) (PVC)</td>
</tr>
<tr>
<td>Surfactants</td>
<td>Sodium dodecylsulphate(SDS), polyethylene glycol, sodium dodecyl benzene sulphonate, trimethyl phosphate, tetrabutylammonium phosphate</td>
</tr>
<tr>
<td>Herbicides</td>
<td>Methyl viologen, atrazine, simazine, prometron, propetryne, bentazon</td>
</tr>
<tr>
<td>Pesticides</td>
<td>DDT, parathion, lindane</td>
</tr>
<tr>
<td>Dyes</td>
<td>Methylene blue, rhodamine B, methyl orange, fluorescein</td>
</tr>
</tbody>
</table>

EDC includes chemicals such as natural hormones, dioxins, biphenol-A etc., and are assumed to be hazardous to both humans and wildlife even at very low concentrations.

Conventional biological methods to remove these EDC chemicals require long periods of time while in general, chemical oxidation methods are not economical for treatment of low concentration pollutants. It has been reported that using TiO$_2$ photocatalysts to treat the water discharged from sewage treatment plants, lead to the decomposition of about
90% of initial estron under UV illumination in a very short time with good reproducibility. This example suggests that the approach should also be suitable for the removal of other low-level EDCs in the aqueous environment.7

1.2.3. Other applications

The principle of photo induced oxidation of organic compounds by TiO₂ semiconductors extends to other applications in a wide range of fields. The major reported practices include photocatalytic destruction of microorganisms, fixation of nitrogen,96-99 clean up of oil spills,100-102 bacteria and virus sterilisation,103-107 cancer treatment,108-112 sunscreen cosmetics113 and superhydrophilicity.114-117 In the environment of low light intensity illumination, TiO₂ photocatalytic oxidation has been applied to air purification and odour removal.118

1.3 Semiconductor Photocatalysts

All of the above-mentioned applications require suitable photocatalysts to sustain photocatalysis performance. The development of appropriate photocatalytic materials has therefore become a major task for researchers in the field.

1.3.1. Energy levels and the band theory

The band model of solids is often used to describe the electronic property of semiconductors. This model is directly from the atomic energy levels in that the sources and sinks of electrons for the electrochemical process are the bands of solids. The Pauli exclusion principle states that levels of identical overlapping electronic orbitals cannot be equal, and orbital overlapping forms bands of energy levels with $2 \times 10^{32}$ levels in each band.119 In the electronic structure of an atom, the orbital completely occupied by the valence electrons is called the “valence band” of the solid. Above the last-filled valence band, there is a band that is associated with first exited state and is normally unoccupied.
by electrons. This is called the “conduction band” of the solid. Unlike metals, in which there exists a continuum of electronic states, semiconductors possess a void energy region where no energy levels are available. This energy level between the filled valence band and an empty conduction band is the energy bandgap \( (E_g) \). In the band model, a hole is an empty level in the valence band with missing electrons.³

**Fermi Energy:** (Fermi Level \( E_f \)) The distribution of electrons in a solid is described by the Fermi distribution function and the Fermi energy level that gives the probability of an electron level of energy being filled by an electron:\(^{120}\)

\[
f(E) = \frac{1}{1 + \exp\left(\frac{E - E_f}{kT}\right)}
\]

where \( k \) is the Boltzmann’s constant and \( T \) is the absolute temperature.

For a first approximation, the Fermi level indicates that all energy levels below it are occupied by electrons and all levels above it are unoccupied by electrons.\(^{119}\) For electric current to be produced by an electric field, the electrons must increase their kinetic energy to move from a lower energy level to a higher one. An insulator is a body whose allowed energy bands are occupied and electrons cannot acquire the additional kinetic energy of orderly motion so that there is no flow of electric current under an electric field.\(^{120}\) If at 0 K the conduction band is partially filled, the crystal has the properties of a metal and electric current is produced under an applied electric field. For metals, as good electrical conductors, there are a large number of electrons in the allowed band and these electrons participate in this motion. If a crystal that is an insulator at absolute zero absorbs kinetic energy (for example, being heated, or under UV illumination), then the electrons in the valence band may move into the upper level of unfilled bands by using the acquired
thermal energy. Crystals that display this electrical conductivity by excitation are called semiconductors with intrinsic conductivity. A crystal may demonstrate the properties of a semiconductor or an insulator depending on the magnitude of electrical conductivity, which is largely decided by the width of the bandgap of the material. A typical semiconductor such as germanium has a bandgap width of 0.67 eV and a typical insulator equals several electron volts.

**Surface energy levels and band bending:** In addition to the energy levels in the bulk of the semiconductor, there are quantum states of energy levels at the surface of a semiconductor that are different to that of the bulk due to thermodynamic equilibrium at the semiconductor-electrolyte boundary.

When a solid bulk semiconductor electrode is in contact with the electrolyte solution containing a reduction-oxidation couple, space charge planes form at the solid/liquid interface by thermodynamic equilibrium in which the major charge carriers move to the surface and minor charge carriers into the inside of the semiconductor. The formation of these charged layers produces electrical double layers that consist of layers of positive charge, negative charge and regions of high electric field between the charge layers. Three distinct double layers generally appear at the solid/liquid interface for a semiconductor in contact with the electrolyte solution (see Figure 1.1). The Gouy layer is often neglected in semiconductor studies because with high concentration solutions, the Gouy layer is very thin and can be considered to have melded into the outer Helmholtz plane.

**Band bending:** Within the space charge layer of the semiconductor, the electronic energy bands in the solid semiconductor within the space charge layer bend upwards at the solid-liquid interface in the case of an n-type semiconductor.
1.3.2. **Photoelectron-hole generation and recombination**

Semiconductors can act as photocatalysts for light-induced oxidation-reduction processes due to their electron structure, which is characterised by a filled valence band and an empty conduction band. The photochemical processes occurring upon irradiation of a semiconductor are well established.\(^{1,2,10,121}\) Primary steps in the photoelectrochemical mechanism are listed below:

**Photo-excitation:** The initial process for heterogeneous photocatalysis by semiconductors is the generation of electron-hole pairs in the semiconductors by light illumination.\(^3\) In this process, the band gap of the semiconductor defines the wavelength sensitivity of the semiconductor to irradiation. Photo-excitation with light energy equal to or greater than the band gap promotes an electron from the valence band of the semiconductor to the conduction band, creating an electron vacancy or “photo hole” (\(h^+\)) at the valence band edge (Figure 1.2).
The excited state of the conduction band electrons and the valence band holes can follow several pathways after the photo-excitation: (i) recombine and dissipate the input energy as heat, (ii) get trapped in the metastable surface states, and (iii) undergo a surface charge transfer process where the electron-hole pair reacts with the electron donors and accepters adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles.\(^1\)

**Charge transfer and recombination:** Unlike metals, the lack of a continuum of interband states in semiconductors enables the life-time of the photo-induced electron-hole pair to be sufficiently long to participate in the interfacial charge transfer process. During the charge transfer process, the semiconductor donates electrons to reduce an electron accepter while electrons from the donor species can combine with the surface hole to oxidise the donor species.\(^2,3\) In circumstances where electron donors or accepters are pre-adsorbed on the semiconductor surface, the electron transfer process will be more efficient.\(^2,122\)
### Table 1.2: Characteristic times for primary processes in TiO$_2$ photocatalysis

<table>
<thead>
<tr>
<th>Primary Process</th>
<th>Characteristic time</th>
<th>Sample description</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge carrier generation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{TiO}_2 + \text{hv} \rightarrow e^- + h^+$</td>
<td>fs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Charge trapping</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$h^+ \rightarrow h^+_{\text{tr}}$</td>
<td>&lt;200 fs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$e^- \rightarrow e^-_{\text{tr}}$</td>
<td>&lt;150 fs</td>
<td>Nanoporous TiO$_2$ film</td>
<td>Tamaki et al.$^{123}$</td>
</tr>
<tr>
<td>$h^+<em>{\text{s-tr}} \rightarrow h^+</em>{\text{d-tr}}$ (relaxation)</td>
<td>~100 ps</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$e^-<em>{\text{s-tr}} \rightarrow e^-</em>{\text{d-tr}}$ (relaxation)</td>
<td>~500 ps</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Charge recombination</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>or $e^- + h^+$</td>
<td>1 $\mu$s</td>
<td>Nanoporous TiO$_2$ film (water)</td>
<td>Yoshihara et al.$^{124}$</td>
</tr>
<tr>
<td>$e^- + h^+<em>{\text{tr}},$ or $h^+ + e</em>{\text{tr}}$</td>
<td>25 $\mu$s</td>
<td>Nanoporous TiO$_2$ film (air)</td>
<td>Perio et al.$^{125}$</td>
</tr>
<tr>
<td>$\rightarrow$ heat (or hv)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interfacial charge transfer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$h^+$ (or $h^+_{\text{tr}}$) + Red</td>
<td>~300 ps (methanol oxidation)</td>
<td>Nanoporous TiO$_2$ film</td>
<td>Tamaki et al.$^{126}$</td>
</tr>
<tr>
<td>$\rightarrow$ Red$^+$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$e^-_{\text{tr}} + O_2 \rightarrow O_2$</td>
<td>~3 ns (2-propanol oxidation)</td>
<td>Nanoporous TiO$_2$ film</td>
<td>Tamaki et al.$^{126}$</td>
</tr>
<tr>
<td>$e^- \rightarrow O_2 \rightarrow O_2$</td>
<td>&lt;2 $\mu$s (water oxidation)</td>
<td>Degussa P25 powder</td>
<td>Ymakata et al.$^{127}$</td>
</tr>
<tr>
<td>$e^- + Pt \rightarrow Pt…e^-$</td>
<td>~10 $\mu$s</td>
<td>Nanoporous TiO$_2$ film</td>
<td>Peiro et al.$^{125}$</td>
</tr>
<tr>
<td>$e^- + Pt \rightarrow Pt…e^-$</td>
<td>2.3 $\mu$s</td>
<td>Degussa P25 powder</td>
<td>Iwata et al.$^{129}$</td>
</tr>
</tbody>
</table>
In competition with the charge transfer process is electron and hole recombination which can occur either within the volume of the semiconductor or on the surface with the release of heat. In order for photocatalysis to be productive chemically, the electron-hole pair recombination process must be retarded to permit an efficient charge transfer process to occur on the semiconductor’s surface. This can be accomplished by trapping either the photo-generated electron, the photo hole or both to suppress recombination and increase the lifetime of the separated electron and hole to more than a fraction of a nanosecond.² Charge carrier traps are associated with surface defect sites that are produced in preparation of colloidal and polycrystalline photocatalysts. The irregularities are associated with surface electron states that serve as charge carrier traps and help suppress the recombination of electrons and holes.³

The time scale for primary process in TiO₂ photocatalysis, including charge carrier generation, charge trapping, interfacial charge transfer and charge recombination, is summarised in Table 1.2.⁷

1.3.3. Band energy

The electrons possess the reducing power of the conduction band energy and the photo holes have the oxidizing power of the valence band energy. The ability of a semiconductor to undergo photo-induced oxidation/reduction with the adsorbed electrolyte is governed by the band energy positions of the semiconductor and the redox potentials of the electrolyte. From the band-edge positions of the valence band and conduction band, the redox capability of a photo-excited semiconductor can be estimated. Figure 1.3 shows the band edge energy levels of some common semiconductors that are in contact with aqueous media at pH 1.¹⁰
In order to donate an electron from a compound to the vacant hole of the semiconductor, the potential level of the donor is thermodynamically required to be above (more negative than) the valence band position of the semiconductor.\textsuperscript{3,10} Therefore, in the photo-induced electron transfer process by semiconductor, the more positive the valence band edge of the potential, the higher the oxidation power of the photo holes.

Band-gap energies are the critical criteria for a semiconductor to be selected for efficient photocatalysis performance. Several simple metal oxide and sulfide semiconductors have band-gap energies sufficient for promoting a wide range of chemical reactions (see Figure 1.3).\textsuperscript{1} These compounds include WO\textsubscript{3} ($E_g = 2.8$ eV), SrTiO\textsubscript{3} ($E_g = 3.2$ eV),\textsuperscript{130} $\alpha$-Fe\textsubscript{2}O\textsubscript{3} ($E_g = 3.1$ eV),\textsuperscript{131} ZnO ($E_g = 3.2$ eV),\textsuperscript{132-134} ZnS ($E_g = 3.6$ eV), SnO\textsubscript{2} ($E_g = 3.6$ eV).\textsuperscript{135,136} Although these semiconductors have the potential to serve as heterogeneous photocatalysts, TiO\textsubscript{2} has proven to be the most suitable for widespread environmental applications due to its advantages over other semiconductors. These include being biologically and chemically inert, inexpensive to produce, and also stable to photo and chemical corrosion.\textsuperscript{3,32,137-139} For example, CdS and CdSe have narrower band gaps, and are sensitive to incident light in the visible spectrum but photo-corrosion is significant. $\alpha$-Fe\textsubscript{2}O\textsubscript{3} is absorptive in the visible region of incident light, but has much lower photocatalytic activity than TiO\textsubscript{2} or ZnO.

Due to its favourable characteristics, TiO\textsubscript{2} has become the benchmark photocatalyst used to evaluate the photocatalytic activity of other catalysts.\textsuperscript{2}
1.4 TiO$_2$ Photocatalysts

A good semiconductor of photocatalytic interest should be (i) photoactive, (ii) able to utilise visible and/or near UV light, (iii) biologically and chemically inert, (iv) highly resistant to photo-corrosion, (v) inexpensive and (vi) non-toxic.$^{140}$ By common consent, the TiO$_2$ semiconductor meets these criteria remarkably well and has been selected as a photocatalyst with many advantages over other semiconductor materials. Due to differences in the material’s properties, such as morphology, crystal phase, specific surface area, particle aggregate size and the surface density of OH$^-$ groups, different samples of TiO$_2$ often exhibit different photocatalytic activities toward a organic.
compound under otherwise identical reaction conditions.\textsuperscript{4,141} These properties of the TiO\textsubscript{2} photocatalyst, in many cases, largely determine the overall efficiency of photocatalytic process involving a particular compound.

1.4.1. Bulk and nano-sized TiO\textsubscript{2}

In the past three decades, photocatalysis by semiconductors has been a subject of intensive research with a wide range of applications in alternative energy production and environmental interests. Development of photocatalysis by semiconductors has followed an evolutionary pathway in regards to the size of the materials, from bulk sized semiconductors to colloidal (~10–100 nm) to nano-sized materials (<10 nm).\textsuperscript{142} According to the size of the semiconductor material, bulk and nano-sized semiconductors have been used as photocatalysts in applications. Although consisting of the same material, these different sized semiconductor photocatalysts have exhibited divergent electronic and photocatalytic properties depending on the size of the material and the surface area.\textsuperscript{2,10,40,119,142-144}

As discussed in 1.3.1, when a bulk semiconductor electrode is in contact with the electrolyte solution containing a redox couple, the valence and conduction bands are bent within the space charge layer to attain equilibrium with the potential of the redox couple (Figure 1.4). The thickness of the space charge layer is usually of the order of 1–10\textsuperscript{3} nm depending on the carrier density and dielectric constant of the semiconductor.\textsuperscript{44} The local electrostatic field existing across this depletion layer is responsible for charge separation upon light illumination in which holes migrate to the surface of the semiconductor where chemical reactions occur, while the electrons drift toward the interior of the electrode and from there to the external circuit.\textsuperscript{2,44}
For the nano-sized TiO$_2$ semiconductor system, charge separation mechanisms for small particles are completely different compared to bulk systems such as macroscopic polycrystalline or single-crystal semiconductors. The potential distribution for the colloidal or nanocrystalline network semiconductor that consists of nano-sized particles is governed by a type of linearised Poisson-Boltzmann equation. The potential drop of such semiconductor types is usually very small (Figure 1.4), and requires high doping levels to produce significant potential gradients. Because the band bending is small for nano-sized semiconductor particles, the charge separation is maintained by a process of diffusion which can be described by a random walk model. Since the diffusion of charge carriers from the interior to the particle surface can occur more rapidly than recombination, high efficiency photocatalytic processes can be achieved if photoelectrons or photo holes are removed fast enough from the surface of the semiconductor.
It is well recognised that an applied potential bias to the TiO\(_2\) semiconductor can increase the photo efficiency of a photocatalytic reaction.\(^{40,146}\) Due to the different charge carrier separation mechanisms for the bulk and nano-sized TiO\(_2\) semiconductors, the potential bias plays different roles in suppressing photoelectron and hole recombination. For a bulk semiconductor electrode, the applied potential bias is mainly to regulate the band bending and hence affects the surface reaction. For the nanoparticulate TiO\(_2\) electrode, photoelectrons drifting to the back contact by diffusion are removed by applied potential bias to the counter electrode and collected as photocurrent through the external circuit.\(^{40}\) In recent years, researchers and engineers have paid special attention to nano-sized TiO\(_2\), which has several advantages compared to the bulk TiO\(_2\) photocatalyst, including quantum size effect, reduced recombination of electron-hole pairs and increased active surface area.\(^{15,147,148}\)

### 1.4.2. Surface structure and morphology

There are three common polymorphs of TiO\(_2\), rutile, anatase, and brookite. Rutile and anatase are the two tetragonal forms that exist in nature. Brookite is extremely difficult to synthesise in the laboratory, but both anatase and rutile can be readily prepared.\(^{59}\) Among the three polymorphs, rutile is the only stable phase while anatase and brookite are metastable at all temperatures.\(^{149}\)

Crystalline anatase can be obtained at low temperature at about 300 – 400 °C while rutile usually forms at higher temperatures. Both anatase and rutile TiO\(_2\) have been used in most photocatalytic studies.\(^{150,151}\) The rutile form of TiO\(_2\) is the most commonly used as white pigment in paints due to its high efficiency in scattering white light and its greater chemical stability compared to the other two TiO\(_2\) polymorphs.\(^{44}\) Rutile however, has attracted less attention in photocatalysis because of its low photocatalytic efficiency.\(^{152}\)
Studies have shown that electron transport in rutile TiO$_2$ layers is about an order of magnitude slower than transport in anatase TiO$_2$.\textsuperscript{153,154}

In photocatalysis, anatase is of much interest and perceived as the more photoactive phase of TiO$_2$ because of higher surface reactivity and potentially higher conduction-band edge energy.\textsuperscript{59} Anatase is the only polymorph that can produce hydrogen without applying an external bias.\textsuperscript{155} Figure 1.5 shows the bulk structure of rutile and anatase (redrawn from ref\textsuperscript{15}).

![Figure 1.5: Bulk structure of rutile and anatase.\textsuperscript{15}](image)

**1.4.3. Photocatalytic degradation**

As discussed in section 1.3.2, light irradiation with matched energy generates charge carriers of photoelectrons and holes across the band gap. If a suitable scavenger or surface defect state is available to trap these charge carriers, recombination can be sufficiently prevented and subsequent redox reactions may occur. The ability of a semiconductor to undergo photocatalytic reaction with adsorbed species on its surface is governed by the band energy position of the semiconductor and the redox potentials of the
adsorbate. For many semiconductors, the valence band holes are very powerful oxidants, and the photoholes are used by most organic degradation reactions to oxidise target species. This has been successfully applied to the remediation of a wide variety of contaminants in water treatment.\textsuperscript{156-161} For most photocatalytic degradation reactions, the oxidising ability of the photoholes was utilised, either directly or indirectly, to completely mineralise the aqueous pollutants that exist in water system. Meanwhile, reducible species, oxygen in most applications, are also provided to react with the photoelectron to avoid the build up of charge carriers on the semiconductor surface that lead to recombination.

In general, the photocatalytic mineralisation of a given organic compound follows the stoichiometric equation:\textsuperscript{162}

\[
C_xH_yO_zX_k + (x + \frac{y - 2z - k}{4})O_2 \rightarrow xCO_2 + kH^+ + kX^- + \frac{y - k}{2}H_2O \quad (1.2)
\]

And under complete mineralization conditions, the number of transferred electrons can be calculated as:

\[
n = 4x + y - 2z - k \quad (1.3)
\]

In studies of photocatalysis by photoelectrochemical methods, the number of electrons expressed in Equation 1.3 can be used to quantify the amount of oxidised molecules for a photocatalytic reaction.

\textbf{1.4.4. Slurry and immobilised TiO$_2$ photocatalytic systems}

Heterogeneous photocatalysis by TiO$_2$ semiconductors has been of considerable interest in wastewater treatment technologies for low organic concentration levels. The TiO$_2$ catalyst has been used in two forms in photocatalytic oxidation reactions: (i) suspended in
aqueous solutions in a form of slurry TiO$_2$ fine powder and (ii) immobilised on a rigid and inert substrate.

**Slurry system:** In water treatment and purification, organic compounds in aqueous solution can be completely mineralised to CO$_2$ and H$_2$O in the presence of TiO$_2$ powder under UV light illumination. In a suspended slurry TiO$_2$ catalyst system, a high ratio of illuminated catalyst surface to effective reactor volume can be achieved for a small, well-designed photocatalytic reactor.$^{37,38}$ As discussed in section 1.3, irradiation of a TiO$_2$ particle with UV light illumination leads to the generation of a photoelectron-hole pair. There is a finite possibility that the electron-hole pair will become spatially separated and diffuse to the surface where the photo electron-holes will be captured by O$_2$ and by the adsorbed hydroxide to form OH$^•$ radicals. During the process of photochemical conversion of light by semiconductor catalysts, recombination is an important source of inefficiency.$^{39,163}$ In practice, if charge recombination is not to be a limiting factor, the particle size must be comparable to, or smaller than, the distance that the holes move to the field-free region before recombination with an electron. Consequently, by using ultrafine (< 30 nm) catalyst particles, there is almost no mass-transfer limitation existing for the photocatalytic degradation process because the maximum diffusional distance is very small.$^{39,164}$

However, in large-scale water treatment applications of photocatalysis by suspended TiO$_2$ slurry, the catalyst particles must be filtered prior to the discharge of the treated water. Hence, the installation and operation of a liquid-solid separator have become necessary following the photocatalytic degradation process. Because this separator installation and operation for ultrafine catalyst particles is a slow and expensive process, it will therefore significantly raise the cost of the overall process. In addition, the depth of penetration of
UV light is also limited in a suspension system due to the strong absorption by the small size catalyst and the dissolved pollutant,\textsuperscript{38} leading to limited practical application of the TiO$_2$ photocatalyst in the form of aqueous slurry suspension.\textsuperscript{38,165}

Due to the problems associated with employing suspended TiO$_2$ catalysts, attention has turned to the application of immobilised TiO$_2$ film catalysts with the design and development of immobilised TiO$_2$ photocatalysts likely to be useful for commercial-scale application in water treatment.\textsuperscript{25,37,39,166,167}

**Immobilised system:** The problems associated with slurry TiO$_2$ photocatalysts can be eliminated by immobilising TiO$_2$ particles onto suitable supports to form TiO$_2$ thin films. This immobilised TiO$_2$ photocatalyst exhibits interesting electrochemical and photoelectrochemical properties.\textsuperscript{168-171} They possess highly porous structures which ensure maximum light absorption as well as guarantee that photoholes are never generated too far from the surface.\textsuperscript{39} This structure retains the photochemical properties of the slurry system with similar selectivity. In practice, a potential bias is often applied to the immobilised TiO$_2$ thin film in a photocatalytic process.

Immobilised TiO$_2$ photocatalysts used in photocatalytic oxidation have several advantages over the traditional suspension/slurry system.\textsuperscript{37}

(i) Because electrochemical methods can be employed to study the photocatalytic process, the oxidation half-reaction at the working electrode is separated from the reduction half-reaction, which occurs at the auxiliary electrode. This separation enables the study each half reaction in isolation. Experimental conditions can be controlled in order to focus on the half reaction of the photo oxidation of organic substances by the TiO$_2$ photocatalyst.
(ii) Immobilising the TiO$_2$ particles on a solid substrate eliminates the problem associated with the separation of the catalyst particles from the treated effluent. This is of great practical benefit for continuous water treatment by photocatalysis.

(iii) Most importantly, an external potential bias can be applied to the immobilised thin film TiO$_2$ photocatalyst to exploit the Electric Field Enhancement (EFE) effect and should lead to an improvement in the efficiency of the photocatalytic process.$^{39,172}$

As discussed in Section 1.4.1, the charge carrier separation occurs on the same particle and charge separation is maintained by diffusion to the surface with a speed that is more rapid than recombination.$^{10}$ For the immobilised TiO$_2$ thin film photocatalyst, the potential bias on the immobilised semiconductor/electrolyte interface generates a space charge region at a depth called the depletion layer within the semiconductor that facilitates the separation of the photo generated electron and holes. This internal electric field is highly dependent on the structure of the electrodes and their degree of doping, and any holes generated within this region will be efficiently transported to the surface.$^{172,173}$

The applied potential bias between the TiO$_2$ photoelectrode and the counter electrode also facilitates drawing the conduction band electron away from the semiconductor film to the counter electrode through the external circuit.$^{173,174}$ The effect of quick electron removal prevents the build up of negative charge at the semiconductor surface, leading to a marked increase in the quantum efficiency for the photochemical generation of holes.$^{25,39,173,175,176}$

In principle, the charge separation and minimisation of electron/hole recombination by immobilised semiconductor film electrodes is analogous to a heterogeneous suspension system which acts as a “shot-circuited microphotocell”.$^{174}$ The photoelectrochemical techniques have proved to be a convenient and powerful method for study of...
photocatalytic reaction by separating the oxidation and reduction occurring at different electrodes.\textsuperscript{42,177-180}

1.4.5. Study of photocatalysis by photoelectrochemical approach

Study of photocatalytic processes on immobilised TiO\textsubscript{2} semiconductors by photoelectrochemical method has several distinct advantages over colloidal suspension systems of semiconductor particles.\textsuperscript{40,168,175,180} The most significant benefit of employing the photoelectrochemical method is the application of a potential bias to the immobilised TiO\textsubscript{2} photocatalyst where the photocatalytic reaction occurs. Under the applied potential bias, the conduction band electrons are drawn away from the semiconductor film, and can migrate to a suitable counter electrode for reduction reaction (usually oxygen reduction).\textsuperscript{39,40} The measurement of the photocurrent passed at the working electrode allows the quantification of the extent of the photocatalytic process.\textsuperscript{40,41,181}

In addition, studying and characterising the photocatalytic process at the immobilised TiO\textsubscript{2} catalyst by photoelectrochemical method, the applied potential bias can be used to manipulate the rate-determining steps of photocatalytic reactions.\textsuperscript{146} For example, the rate-determining steps of a photocatalytic reaction can be altered by the applied potential bias to allow study of photocatalytic oxidation mechanisms.

Based on the photoelectrochemical principle, a great variety of investigations have been conducted to characterise the photocatalytic process at immobilised TiO\textsubscript{2} photocatalyst, particularly with respect to issues such as electron transport in the film,\textsuperscript{40,143,182-184} and the kinetics and thermodynamics of the photocatalytic oxidation for a wide range of organic compounds.\textsuperscript{39,40,76,146,185-190}
Figure 1.6 schematically demonstrates the path of electron transport in a photocatalytic oxidation reaction. The generated electrons from the photocatalytic reaction are collected as the photocurrent that can be employed to characterise the photocatalytic process.

This thesis focuses on the study of the photocatalytic reaction at immobilised TiO$_2$ thin film photocatalysts. Photoelectrochemical methods were employed to investigate the photocatalytic degradation of organic substances in relation to the three separated steps in a photocatalytic process.

**Figure 1.6**: Electrochemical approach in the study of photocatalytic processes

### 1.5 Photoelectrocatalysis

In general, heterogeneous photocatalysis by immobilised TiO$_2$ photocatalyst is composed of three major steps that are interactively related to each other (Figure 1.7):
(i) the mass transfer step in the solution phase involving processes of transportation of reactants to and removal of products from the catalyst surface;

(ii) the interfacial step comprised of multiple processes. It generally includes physical and chemical activities occurring at the phase boundary of the heterogeneous photocatalytic process;

(iii) the photoelectrons/holes migration within the semiconductor photocatalyst

Figure 1.7: The three major steps for photocatalysis

1.5.1. Mass transfer process

The photocatalytic degradation technology in wastewater treatment is competitive with several other thermal and non-thermal technologies with several advantages: (i) the organic contaminant can be destroyed completely, (ii) it avoids the formation of polycyclic products, (iii) it requires inexpensive catalysts with high turnovers, and most
importantly (iv) photocatalytic procedures can be applied to wastewater treatments containing contaminants in the ppb concentration range.\textsuperscript{17}

In practice, for a photocatalytic oxidation reaction such as water treatment where the reactant concentration is low, mass transfer may become a factor that limits the overall photocatalytic efficiency for the photocatalytic process.\textsuperscript{37,86}

In the TiO\textsubscript{2} slurry photocatalytic system, a high ratio of illuminated catalyst surface to the effective reactor volume can be achieved for the aqueous suspended TiO\textsubscript{2} photocatalysis in a small and well-designed photocatalytic reactor.\textsuperscript{191} In these superfine suspension TiO\textsubscript{2} photocatalyst systems, the diffusion distance between the solute molecules and catalyst surface is short, and mass transfer limitations are usually not believed to be the limiting factor.\textsuperscript{37} It has been reported that in a slurry TiO\textsubscript{2} system, mass transfer phenomena did not affect reaction rate measurements in photocatalytic decomposition of phenol over anatase TiO\textsubscript{2} powder.\textsuperscript{23}

In a study of the mass transfer and photocatalytic degradation of leather dye in a TiO\textsubscript{2} suspension system,\textsuperscript{192} the adsorption of dye by a suspended TiO\textsubscript{2} photocatalyst was calculated using a film and pore diffusion model. It was reported that there was no diffusion limitation for dye degradation by the suspended TiO\textsubscript{2} and the controlling step for the overall photocatalytic degradation reaction was identified as the reaction on the particle surface.

However, for immobilised TiO\textsubscript{2} photocatalyst, both external and internal mass transfer play significant roles in the overall photocatalytic process owing to the increasing diffusional length of the reactant from the bulk solution to the photocatalyst surface.\textsuperscript{37} In photocatalytic degradation of water contaminants by immobilised catalysts, mass transfer is often the only means by which reactants are supplied to and products removed from the
Chapter 1: General Introduction

catalyst surface. In a comparison of suspended and immobilised TiO$_2$ photocatalyst efficiency, it was reported that under identical illumination conditions in the photocatalytic degradation of phenol, the degradation rate with the TiO$_2$ free suspension was approximately 2.6 times faster than that with the immobilised catalyst.$^{86}$

Photocatalytic degradation of organic compounds by suspended catalysts often follows different kinetic models from that of reaction by immobilised TiO$_2$ catalysts. In a study of photocatalytic degradation of formic acid, the efficiency of immobilised and suspended systems was compared and reported by Dijkstra and others.$^{193}$ In the study, the degradation in the suspended system was described with the pseudo zeroth order model while in an immobilised catalyst system, the degradation rate followed a Langmuir-Hinshelwood kinetic model due to the mass transfer limitation. This conclusion was in accordance with experimental results for the degradation of phenol in immobilised TiO$_2$ photocatalyst reported by Matthews.$^{170}$ In an investigation of phenol photocatalytic degradation over titanium dioxide beads, Sclafani and others$^{194}$ concluded that diffusional processes were of primary importance, particularly at low reactant concentrations. Mass transfer limitation during the photocatalytic degradation depends mainly on phenol diffusion.$^{194}$

To investigate diffusion phenomena in photocatalysis, different experimental techniques have been established:

**Diaphragm cell:** The traditional diaphragm cell method is a simple experimental procedure in which diffusion takes place through a porous glass diaphragm that separates two cells. Liquid concentrations are monitored after the steady state condition has been set up in the diaphragm. Diffusion coefficients can be determined from the change of
concentrations of solutions in the two cells.\textsuperscript{195,196} The applicability of the diaphragm method depends on the careful choice of suitable pore size of the glass diaphragm.

**Hydrodynamic voltammetry:** Electrochemical methods can be useful for the determination of diffusion coefficients in various media with high sensitivity. This technique has been employed to determine diffusion coefficients of a variety of aromatic amino and phenolic compounds.\textsuperscript{197-199}

**Chronoamperometry:** The chronoamperometry method has proven useful for the measurement of diffusion coefficients of electroactive species. With a known area of electrode and solution concentration, the diffusion coefficient can be then calculated from the Cottrell equation when the reaction at a planer electrode is under diffusion control.\textsuperscript{200-203}

**Taylor dispersion technique:** In liquid systems where diffusion quantity is strongly dependent on composition, the Taylor dispersion technique has provided a good alternative to classical methods such as diaphragm cell techniques.\textsuperscript{204,205} Taylor methods are relatively fast, and relatively small concentration gradients can be used for measurement. For the determination of multi-component diffusion coefficients for organic compounds and electrolyte solutions, the Taylor dispersion technique and algebraic techniques of matrix diagonalization have been reported for binary and ternary systems.\textsuperscript{206-209}

**Optical method:** A variety of optical methods have been employed in the investigation of diffusion properties for the measurement of mutual diffusion coefficients. Optical methods are believed to be the most precise for determining diffusion coefficients in binary and ternary systems.\textsuperscript{210}
However, in a photocatalytic process by immobilised TiO$_2$ photocatalyst, the effect of mass transfer to the overall photocatalytic process is highly circumstantial to the experimental conditions and the system configuration. The diffusion coefficient of a compound measured under different experimental conditions often cannot be directly applied to characterise the mass transfer property of a photocatalytic process. Therefore, to develop a method that can obtain the effective diffusion coefficient of the reactant under given experimental conditions of the photocatalytic reaction has become necessary.

In this thesis, an *in-situ* photoelectrochemical method to determine the effective diffusion coefficient of organic compounds is developed and validated in an attempt to provide a useful tool for studying mass transfer properties involved in photoelectrocatalytic processes.

### 1.5.2. Interfacial steps

Interfacial steps for photocatalysis generally include the interaction of light with the photocatalyst, photohole/electron generation and recombination, surface adsorption and desorption, and heterogeneous electron transfer across the phase boundaries.$^{35}$

Significant effort has been put into the improvement of each related step in order to achieve the best overall efficiency for a given photocatalytic system. Fundamental surface adsorption and kinetic studies have provided important information about the photocatalytic processes to improve the overall performance.$^{190,211-213}$

**Surface adsorption in heterogeneous photocatalysis:** For a high photo efficient photocatalytic process, the interfacial electron transfer is kinetically competitive only when the relevant reactant is pre-adsorbed on the surface of the photocatalyst and the surface oxidation-reduction reaction sustained by surface charge carrier trapping must exceed the rapid recombination of photogenerated electrons and holes (in a picosecond
timescale). It has been suggested that preliminary surface adsorption is prerequisite for highly efficient detoxification. In this regard, much effort has been put into the understanding of surface adsorption properties at the TiO$_2$ photocatalyst.

In photocatalytic degradation processes the Langmuir adsorption model has been employed to describe the adsorption behaviour of organic compounds on metal oxide surfaces:

$$\theta = \frac{KC}{1 + KC}$$  \hspace{1cm} (1.4)

where the $\theta$ is the surface coverage of the reactant, $K$ the adsorption equilibrium constant and $C$ the concentration of the reactant in the solution in contact with the solid adsorbent.

The Langmuir isotherm involves the following assumptions for the equilibrium of adsorption/desorption process: (i) the surface of the adsorbent is uniform; (ii) the adsorbed molecules form a monolayer at the surface of the adsorbent; and (iii) the ability of a particle to bind to a site is independent of whether or not nearby sites are occupied.

In study of the reaction rates of photocatalytic degradations of organic pollutants present at various dilute concentrations, and assuming adsorption of one or more of the reactions is one step of the reaction mechanism, the rate equation of a degradation reaction has been described by the classical Langmuir-Hinshelwood expression:

$$r = \frac{kKC}{1 + KC}$$  \hspace{1cm} (1.5)

where $C$ is the bulk concentration of the reactant, $r$ is the reaction rate and $k$ the rate constant respectively. $K$ is the adsorption equilibrium constant. The Langmuir-
Hinshelwood kinetic model employs the surface coverage of reactants to describe the reaction rate.

In theory, if the adsorption equilibrium constant, $K$, is a true reflection of the adsorption affinity of the substrate for the TiO$_2$ surface, the $K$ value is expected to remain relatively constant under various conditions.$^1$ However, significant differences in $K$ values are reported by independent determination from adsorption isotherms and from kinetic data obtained in photocatalytic systems.$^{20,222}$ The reaction rate of photocatalytic degradation determined by using the adsorption equilibrium constant is much lower than the actual photocatalytic degradation rate at low concentrations of the reducing agent. A rapid release of photogenerated OH• radicals from the photo adsorption surface of substrates may be responsible for these differences. Various possible mechanisms based on models of OH• attack by the organic reactant have been suggested to explain the behaviour of adsorption equilibrium constants and the dependence on the photodegradation rate constant $k$.  

**Measurement of adsorption:** Establishment of thermodynamic and kinetic models to describe the behaviour of surface adsorption in heterogeneous photocatalysis is often largely reliant on accurate measurements of the quantity of adsorbate at the surface of the photocatalyst. Despite the progress that has been made, development of a method that can be employed to accurately measure the amount of organic compounds with diverse adsorption properties at the TiO$_2$ surface still remains a challenge. In this regard, many attempts have been made to directly determine the adsorbed species using various techniques, including Raman spectroscopy,$^{224}$ IR,$^{225}$ sum frequency generation spectroscopy,$^{226,227}$ UV absorption spectroscopy,$^{228}$ electrophoresis,$^{229}$ quartz crystal
microbalance\textsuperscript{230} and combined techniques such as attenuated total Reflection inferred (ATT-IR) and Resonance Raman Spectroscopy.\textsuperscript{231}

Traditionally, the determination of adsorption of organic compound at the surface of nanoparticulate TiO\(_2\) slurries is carried out by adding the TiO\(_2\) nanoparticles into the aqueous organic solution to allow pre-adsorption. TiO\(_2\) particles with large surface areas are often chosen to assure a measurable amount of adsorbates adsorbed into the TiO\(_2\) slurry from the solution. The quantity of adsorption is then usually calculated by measuring the decrease in concentration of the adsorbate in the solution after separating the slurry of TiO\(_2\) nanoparticles from the solution by filtration or centrifuge.\textsuperscript{185,187-189,216}

In practice however, this method is often associated with problems such as low precision outcomes and being time-consuming in the separation of the fine TiO\(_2\) particles from the solution. Furthermore, this approach involves many uncontrollable factors in the measurement. For example, adsorbate concentration in the bulk solution can change rapidly during adsorption, the pH of the solution can change during adsorption due to deprotonation or protonation.\textsuperscript{41} The measurement results may be affected by these changes in experimental conditions.

In a study of phthalic acid adsorption on porous TiO\(_2\) thin film electrodes, Jiang and others reported an \textit{ex-situ} photoelectrochemical method to measure the adsorption isotherm of the phthalic acid on the porous TiO\(_2\) thin film electrode.\textsuperscript{41} Analysis of the adsorption data indicated that the adsorption of phthalic acid in the concentration range of 0.20 mM followed a Langmuir model, and the equilibrium constant was determined by the \textit{ex-situ} photoelectrochemical approach.\textsuperscript{41} The measurement of phthalic acid adsorption at the immobilised TiO\(_2\) thin film was conducted in two steps. Firstly, the adsorption of phthalic acid onto the surface of an immobilised TiO\(_2\) thin film electrode
was carried out by immersing the electrode into a phthalic acid solution of a given concentration for a period of time. After pre-adsorption, the TiO$_2$ photo electrode was removed from the solution and washed by the supporting electrolyte before it was transferred into a photoelectrochemical cell in which the pre-adsorbed phthalate were degraded under UV illumination. Surface coverage was determined by the photocurrent generated from the photocatalytic degradation of the pre-adsorbed phthalate molecules at the surface of the immobilised TiO$_2$ photo electrode.

This *ex-situ* photoelectrochemical approach has demonstrated its usefulness in investigating the adsorption behaviour of the compound at the semiconductor surface in a simple, rapid and sensitive manner. It directly quantifies the surface coverage from the photocurrent generated by oxidation of the adsorbed organic compound at the surface of the TiO$_2$ thin film electrode.

However, due to the time delay in the washing step and in the transferring of the electrode from the organic solution to the photoelectrochemical cell, this *ex-situ* method is unable to provide an accurate measurement of the quantity of the pre-adsorbed organic compound over a short time scale (e.g. seconds). Furthermore, accuracy of the measurement for weak adsorbate in particular may be compromised by the washing step between the pre-adsorption and photocatalytic oxidation processes in which adsorbates at the TiO$_2$ film surface may be partially or completely removed.

To solve the aforementioned problems in the *ex-situ* method, this thesis project proposed an *in-situ* photoelectrochemical method that allowed for accurate quantification of the adsorption of organic compound on the TiO$_2$ surface over a short time scale. This method was validated by measuring the adsorption equilibrium constant of phthalic acid and
methanol as model compounds to represent strong and weak adsorbates respectively to the TiO$_2$ surface.

**Water adsorption:** Almost all of the applications discussed in Section 1.2 of this chapter are performed in aqueous media. Water is probably the most important adsorbate at the TiO$_2$ surface and the interaction of water with the TiO$_2$ surface has been subject of intensive studies of practical and fundamental interest. Due to its high concentration and highly polarised molecular structure, water interaction with the TiO$_2$ thin film photocatalyst surface has a strong influence on the catalytic activity.$^{15,232}$

Literature on the adsorption of water on solid surfaces is extremely vast,$^{233}$ and conclusions remain controversial regarding the dissociation state of TiO$_2$ under bulk water.$^{15,234,235}$ Early work on the water/TiO$_2$ surface interaction mainly involved conventional surface science methods. More recent work has been undertaken by using theoretical calculation and experimental studies.$^7$

Theoretical first-principles density functional calculations have been used to study the adsorption on a particular surface for different H$_2$O coverage levels. Several factors are important to the structure of adsorbed water overlayers at the TiO$_2$: the surface symmetry and corrugation, the spacing between surface adsorption sites, and the relative strength of water-water and water surface interactions.$^{236}$ In this regard, first principle molecular dynamics simulation have been a useful tool in understanding the structure and energetics of thin water overlayers on a particular surface of TiO$_2$ either in anatase or rutile form.$^{236-239}$

Because many applications of TiO$_2$ photocatalysis are heavily dependent on the surface properties of the TiO$_2$ material, several experimental techniques have been developed in the study of the interaction of water with the TiO$_2$ surface: Temperature-Programmed
Desorption (TPD),\textsuperscript{240,241} Scanning Tunnelling Microscopy (STM),\textsuperscript{242,243} Density Functional Theory (DFT),\textsuperscript{244} X-ray Photoelectron Spectroscopy (XPS),\textsuperscript{245,246} Fourier transform infrared spectroscopy (FTIR),\textsuperscript{245} Visible-infrared Sum Frequency Generation (SFG) spectroscopy,\textsuperscript{247,248} High-Resolution Electron Energy Loss Spectroscopy (HREELS)\textsuperscript{241,249} and solid state IH NMR.\textsuperscript{250}

A fundamental question that has been the focus of study is whether water adsorption is molecular or dissociative, as the existence of OH radicals associated with water dissociation would have dramatic influence to the chemical properties of the surface.\textsuperscript{7,238,251,252}

In general, it has been recognised that for water adsorption on TiO\textsubscript{2} surfaces, some of the water is adsorbed into the anatase surface in the form of dissociated hydroxy groups, but the majority is adsorbed molecularly.\textsuperscript{253,254} Results from molecular dynamics simulations concur with the experimental results of studying water adsorption on anatase (101) and (001) surfaces and the calculated energetics of multilayer adsorption.\textsuperscript{236,238} However, because most of the experimental information on water adsorption is based on samples that have been prepared by various techniques, and theoretical studies have used simplified models to represent particular surfaces of the material, different and even controversial experimental results have been reported in literature.\textsuperscript{238} More importantly, the experimental conditions for the available information could not be directly used for large scale applications of photocatalytic process by TiO\textsubscript{2} photocatalysts.

Photoelectrochemical methods used to study surface adsorption of TiO\textsubscript{2} photocatalyst have proven to be an effective tool in obtaining information on the adsorption process of organic compounds on the surface of immobilised TiO\textsubscript{2} films.\textsuperscript{41,42,181} Kinetic studies of the photocatalytic oxidation of adsorbed carboxylic acids at TiO\textsubscript{2} films have revealed
different kinetic behaviours of photocatalytic degradation. These differences may contribute to the adsorption of the carboxylic acid to the TiO$_2$ surface forming different types of surface complexes. Each of the surface complexes has distinctive binding affinities to the TiO$_2$ surface, and displays typical reaction kinetic characteristics in photocatalytic degradation under UV illumination. Titanium ions from the perfectly cleaved (001) and (011) crystal faces of anatase have been reported to be responsible for the formation of the two types of complexes.$^{42}$

Based on this principle, this study employs a photoelectrochemical technique to study the interaction of water with the immobilised TiO$_2$ thin film photocatalyst.

1.5.3. Photoelectrons transport

The achievement of high quantum yields for a photocatalytic oxidation process by TiO$_2$ photocatalyst depends on the rapidity of removing surface charge carriers at the interface of the photocatalyst.$^{10}$ In a study of reaction mechanisms, the charge removal and recombination processes are important factors that determine the kinetics, efficiency and reaction pathway of a photocatalytic degradation process.$^{40}$

The dynamics of charge recombination following electron injection into the conduction band of the semiconductor have been examined under potentiostatic control of the electric field within the space charge layer of the membrane. It was reported that a 1000–fold decrease in recombination rate was observed due to the potential change within range of 300 mV.$^{171}$ Conductivity of the nanostructured TiO$_2$ film has been found low without UV illumination at room temperature, and it was reported to be less than $10^{-7}$ S when measured by the four-point technique under dry nitrogen. The conductivity is strongly increased by exposure to UV light radiation, indicating that the low conductivity is due to a low electronic concentration in the conduction band rather than the poor electrical
contact between the particles. A moderate illumination on the TiO$_2$ film surface in vacuum would result in an increase in conductivity, possibly due to a lowering of the conductivity activation energy and an upward shift of the Fermi level of the semiconductor. In study of charge transport properties in nanostructured TiO$_2$ thin film electrodes, the charge transport in TiO$_2$ has been described by diffusion. The apparent diffusion coefficient for electrons has been reported to be in the range of $(3 - 8) \times 10^{-6}$ cm$^2$ s$^{-1}$ at $+300$ mV in 0.1 M KI in propylene carbonate. The charge transport was highly dependent on electrolyte composition and light intensity.

In a study of band edge movement and recombination kinetics in DSSC by Intensity Modulated Photo-Voltage Spectroscopy (IMVS), Schlichthorl and others proposed a model to reveal that the transfer of photo injected electrons from TiO$_2$ to the redox electrolyte taking place predominantly via surface states, and the electron trapping and detrapping are much faster than recombination as evidenced by the calculated average time constant between the photo-injection and recombination of electrons. It was also found that the movement of Fermi levels by surface modification increased the negativity of the open circuit voltage, reflecting the decrease of the average activation energy for electron transfer.

The efficiency of electron transport through nano-crystalline TiO$_2$ film electrodes without electron recombination may be experimentally measured by the incident photon to current conversion efficiency (IPCE). For dye-sensitised solar cells, it was reported that the decrease of IPCE at both high and low light intensity were controlled by different limiting mechanisms of the photocatalytic process: the decrease of the IPCE at large light intensity is due to the diffusion limitation of the electrolyte and at low light intensity, it
was due to recombination of TiO$_2$ conduction band electrons transferring into the electrolyte.$^{184}$

One natural direction to take in study electron transport in the TiO$_2$ thin film would be the direct measurement of the conductivity of the material. However, relatively few studies have investigated conductivity of TiO$_2$ films, and the details regarding the charge transport mechanisms in nanostructured TiO$_2$ films are not fully understood.$^{257}$

Electrochemical impedance spectroscopy has been employed to study electrical conductivity for nanostructured TiO$_2$ electrodes. This technique has proven to be excellent for characterisation of electrochemical systems in which the overall response to the applied potential bias was contributed from several simultaneous processes.$^{258,259}$

While the intrinsic conductivity should be a fundamental feature of a given TiO$_2$ semiconductor film electrode, the behaviour of charge transport in a photocatalytic oxidation reaction also depends on the presence of redox species in the solution. Jiang and others proposed a model to describe the charge transport of a TiO$_2$ film electrode in a photocatalytic oxidation reaction. The overall photocatalytic reaction was characterised by a reaction resistance of the TiO$_2$ thin films photocatalyst under an applied potential bias. The reaction resistance was found to consist of two components: (i) the variable part that depends on the reaction rate and (ii) a constant value representing the contact resistance between the TiO$_2$ particles, and the contact with the conducting substrate of the electrode.$^{40,260}$ Because the effectiveness of a photocatalytic reaction largely depends on the rapid removal of electrons across the TiO$_2$ thin films to surpass recombination, the reaction resistance measured by these photoelectrochemical approaches should reflect the characterisation of the TiO$_2$ thin film photocatalyst.
Clearly, the film thickness, the light intensity of UV illumination, and the applied potential bias on the TiO\textsubscript{2} film electrode during the photocatalytic oxidation reaction are factors that play an important role in the photocatalytic performance. The aim of the present study was to investigate the electron transport process in photocatalytic oxidation of organic compounds by TiO\textsubscript{2} thin film electrodes. A photoelectrochemical method was proposed to study the effect of the incident light intensity, applied potential bias, concentration of photogenerated holes scavenger and film thickness of the photo electrode on the photocatalytic reaction.

1.6 Scope of Thesis

This work aims to develop a suite of characterisation methods for studying nanostructured photocatalyst and catalytic systems.

Compared to the slurry/suspension TiO\textsubscript{2} catalyst, the use of immobilised TiO\textsubscript{2} thin film for photocatalysis has several advantages. Immobilisation of TiO\textsubscript{2} avoids the costly and time-consuming process of separating the TiO\textsubscript{2} fine powder from the aqueous media. The applied potential bias appears to facilitate removal of photo-generated electrons and therefore effectively reduce the recombination of photoelectrons and holes, allowing the study of the photocatalytic process by photoelectrochemical methods.

Generally, photocatalysis by immobilised TiO\textsubscript{2} photocatalysts involves three major steps, and the best performance of a given photocatalytic system relies on the effectiveness of each interactively related steps. This thesis focuses on characterisation of immobilised TiO\textsubscript{2} thin film photocatalyst in each of the individual steps by newly developed methodologies. A group of organic compounds were chosen as the model compounds. Photocatalytic degradation of these compounds was investigated in a collective and synergetic manner.
In this thesis, Chapter 1 reviews and highlights the general history and recent developments in the field of TiO$_2$ photocatalysts. This introductory chapter includes an extensive literature review necessary to understand the principles and properties of photocatalysis by TiO$_2$ photocatalysts.

Following the introduction, Chapter 2 presents the details of experimental procedures and methods that were employed in this thesis to characterise TiO$_2$ thin film photocatalysts. The TiO$_2$ colloid was prepared by hydrolysis of titanium butoxide, and immobilised into a conducting substrate to fabricate a TiO$_2$ thin film electrode. Surface properties and morphology of the TiO$_2$ photocatalyst are characterised by XRD diffraction and by SEM analysis. The experimental set-up and photoelectrochemical characterisation are also illustrated in Chapter 2.

In Chapter 3, an in-situ photoelectrochemical method to study mass transfer process is presented and validated by measuring the diffusion coefficient of a group of organic compounds. This in-situ method of determining diffusion coefficient is based on the photoelectrochemical principle for a photocatalytic process where the overall reaction is under diffusion control. The Nernst diffusion layer thickness for the experimental conditions is experimentally determined by a group of compounds whose diffusion coefficient values are known.

Chapters 4, 5 and 6 focus on the study of surface adsorption of organic compounds and water at immobilised TiO$_2$ thin film photocatalyst. Investigations of the adsorption properties of organics at the TiO$_2$ surface are presented in Chapters 4 and 5. Compared to the ex-situ measurements of adsorption where the adsorption and measurement occur in different reaction cells, the proposed in-situ method has several advantages, in particular, the adsorption time can be accurately controlled in order to obtain reliable adsorption
measurements over a short time scale (i.e. in seconds). Phthalic acid was chosen to represent a group of organic compounds that would strongly adsorb to the surface of TiO₂ thin film photocatalyst. Methanol was chosen as the model compound for weak adsorbate. The adsorption behaviours of phthalic acid and methanol investigated by the proposed in-situ method are described in Chapter 4 and Chapter 5, respectively. Analysis of the obtained data from the in-situ measurement has indicated that the adsorption process of both strong and weak adsorbates can be described by the Langmuir adsorption model.

In Chapter 6, adsorption of water at the TiO₂ thin film photocatalyst is studied using the photoelectrochemical method. The two types of water adsorption sites at the TiO₂ surface, possibly due to the multilayer of water adsorption and the heterogeneity of the TiO₂ crystalline structure, are evidenced in the components of the photocatalytic oxidation current. Kinetic information on water adsorption was also obtained by analysing the photocurrent generated from the photocatalytic oxidation of adsorbed water at the thin film TiO₂ electrode.

Electron transport processes within the thin film electrode are studied using a photoelectrochemical method and results discussed in Chapter 7. Photocurrent responses to the applied potential bias, light intensity and the concentration of the photohole scavenger were investigated. Due to surface trapping of the charge carriers in competition with recombination, the rapid removal of photoelectrons appeared to greatly reduce the recombination of photoelectrons and holes. The effect of film thickness to the charge transport was also investigated in this chapter. Reaction resistance and the intrinsic resistance of the photoanode were employed to characterise the photo efficiency of the photocatalysis of a TiO₂ thin film electrode.
Finally, Chapter 8 summarises the contents of the thesis and presents future research in this area.

1.7 References

(2) Fox, M.; Dulay, M. Chem. Rev. 1993, 93, 341.


(49) Ganesan, P.; Huang, S.; Popov, B. *ECS Trans. 2008*, 16, 1143.
(51) Jung, H.; Huang, S.; Ganesan, P.; Popov, B. J. Power Sources 2009, 194, 972


Chapter 1: General Introduction


Chapter 1: General Introduction


(224) Lana-Villarreal, L.; Perez, J.; Gomez, R. Comptes Rendus Chimie 2006, 9, 806.


(232) Henderson, M. Surface Science Reports 2002, 46, 1
(233) Thiel, P.; Madey, T. Surface Science Reports 1987, 7, 211.


Chapter 2

Experimental
Chapter 2 Experimental

2.1 Introduction

In this chapter, detailed procedures and experimental setups for the synthesis of colloidal TiO$_2$ are provided, followed by fabrication procedures for TiO$_2$ photoanodes. Physical characterisation of the immobilised TiO$_2$ photocatalyst by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) are also presented. Finally, the use of photoelectrochemical techniques, including Cyclic Voltammetry (CV), Linear Sweeping Voltammetry (LSV) and Chronoamperometry, (CA), used to investigate the photocatalytic processes is discussed.

2.2 TiO$_2$ photocatalyst preparation

A number of methods have been employed to fabricate TiO$_2$ thin films, including the sol-gel method, electron beam evaporation, sputtering, chemical vapour deposition, electron beam deposition, and flame synthesis. Among them, the sol-gel method is a simple approach providing excellent chemical homogeneity at low reaction temperatures with good optical properties. Also, it requires considerable less equipment, and is convenient for composition control and for large area coatings. Employing this method is potentially less expensive than other methods. Most importantly, the advantage of the sol-gel method over conventional coating methods is the ability to tailor the microstructure of the deposited film. For these reasons, the sol-gel method was employed in this study in the preparation of TiO$_2$ photoanodes.

2.2.1. TiO$_2$ colloid synthesis

In this study, a recognised procedure was followed to prepare aqueous TiO$_2$ colloid by the hydrolysis of titanium butoxide.
Figure 2.1 shows the schematic illustration of the experimental reaction setup for the hydrolysis reaction.

![Schematic Illustration of Reaction Setup](image)

**Figure 2.1: Schematic illustration of the reaction setup for TiO$_2$ colloid synthesis**

The hydrolysis procedure consists of the following steps: 16 mL of isopropanol and 50 mL of titanium butoxide were accurately measured into a 150 mL separating funnel, and then added to an Erlenmeyer flask that contained 600 mL of Milli-Q water. 4.0 mL of 70% nitric acid was added as a peptising agent to the mixture. The Erlenmeyer flask was then immersed in a water bath at temperature of 80°C and stirred continuously for 10 hours. 100 mL of the resultant colloid was placed into a 200 mL Pyrex glass-lined stainless steel autoclave Parr-bomb (Parr Instrument, USA). The sample was treated for 15 hours at 200°C in a convection oven (1300 W, SEM Australia). The suspended products were allowed to stand for 24 hours. The colloid was then concentrated on a rotary evaporator to a concentration of 60 g/L. 30% of polyethylene glycol Carbowax (Supelco) relative to the dry weight of TiO$_2$ was added.
to the colloidal suspension. The TiO\textsubscript{2} colloid was stirred for approximately 20 minutes before the dip-coating.

2.3 Fabrication of TiO\textsubscript{2} thin film electrode

Various materials have been reported as the supporting substrate for immobilised photocatalyst.\textsuperscript{5,14,15} For photoelectrochemical processes, the supporting substrates need to be electrically conductive, but direct electrochemical reaction at the uncovered site of the substrate should be avoided during the photocatalytic oxidation reaction. In photocatalysis application, ITO film is commonly used for transparent electrodes.\textsuperscript{16-18} In this study, ITO conducting glass was chosen as the supporting substrate for immobilised TiO\textsubscript{2} photocatalyst due to the high overpotential for water electrolysis and oxygen reduction,\textsuperscript{19} resulting in negligible currents from pure electrochemical reactions.\textsuperscript{20}

Before the TiO\textsubscript{2} colloid was immobilised onto the ITO substrate, the surface of the ITO glass slides were washed in turn with detergent, water, chromic acid washing solution, water and ethanol. The contact time of the ITO glass slides with the acidic washing solution was carefully controlled to avoid damage to the ITO layer by the chromic acid. Conductivities of the substrate were examined before and after the treatment to assure there was no measureable change caused by the treatment process.\textsuperscript{21}

The dip-coating method consists of steps of withdrawal of the substrate from the TiO\textsubscript{2} colloid, gravitational draining and solvent evaporation. This method was employed in this study to immobilise TiO\textsubscript{2} colloid onto the ITO glass substrate to prepare TiO\textsubscript{2} thin film photoanodes for the characterisation of the photocatalytic system. Film thickness was regulated by controlling the speed of the ITO substrate being vertically
withdrawn from the TiO$_2$ colloid. The thickness of the thin film is sensitive to a variety of factors including colloid composition and viscosity and the relative rates of condensation and evaporation.$^4$

2.4 Physical characterisation of TiO$_2$ photocatalyst

2.4.1. XRD

XRD is primarily used to identify the crystalline composition of the TiO$_2$ samples.$^{15,22-25}$ It has been reported that anatase is predominant in the TiO$_2$ film samples after treatment at temperatures below 600$^\circ$C, while anatase/rutile mixture phases were produced after treatment at higher temperature.$^{19}$

In this study, the TiO$_2$ thin film photoanodes used in the photocatalytic processes were prepared at 500$^\circ$C and 700$^\circ$C, respectively. XRD (Philips PW3020) was used to study the crystalline phase of the TiO$_2$ thin film electrodes calcined at various temperatures (Figure 2.2).

The anatase/rutile composition of the TiO$_2$ thin film photocatalyst was analysed by the intensity ratio of the two phases in the XRD diffraction pattern. The equation developed by Spurr and Myers was used to calculate the anatase/rutile composition of the TiO$_2$ sample prepared at different treatment temperatures.$^{26}$

$$f = \frac{1}{1 + 1.26 \frac{I_R}{I_A}} \quad (2.1)$$

where $f$ is the weight fraction of anatase present, $I_R/I_A$ is the intensity ratio of rutile reflection to the anatase reflection. Table 2.1 shows the phase compositions of the TiO$_2$ samples calcined at different temperature and duration.
Table 2.1: Effect of calcination temperature and duration on the crystalline phase composition

<table>
<thead>
<tr>
<th>Calcination Temperature</th>
<th>Duration</th>
<th>Phase Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>500°C</td>
<td>0.5 hour</td>
<td>Anatase (100%) Rutile (0%)</td>
</tr>
<tr>
<td>700°C</td>
<td>0.5 hour</td>
<td>Anatase (96.5%) Rutile (3.5%)</td>
</tr>
<tr>
<td>700°C</td>
<td>16 hours</td>
<td>Anatase (92.9%) Rutile (7.1%)</td>
</tr>
</tbody>
</table>

Figure 2.1: An X-ray diffraction pattern

XRD pattern for the TiO₂ films calcined at (a) 500°C for 0.5 h, (b) 700°C for 0.5 h and (c) 700°C for 16 h.

2.4.2. FESEM

Surface structure and morphology of the TiO₂ thin film was characterised by field emission scanning electron microscope (FESEM). It was observed that the typical size of the TiO₂ particles fell within the range of 20-50 nm under preparation conditions (Figure 2.3).
Figure 2.3: SEM images of TiO$_2$ thin film

The TiO$_2$ thin film was calcined (a) at 700°C for 16 h in air, and (b) at 500°C for 0.5 h.

2.5 Photoelectrochemical characterisation

2.5.1 Apparatus and experimental setup

The photoelectrochemical method used to study the photocatalytic process can provide useful kinetic and thermodynamic information about the TiO$_2$ thin film photocatalyst. In this study, a three-electrode electrochemical cell is employed for all
experiments. The electrochemical cell consists of the immobilised TiO₂ thin film as the working electrode, a saturated Ag/AgCl reference electrode, and a platinum mesh auxiliary electrode. The TiO₂ thin-film working electrode was mounted in a special holder with a quartz window for UV illumination. A 0.10 M NaNO₃ supporting electrolyte solution was employed to allow electrochemical measurement. The pH of the solution was adjusted by adding either NaOH or HNO₃ to the solution for desired experimental conditions.

The applied potential bias was supplied by a voltammograph (CV-27, BAS) and an AD converter (Maclab 400, AD Instruments) coupled to a computer which was used for photocurrent monitoring and data recording. The light source was a 150 W xenon lamp (HFC-150, TrustTech.) with regulated optical output and a UV-band-pass filter (UG-5, Schott) placed in front of the quartz window to prevent the testing solution from being heated. Light intensity radiating on the thin film surface was controlled by adjusting the distance of the electrochemical cell from the UV light source. The output UV light intensity was measured at 365 nm wavelength using a UV irradiance meter (UV-A, Instruments of Beijing Normal University).

The experimental system setup is schematically illustrated in Figure 2.4.

2.5.2. LSV and CV

A three-electrode photoelectrochemical system as illustrated in Figure 2.4 was used to investigate the photocatalytic processes. The electrochemical behaviour of a photocatalytic process can be obtained through the technique linear sweep voltammetry (LSV). In linear sweep voltammetry, the potential applied across the electrode-solution interface is linearly scanned from an initial value to a final value at a constant rate.²⁷,²⁸
To obtain a voltammogram, the current is measured during the potential scan in an unstirred solution. Information can be obtained in an experiment by linearly sweeping the potential over time and directly recording the current-time and potential-time curves directly.

An extension of LSV is cyclic voltammetry (CV). Cyclic voltammetry takes the LSV experiment one step further by reversing the potential scan in the opposite direction once the LSV potential sweep reaches the final value. Therefore, when the potential sweep in CV reaches a set potential, the potential applied to the working electrode is inverted. In practice, the potential scan can be continued for any number of cycles, hence the term cyclic voltammetry.\(^{28}\)

Cyclic voltammetry is one of the most effective and versatile electroanalytical techniques available for the mechanistic study of redox systems. The effectiveness of CV results from its capability to rapidly observe the redox behaviour of an electrochemical system over a wide potential range.\(^{29}\)
Typical current-time and potential-time profiles obtained during the CV under UV illumination are illustrated in Figure 2.5 in the presence of 1.0 mM and 5.0 mM glucose.

![Graph showing current vs. time and potential vs. time profiles](image)

**Figure 2.5:** The E-t and i-t in a CV experiment

In data analysis of cyclic voltammetry experiments, it is customary to record and display the current as a function of potential. Figure 2.6 shows the photocurrent response as a function of the applied potential bias in the oxidation of glucose.

It was observed that the i-E curve drawn from Figure 2.5 consists of two stages (Figure 2.6). In the first stage, the photocurrents increase linearly with the potential bias up to approximately -0.1 V. In the second stage, the photocurrents saturate. The two stages of the i-E curve correspond to different limiting steps of the photocatalytic processes:
(i) In the linear increase part of the $i-E$ curve, the limiting step is the electron transport process within the TiO$_2$ thin film.

(ii) The saturated part of the curve indicates that the overall reaction is controlled by the interfacial reaction. In studies of interfacial reaction at the TiO$_2$ thin film surface, the applied potential bias selected must be high enough to insure that the overall photocatalytic reaction is not limited by the electron transport step. Therefore, in this work, the applied potential bias in the study of adsorption and mass transfer processes for a photocatalytic system was chosen to be greater than +0.3V (vs Ag/AgCl) to maintain the required controlling step.

2.5.3. **Photocurrent from photocatalytic oxidation**

Chronoamperometry (CA), i.e., current measured as a function of time, is an important electrochemical technique in the study of electrochemical behaviour. In chronoamperometric experiments, the electrode potential is controlled at a value

![Figure 2.6: Photocurrent response to the applied potential bias](image-url)
sufficient to immediately react to any sample molecule at the photoanode surface.\textsuperscript{27,28} In the subsequent experiments in this thesis, the photoelectrochemical approach is employed to study the properties of a photocatalytic system. In photocatalysis studies, UV illumination is employed as the excitation signal to initiate and maintain the photocatalytic process instead of the applied potential as in the electrochemical process.

Figure 2.7 shows a typical photocurrent originating from the oxidation of an organic compound under given potential bias and light intensity. For a fixed potential without UV illumination, there is no significant current observed, suggesting that no typical electrochemical oxidation of water and the organics occurs under the potential. Immediately after the UV illumination, photocurrent increases sharply to form a current spike, then the current decreases with time to reach a steady state.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_7.png}
\caption{A typical photocurrent-time profile obtained under UV illumination.}
\end{figure}
Chapter 2: Experimental

The peak current is considered to be the photoelectrochemical reaction of oxidation of the adsorbed organic compound. The magnitude of the initial peak current can be used to quantify the amount of organic compounds adsorbed at the TiO$_2$ thin film surface. For photocatalytic oxidation that is under diffusion control, the amount of adsorbed organic compound can be determined from the net charge calculated from the photocurrent.

The steady photocurrent illustrated in Figure 2.7 can be employed to study the mass transfer properties of the organic compounds if the photocatalytic reaction is under diffusion control for the given experimental conditions. Under the diffusion control condition, the limiting current can be obtained by subtracting the blank photocurrent from the total photocurrent. The diffusion coefficient of the organic compound can be determined from the limiting current according to Fick’s first law.

2.6 Conclusions

This chapter has described experimental procedures of TiO$_2$ colloid synthesis and preliminary characterisation results. The XRD patterns suggest that the TiO$_2$ thin film obtained at 500°C was mainly the anatase phase, while the thin film sample calcined at 700°C consisted of anatase and rutile mixed phases. SEM images show that the particles are well crystallised with particle sizes in the range of 20-50 nm.

2.7 Reference

(22) Cullity, B. Addition-Wesley, Reading, WA 1978.
Chapter 3

Chapter 3: Study of Mass Transfer Process

3.1 Introduction

Mass transfer is one of the three aforementioned photocatalytic processes. This chapter proposes an \textit{in-situ} photoelectrochemical method to study mass transfer behaviour of the photocatalytic system.

Since the discovery of splitting water to produce hydrogen and oxygen over an illuminated TiO$_2$ semiconductor electrode by Fujishima and Honda in 1972,\textsuperscript{1} numerous efforts have been made to research on semiconductor photocatalysts. Discoveries of nanosized TiO$_2$ semiconductor photocatalysts with enhanced photocatalytic activity\textsuperscript{2} and their applications to solar energy conversion\textsuperscript{3,4} and removal of organic pollutants\textsuperscript{2,5} have set off a new upsurge of research activities in this field, leading to better understanding of photocatalysis processes.\textsuperscript{6-11} In general, a TiO$_2$ photocatalysis process consists of three consecutive major steps: (i) the mass transfer step in the solution phase involving processes of transportation of reactants to and removal of products from the catalyst surface; (ii) the interfacial step comprising multiple processes e.g. the interaction of light with the photocatalyst, photohole/electron generation and recombination, surface adsorption and desorption, and heterogeneous electron transfer; (iii) the photoelectrons/holes migration inside the semiconductor photocatalyst. In practice, the best performance of a given photocatalysis system can be achieved only when all interactively related steps are optimised in a collective and synergetic manner. Therefore, acquiring the information regarding the maximum capacity of an individual step involved is highly beneficial,
as such information can be used as a benchmark to estimate the potential improvement of a reaction system and identify the limiting step that allows the optimisation to be carried out with a precise focus. In this regard, although the mass transfer step is one of the key steps involved in the photocatalysis, the majority of published literature to date has been focused on the interfacial and photoelectrons/holes migration steps\textsuperscript{12-18} while little attention has been paid to the aspect of solution mass transfer.

In a slurry/suspension TiO\textsubscript{2} photocatalysis system, the effective diffusion coefficient is useful for reactor design, though the mass transfer step is less likely to be the control step of the overall process due to the freedom of movement of both catalysts and reactants under the convection conditions. The immobilised TiO\textsubscript{2} photocatalysis systems have been widely employed for solar energy conversion applications, such as dye-sensitized solar cells, hydrogen production using sacrificing agent and photoelectrocatalytic degradation of organic pollutants\textsuperscript{19-23} With such systems, the mass transfer step becomes important because the immobilised photocatalyst loses its freedom of movement and the reaction that could take place is solely relied on the transport of the reactant to the catalyst surface\textsuperscript{24} Under these circumstances, the quantitative insight knowledge of mass transfer process benefits not only the system optimisation but also mechanistic studies. For example, the adsorption is one of the important interfacial processes that directly relates to the mass transfer conditions. An actual understanding of the adsorption kinetics (e.g. rate of adsorption) and thermodynamics (e.g. adsorptivity and adsorption constant) would require precise knowledge of mass transfer conditions\textsuperscript{25-27} Therefore, developing a simple and effective method that serves these needs is of interest to the researchers in the field. It will also be beneficial to researchers in other fields involving mass transfer process.
According to Fick’s law, the maximum flux of the mass transport under diffusion-controlled conditions can be obtained if the diffusion coefficient is known.\textsuperscript{28} In this regard, physical chemistry handbooks or other sources can provide diffusion coefficients of some, but limited, inorganic and organic substances. As a result, for photocatalysis applications, especially for a system involving organic reactants, difficulties for finding diffusion coefficients arise when the required diffusion coefficients are either unavailable from the literature, or they cannot be directly applied to a particular system of interest, because of differences in the measurement conditions where they were determined and applied to. Under such circumstances, the experimental determination of the diffusion coefficient becomes unavoidable. In practice, however, the experimental determination of the diffusion coefficient is a formidably difficult task.\textsuperscript{28-30} Many experimental techniques have been developed for determining the diffusion coefficient, including the traditional diaphragm cell method,\textsuperscript{29,31} the chronoamperometry technique,\textsuperscript{32} hydrodynamic voltammetry method,\textsuperscript{33-35} more recently developed optical light scattering method,\textsuperscript{36} and thin-layer microdevice electrochemical method.\textsuperscript{37} Nevertheless, the diffusion coefficients obtained by these methods can barely be applied directly for the purpose of evaluating photocatalysis systems, because the value of a diffusion coefficient is highly circumstantial to the reaction matrix (compositions) and system configuration.

Herein, we propose a simple, rapid yet effective photoelectrochemical method for \textit{in situ} determination of effective diffusion coefficients of organic compounds that could be directly applied to a photoelectrocatalysis system.
3.2 Experimental

3.2.1. Materials.

Indium Tin Oxide (ITO) conducting glasses (8-10 Ω/square, Delta Technologies Limited) were used as substrates for fabrication of TiO$_2$ thin-film electrodes. Titanium butoxide (Aldrich), oxalic acid (Ajax), malonic acid (Sigma), succinic acid (Sigma), D-glucose (BDH), glutaric acid (Aldrich), benzoic acid (Aldrich), phthalic acid (Chem. Supply), catechol (Sigma) and glycerol (Sigma) were of analytical grade and used as supplied without further purification. All inorganic reagents used were of analytical grade unless otherwise stated. All solutions were prepared with high purity water (Millipore Corp., 18MΩcm). The pH of solutions was adjusted by adding diluted nitric acid or sodium hydroxide.

3.2.2. Preparation of TiO$_2$ thin-film electrodes.

The TiO$_2$ colloidal solution was prepared by hydrolysis of titanium butoxide according to a published procedure.$^{14,38}$ Fabrication of electrode follows the procedures as per Chapter 2. After the coating, the electrode was placed on a leveled platform in an oven and dried in air at 115°C for 30 minutes. The air-dried electrode was then calcined in a muffle furnace at 500°C for 30 minutes in air. The resultant TiO$_2$ film consists of 100% of anatase, as confirmed by the XRD analysis. The thickness of the resultant TiO$_2$ film was ca.0.7µm measured with a surface profilometer (Alpha-step 200, Tencor Instrument).

3.2.3. Apparatus.

The system set up for measuring photocurrent is schematically illustrated in Figure 2.4 in Chapter 2. All experiments were carried out at 25°C in a three-electrode photoelectrochemical cell with a TiO$_2$ thin-film working electrode, a saturated
Ag/AgCl reference electrode and a platinum mesh auxiliary electrode. The TiO$_2$ thin-film working electrode was mounted in a special holder with an area of 0.78 cm$^2$ exposed to a quartz window for UV illumination. A 0.10 M NaNO$_3$ supporting electrolyte solution with pH = 4.0 was employed to allow electrochemical measurement. A voltammograph (CV-27, BAS) was used to apply the potential bias. An AD converter (Maclab 400, AD Instruments) coupled to a Macintosh computer was used for data recording. The light source was a 150W xenon lamp (HFC-150, TrustTech.) with regulated optical output and an UV-band pass filter (UG-5, Schott) placed in front of the quartz window to prevent the testing solution from being heated. The output UV light intensity was measured at 365nm wavelength using an UV irradiance meter (UV – A, Instruments of Beijing Normal University).

### 3.3 Results and Discussion

#### 3.3.1. Measurement principle.

For an electrochemical reaction under steady-state mass transfer conditions, assuming that the migrational and convectional mass transfer components can be reduced to negligible levels, and the concentration gradient within the diffusion layer is linear, then the flux ($J(x)$) can be given by the semi-empirical equation:\textsuperscript{28}

$$J(x) = -\frac{i}{nFA} = -\frac{D}{\delta}(C_b - C_0(x = 0)) \tag{3.1}$$

where $i$ is the faradic current; $A$ and $n$ refer to the electrode area and the number of transferred electrons, respectively; $F$ is Faraday constant; $D$ is the diffusion coefficient; $\delta$ is the thickness of Nernst diffusion layer; $C_b$ and $C_0$ represent the bulk and the surface concentration, respectively.
The limiting current, $i_l$, can be obtained under the diffusion controlled conditions, where $C_0(x = 0) << C_b$, therefore, $C_b - C_0(x = 0) \approx C_b$:

$$i_l = \frac{D}{\delta} nFAC_b \quad (3.2)$$

For photoelectrocatalysis, $i_l$ represents limiting photocurrent originated from the photocatalytic oxidation of organics under the diffusion controlled steady-state mass transfer conditions. Equation 3.2 quantifies the relationship between the measured limiting photocurrent, $i_l$, and diffusion coefficient, $D$.

A set of necessary conditions must be met for Equation 3.2 to be employed for determination of diffusion coefficient. For a given system, the electrode area, $A$, is known. The bulk concentration, $C_b$, needs to be a constant during the measurement process, which can be achieved by large volume of solution with relatively small electrode area (i.e. a large volume to electrode area ratio).

The number of electron transferred, $n$, needs to be a constant and a known value. In general, the stoichiometric mineralization of a given organic compound can be given as:

$$C_xH_yO_zX_k + (x + \frac{y - 2z - k}{4})O_2 \rightarrow xCO_2 + kH^+ + kX^- + \frac{y - k}{2}H_2O \quad (3.3)$$

Under complete mineralization conditions, the number of transferred electrons can be calculated as:

$$n = 4x + y - 2z - k \quad (3.4)$$
where, $x$, $y$, $z$, and $k$ represent number of carbon, hydrogen, oxygen, and halogen atoms, respectively. Equation 3.4 can be used to calculate the $n$ value of a given compound if the complete mineralization is achieved, which requires further experimental proof.

In order to determine $D$ value using Equation 3.2, the Nernst diffusion layer thickness, $\delta$, must be a known value. For majority electrochemical reactions under diffusion controlled conditions, the $i_i$ is determined by the number of molecules transported to the reaction zone per unit time and the $\delta$ value is dependent of molar mass and molar concentration of the compound. For a given $i_i$ and bulk molar concentration, the $\delta$ value is normally increased as the molecular mass is increased, since a larger molecule tends to move at a lower velocity than a smaller molecule, causing a greater concentration depletion. For these reasons, the experimental determination of $\delta$ value is generally reputed to be extremely difficult, which has led to the use of a proportional constant, the mass transfer coefficient ($m = D/\delta$) to treat the mass transfer process instead.\textsuperscript{28}

In the case of a photocatalysis oxidation reaction, the circumstances regarding the experimental determination of $\delta$ values can be greatly simplified when stoichiometric mineralization is achieved. Under such conditions, the obtained limiting photocurrent ($i_l$) represents maximum rate of reaction in terms of the number of electrons per unit of time captured from the reactant (or the number of photoholes per unit of time demanded by the reactant). Such a reaction process is essentially a process of the electron demand (by the photogenerated holes) to be met by moving reactant to the electrode surface. To attain a given $i_l$ during the photoelectrocatalytic mineralization, the required molar concentrations are generally very different for different organic
compounds, because the number of electrons to be captured from different organic compounds vary significantly according to their molar mass (see Equation 3.4). Nevertheless, if we normalize the reactant concentration with respect to the equivalent number of electrons by defining a new concentration scale, \( N_e = n \times C \) (the electron normality concentration), then Equation 3.2 can be rewritten as:

\[
i_l = \frac{D}{\delta} \cdot FAN_e \tag{3.5}
\]

Equation 3.5 states that during the photocatalytic mineralization reaction, the limiting current, \( i_l \), is directly proportional to the electron normality concentration \( (N_e) \), regardless of the identity of the organic compounds. This new concentration unit effectively normalises the molar concentrations of different reactants into the same measurement scale in term of photohole demand (the photoholes required for the mineralisation of a molecule). Hence, the photohole demand for different reactants with the same \( N_e \) is the same. This means that the total photohole demand \( (N_e = n \times C) \) rather than the molar concentration \( (C_b) \) is the decisive factor. Consequently, the concentration depletion or the thickness of the Nernst diffusion layer \( (\delta) \) is also determined by the total photohole demand, which leads to a possibility that the Nernst diffusion layer \( (\delta) \) is a close value for different organic compounds under these conditions. If this is proven to be true, then the \( \delta \) value can be experimentally measured according to Equation 3.5 with selected organic compounds whose diffusion coefficients are known. The measured \( \delta \) value can subsequently be used to determine the diffusion coefficient of other compounds.
3.3.2. Optimisation of experimental conditions.

Equation 3.5 is valid for determination of diffusion coefficient only when the overall reaction is under diffusion controlled conditions. Therefore, the key parameters were firstly optimised to ensure such conditions.

Figure 3.1(a) shows a set of typical voltammograms obtained from the blank solution of 0.1M NaNO₃ and solutions containing different concentration of benzoic acid, under illumination with a constant light intensity of 6.0mW/cm². All other organic compounds investigated exhibit similar characteristics of voltammogram as those shown in the figure. It was found that the photocurrent initially increased linearly with applied potential bias and then saturated at higher applied potentials. The linear response range corresponded to the process where the overall photocatalysis reaction was limited by the freed photoelectrons transport inside the TiO₂ film, while the photocurrent saturation indicated the overall photocatalysis reaction was controlled by the photohole capture process at TiO₂ surface.³,¹⁴,⁴⁰ Figure 3.1(b) shows the plot of the saturation photocurrent ($i_{sph}$) against the concentration under a constant light intensity. It was found that the saturation photocurrent initially increased linearly with the concentration, because the rate of the photohole capture process was limited by the mass transfer in the low concentration range. However, as concentration increased to a point where the mass transfer was no longer the limiting step, the photohole generation (light intensity dependent) became the limiting step of the photohole capture process, leading to the photocurrent saturation at high concentrations.¹⁴,⁴⁰ These observations suggest that at a given light intensity of 6.0 mW/cm², the system can attain its diffusion controlled conditions if the applied potential bias is more positive than +0.30V (vs Ag/AgCl) and the concentration of the substrate is below 0.8mM for benzoic acid. This concentration is equivalent to a total
Figure 3.1 Voltammograms and saturation photocurrent

(a): Voltammograms obtained from solutions containing 0.1 M NaNO₃ and different concentrations of benzoic acid. The concentrations of benzoic acid for the curves from the bottom to the top in turn were: 0, 0.10, 0.20, 0.30, 0.40, 0.50 and 0.60 mM. Scan rate: 5.0mV/s; light intensity of 6.0mW/cm². (b): A plot of saturation photocurrent against the concentration. Data derived from (a).
photohole demand of 2.4mNe \((Ne = n \times C = 30e^r \times 0.08mM = 2.4mNe)\). These conditions were employed for the subsequent experiments.

The effect of the solution pH on the measured signal was investigated. The photocurrent observed was independent of pH within the range of 2.0 to 10.0, which was in agreement with our previous observation.\(^{30,41}\) Since the diffusion coefficient of a given organic compound is dependent on its chemical forms resulting from the association/dissociation in which the solution pH is a decisive factor, all solutions used for this study were therefore adjusted to pH 4.0.

The effect of dissolved oxygen concentration on the photocurrent response was also investigated. No significant change in photocurrent response was observed when the concentration of dissolved oxygen was changed from 0ppm (purging with pure N\(_2\)) to 25ppm (purging with pure O\(_2\)), which was in agreement with our previous observations.\(^{39,42}\) In addition, the data obtained from the temperature effect experiments indicated no significant change in photocurrent response when the temperature was altered from 10\(^{\circ}\)C to 35\(^{\circ}\)C. Nevertheless, all experiments were performed under a constant temperature of 25\(^{\circ}\)C.

### 3.3.3. Experimental validation.

The measurement and quantification of the limiting photocurrent are illustrated in Figure 3.2 with a set of typical photocurrent profiles obtained under a constant light intensity of 6.0 mW/cm\(^2\) and an applied potential bias of +0.30V (vs Ag/AgCl). A steady-state photocurrent was attained for all cases after a transient period. For the blank solution, the steady-state photocurrent \((i_b)\) originated from the photocatalytic oxidation of water can be treated as a constant for a given system.\(^{30,42,43}\) For the sample solution containing organics, the overall steady-state photocurrent \((i_{total})\)
Figure 3.2: Photocurrent-time profiles

(a) Determination of net limiting photocurrent current: The net limiting photocurrent ($i_l$) can be obtained by deducting the blank photocurrent ($i_b$) from the total photocurrent ($i_{total}$). (b) A set of typical photocurrent-time profiles obtained from solutions containing 0.1 M NaNO$_3$ and different concentrations of benzoic acid. The concentrations of benzoic acid for the profiles from the bottom to the top in turn were: 0, 0.01, 0.02, 0.03, 0.04, 0.05 and 0.06 mM.
consisted of two components, due to the photocatalytic oxidation of water \((i_b)\), which is essentially the same as the blank photocurrent and the photocatalytic oxidation of organic compound \((i_l)\), respectively.\(^{42}\) Considering the measurements were carried out under the diffusion controlled conditions, the net limiting photocurrent \((i_l)\) originated from the oxidation of organics, as defined by Equation 3.5, can be obtained by subtracting the blank photocurrent from the total photocurrent:

\[
i_l = i_{total} - i_b
\]  

(3.6)

To validate that the photoelectrochemical mineralization of organic compounds was under diffusion control for the given experimental set-up, photocurrents from oxidation of 1.2 mN\(_e\) glucose were measured under light intensity ranging from 1 to 10 mW/cm\(^2\). Figure 3.3 shows the measured overall photocurrent, \(i_{total}\), and the blank photocurrent \(i_b\). The limiting photocurrent, \(i_l\), then was obtained by using Equation 3.6.

Light intensity of 6.0mW/cm\(^2\) was therefore selected for subsequent experiments in measuring photocurrent based on our experimental data showed in Figure 3.3. With the system set up and experimental conditions employed, the net photocurrent became light intensity independent when the light intensity was greater than 4.0 mW/cm\(^2\) though the overall photocurrent continued to increase as the light intensity increased. The obtained net photocurrent independent of light intensity at higher intensity range was because the transport of organics to the photoanode became the rate limiting step.

This indicates that the light intensity employed was sufficient to ensure the photohole generation was not the limiting step of the overall photocatalysis processes.
The overall photocurrent increased with the increased light intensity can be attributed to the increased water oxidation because of the overwhelmingly high water concentration. In fact, it is extremely unlikely (if it is not impossible) the transport of water to the photoanode surface would become the rate limiting step of a photocatalysis process in an aqueous solution under the experimental conditions employed. For the reason of water oxidation at the TiO$_2$ electrode surface, an increase in the light intensity will lead to an increase in the overall photocurrent. As aforementioned, the proposed method is valid only when the complete mineralization of substrate is achieved. The complete photoelectrochemical mineralisation of a wide spectrum of organic compounds under exhaustive degradation model has been previously demonstrated.\cite{39,42,44} Under such conditions, the degree of the mineralization can be evaluated based on the measured charge against the theoretical charge calculated by Faraday’s law.\cite{42,44} However, under non-
exhaustive degradation conditions, a direct experimental proof of complete mineralization using the same method is difficult. Nevertheless, other types of evidences can be obtained experimentally to support the argument. Figure 3.4 shows the $i_l$ vs $C_b$ curves of different organic compounds under diffusion controlled conditions. A linear relationship between the limiting photocurrent and molar concentration was observed for all cases investigated. This suggests that both $n$ and $D/\delta$ in Equation 3.2 are constant. More importantly, that the slopes of the curves were found to be directly proportional to $n$, indicating the complete mineralization had been achieved.

![Figure 3.4: The net limiting photocurrent](image)

*Figure 3.4: The net limiting photocurrent*

*The relationship between the net limiting photocurrent and the concentration for benzoic acid, glucose, succinic acid and oxalic acid.*

In order to utilize Equation 3.5 for determination of diffusion coefficient, the thickness of the Nernst diffusion layer ($\delta$) must be known. As discussed in the previous section, experimental determination of the $\delta$ value is possible due to the
unique mass transfer conditions required by a photocatalytic mineralisation process. That is, the extent of the photohole demand by the organic compound determines mass transport property of the mineralisation process at the electrode surface, regardless the chemical identities of the organic compound. According to Equation 3.5, employing the normalized concentration, $N_e$, could lead to an assumption that the diffusion layer thickness $\delta$ is a close value for different organic compounds. For the purpose of experimentally determining $\delta$ value, four representative organic compounds with known $D$ values (see Table 3.1) were selected, among which glucose is a weak adsorbate and three organic acids (oxalic, succinic and benzoic acid) are strong adsorbates. Benzoic acid represents the aromatic compounds with the photohole demand, $n = 30$, for complete mineralisation. The required electron transfer numbers (photohole demand) of the selected organic compounds for complete mineralisation vary from 2 for oxalic acid to 30 for benzoic acid per molecule.

Under the assumption that during a photocatalytic oxidation process, a constant Nernst diffusion layer thickness $\delta$ possesses similar value for different organic compounds, a plot of $i_i$ vs $FADN_e$ for different organic compounds, according to Equation 3.5, should show a single linear relationship for all compounds, by using values of diffusion coefficient $D$ from the literature.\(^{45,46}\) Figure 3.5 confirms such a relationship with a best-fit linear equation of $y = 22.424x + 0.1069$ ($R^2 = 0.9865$), which in turn attests to the assumption of complete mineralization for different compounds under the experimental conditions. The mean (collective) diffusion layer thickness, $\delta = (4.46 \pm 0.06) \times 10^{-2}$ cm, can be obtained from the reciprocal of the slope in Figure 3.5. Table 3.1 gives the slopes of each compound and the corresponding $\delta$ values. It was found that the $\delta$ values of individual compounds ranged from $3.68 \times 10^{-2}$ to $4.55 \times 10^{-2}$ cm, indicating the small variation of the $\delta$ value for the organic
compounds tested in this experiment. The collective $\delta$ value of $4.46 \times 10^{-2}$ cm was used for the subsequent experiments to determine diffusion coefficients of other organic compounds.

![Figure 3.5: Limiting photocurrent and AFDNe](image)

**Table 3.1:** $\delta$ values of individual organic compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$n$</th>
<th>$D$ ($10^{-5}$ cm$^2$s$^{-1}$)</th>
<th>Regression Equation</th>
<th>$\delta$ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic Acid</td>
<td>2</td>
<td>$0.987^{45}$</td>
<td>$y = 27.148x - 0.4356$</td>
<td>0.037</td>
</tr>
<tr>
<td>Succinic Acid</td>
<td>14</td>
<td>$0.783^{45}$</td>
<td>$y = 23.533x - 0.1778$</td>
<td>0.042</td>
</tr>
<tr>
<td>Benzoic Acid</td>
<td>30</td>
<td>$0.863^{45}$</td>
<td>$y = 21.969x - 0.0381$</td>
<td>0.046</td>
</tr>
<tr>
<td>Glucose</td>
<td>24</td>
<td>$0.67^{46}$</td>
<td>$y = 23.133x - 0.100$</td>
<td>0.043</td>
</tr>
</tbody>
</table>

3.3.4. Determination of diffusion coefficient.

Glutaric acid, phthalic acid, malonic acid, catechol and glycerol were selected as the test compounds. All solutions were adjusted to pH = 4.0. Under such a pH, 37% of
glutaric acid, 7.9% of phthalic acid, 6.2% of malonic acid, 100% of catechol and 100% of glycerol exist in their molecular forms in the solution (see Table 3.2). Figure 3.6(a) and Figure 3.6(b) show the plot of \( i_l \) against \( \frac{AFN}{\delta} \), with diffusion layer thickness \( \delta = 4.46 \times 10^{-2} \) cm for organic compounds that represent strong and weak adsorbates, respectively. Table 3.2 summarized the determined diffusion coefficients of all test compounds calculated from the slope of the corresponding curve shown in Figure 3.6.

The determined diffusion coefficients for malonic acid, glutaric acid and phthalic acid were found to be \( 7.26 \times 10^{-6} \) cm\(^2\) s\(^{-1} \), \( 7.40 \times 10^{-6} \) cm\(^2\) s\(^{-1} \) and \( 8.11 \times 10^{-6} \) cm\(^2\) s\(^{-1} \), respectively. The measured \( D \) values for glutaric acid and phthalic acid were 5.7% and 16.5% higher than the literature values, respectively.\(^45\) However, for malonic acid, the measured diffusion coefficient was 14.1% lower than the literature value (see Table 3.2).

**Table 3.2: Diffusion coefficients of individual organic compound**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecule Form (%)</th>
<th>( D ) (10(^{-5}) cm(^2) s(^{-1} )) (Measured)</th>
<th>( D ) (10(^{-5}) cm(^2) s(^{-1} )) (Literature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malonic Acid</td>
<td>8</td>
<td>6.2</td>
<td>0.726</td>
</tr>
<tr>
<td>Glycerol</td>
<td>14</td>
<td>100</td>
<td>0.718</td>
</tr>
<tr>
<td>Glutaric Acid</td>
<td>20</td>
<td>37</td>
<td>0.74</td>
</tr>
<tr>
<td>Phthalic Acid</td>
<td>30</td>
<td>7.9</td>
<td>0.811</td>
</tr>
<tr>
<td>Catechol</td>
<td>26</td>
<td>100</td>
<td>0.909</td>
</tr>
</tbody>
</table>
Figure 3.6: Determination of diffusion coefficients for strong and weak adsorbates

(a): The plots of $i_i$ vs AFNe/$\delta$ for determination of diffusion coefficient values of organic compounds that represent strong adsorbates. (b): The plots of $i_i$ vs AFNe/$\delta$ for determination of diffusion coefficient values of different organic compounds that represent weak adsorbates.
These differences can be attributed to the differences in measurement conditions, as the reported $D$ values in the literature were determined using an indefinitely diluted aqueous solution at 25°C without specified pH condition, while in this study, the measurements were conducted in an aqueous solution containing organic compounds and the supporting electrolyte at 25°C with a specific pH of 4.0. The diffusion coefficients determined for catechol was $9.09 \times 10^{-6}$ cm$^2$s$^{-1}$. This is significantly higher than that of literature value of $6.61 \times 10^{-6}$ cm$^2$s$^{-1}$, measured by a hydrodynamic voltammetry method with a tubular graphite electrode in 0.10M H$_2$SO$_4$ medium. For glycerol, the determined diffusion coefficient was $7.18 \times 10^{-6}$ cm$^2$s$^{-1}$, which is again significantly lower than that of reported value of $8.684 \times 10^{-6}$ cm$^2$s$^{-1}$, measured by a Taylor dispersion method in water with 0.28 M of glycerol at 20°C. However, it is noteworthy that the conditions used to obtain diffusion coefficients by the methods reported in the literature are unlikely attainable in most photocatalysis applications, while the conditions used to determine diffusion coefficients by this newly proposed in situ method are close to that of photoelectrocatalysis applications. In fact, the proposed method can be directly employed to in situ determine the effective diffusion coefficient in many photoelectrocatalysis systems without the need to alter the solution composition.

Since liquids are densely packed with molecules and interactions between neighbouring molecules are strong by the force in the fields, liquid state theories for calculating diffusion coefficients are quite idealised and none is able to provide satisfactory results from the liquid model. Stokes-Einstein equation is based on the hydrodynamic theory in analysing model of large spherical molecules diffusing in a dilute solution:
\[ D = \frac{kT}{6\pi \eta a} \]  

(3.7)

Where \( \eta \) is the solution viscosity and \( a \) is the effective hydrodynamic radius of the spherical particles, \( k \) is Boltzmann’s constant.\(^{29,48}\) Although calculation of diffusion coefficient using the Stokes-Einstein equation are accurate to only approximately twenty percent, this equation is most commonly used in estimating diffusion coefficients in liquids.\(^{49,50}\) The diffusion coefficient variation with temperature suggested by the equation (3.7) is apparently a linear relationship assuming viscosity of the solution remains constant for the temperature range under test.

In this proposed \textit{in-situ} photoelectrochemical method, diffusion coefficient of the organic solute is determined by the Fick’s law using the limiting photocurrent from the photocatalytic reaction. Experimental parameters such as light intensity, solution concentration, and temperature for the given system configuration must be optimised for the condition that the photocatalytic reaction must be under diffusion control. Because the photocatalytic reaction at the TiO\(_2\) surface is composed of three major steps, the measurement condition of this \textit{in-situ} photoelectrochemical method in determining diffusion coefficient is highly subject to the given experimental condition. The insignificant change of net photocurrent to varying temperature in the test may be due to the competitive photocatalytic oxidation process between oxidation of the organic compound and water, and concentration of the later is overwhelmingly high in the solution.

In this \textit{in-situ} photoelectrochemical method, the temperature has been chosen at 25°C, because of (a) most photocatalytic reactions in study of photocatalytic process in mineralisation of organic pollutants present in water are carried out at room temperature,\(^{43,51,52}\) (b) available diffusion coefficients in literature used to calculate
the thickness of the Nernst diffusion layer (Equation 3.5) are mostly measured at temperature of 25°C.\textsuperscript{45}

### 3.4 Conclusions

A photoelectrochemical method for determination of effective diffusion coefficients of organic compounds has been proposed and experimentally validated. The study has successfully demonstrated that diffusion coefficients of various organic compounds can be \textit{in-situ} determined in a simple and rapid manner. It is envisaged that this new method can be a useful tool for studying the mass transport process involved in the photoelectrocatalysis process. Theoretically, the proposed method can be extended to determine any oxidisable species including the inorganic compounds such as I\textsuperscript{-}, which is widely used as an electron mediator in dye-sensitized solar cell.

### 3.5 Reference


Chapter 4

Study of Strong Adsorbate: *in-situ* Photoelectrochemical Measurement of Phthalic Acid on Titania
Chapter 4 Study of Strong Adsorbate: *in-situ*

Photoelectrochemical Measurement of Phthalic Acid on Titania

4.1 Introduction

In Chapter 3, the photoelectrochemical method has been demonstrated to be simple and effective to study the mass transfer processes in the heterogeneous photocatalytic systems.

The interfacial step for a photocatalytic process includes physical and chemical activities at the phase boundary of the solid-liquid interface. The adsorption process of organic compounds at the TiO$_2$–liquid interface plays an important role on photocatalytic oxidation reaction.$^{1-8}$ This chapter and Chapter 5 focused on the study of adsorption behaviour of organic compound at the TiO$_2$ surface.

In order to improve the efficiency of photocatalytic oxidation processes, adsorption kinetics and thermodynamics at the interface should be investigated quantitatively. The measurement of adsorption amount at the TiO$_2$ surface is inevitably involved in the investigation of adsorption process. Traditionally, the amount of adsorbed species on the TiO$_2$ nanoparticles in suspension can be determined directly via an *ex-situ* method described by the following steps:$^{8-10}$ 1) sufficient amount of TiO$_2$ nanoparticle slurries is added in adsorbate solution in order to ensure a measurable amount to be adsorbed from the solution to the surface of TiO$_2$ catalyst; 2) TiO$_2$ slurry is separated from the solution using filtration or centrifuge instrument; 3) post-adsorption washing with water to remove residue solution on the particles; 4) dissolve the adsorbates with organic solvent; 5) determination of the adsorbate amount using chemical analysis.
tools, such as UV-vis spectrophotometer or HPLC. The results from the ex-situ method are often insensitive, have low precision and the process is time-consuming. More importantly, the ex-situ method is unable to provide reliable measurements in short time scales (e.g., seconds). This is mainly because adsorption time cannot be quantified accurately due to the fact that adsorption reaction continues during the separation of TiO$_2$ nanoparticles from the reaction solution.

Owing to the aforementioned problems, many attempts have been trialled to directly probe and determine the adsorbate amount using various ways, such as sum frequency generation spectroscopy$^{11,12}$, photoelectrochemical techniques,$^8$ IR,$^{13}$ Raman spectroscopy,$^{14}$ UV absorption spectroscopy,$^{15}$ electrophoresis,$^{16}$ quartz crystal microbalance (QCM),$^{17}$ and even combined techniques, such as, incorporation of photoelectrochemical and spectroscopic techniques, i.e., Attenuated Total Reflection Inferred (ATT-IR), and Resonance Raman Spectroscopy.$^{18}$ These attempts have provided significant insights into the adsorption process a function of time (i.e., QCM method). However, difficulties remain for in-situ determination of the quantity adsorbed of small molecules in aqueous solution on very short time scales.

Jiang et al. has reported the development of an ex-situ photoelectrochemical method to measure the amount of phthalic acid (PA) adsorption on TiO$_2$ electrode surface.$^8$ In the ex-situ method, TiO$_2$ nanosized catalyst was immobilised into ITO conducting glass to act as an electrode. The adsorption of PA onto the TiO$_2$ surface was carried out by immersing the TiO$_2$ electrode into a PA solution for a given period of time, then the electrode was washed by the supporting electrolyte and transferred to a photoelectrochemical reactor where the adsorption amount of PA was measured.
In this chapter, the author proposes and develops an *in-situ* photoelectrochemical method where both the adsorption process and the photoelectrochemical measurement are conducted in the same solution of the target organic compound in the same reactor. This arrangement of experiment has overcome the aforementioned short-time scale problems associated with the quantification of the adsorbate amount on the TiO₂ surface by eliminating the washing step. The adsorption process of PA on the TiO₂ was investigated to demonstrate the applicability of the proposed *in-situ* approach. PA is an aromatic compound with two carboxyl groups (\( \text{H}_2\text{C}_8\text{H}_4\text{O}_4, pK_{a1} = 2.95, pK_{a2} = 5.41 \))\(^1\) which are known to strongly adsorb to the surface of TiO₂.\(^2\) The speciation of PA at different pH was discussed in our previous work.\(^3\) At pH 4, the dominant form of PA is HC₈H₄O₄⁻ that can be most favourably adsorbed to TiO₂ surface.\(^4\) The proposed *in-situ* method is expected to be a simple and accurate alternative for determination of the adsorption amount for small molecules in a very short time scale.

### 4.2 Experimental

#### 4.2.1. Materials.

Indium Tin Oxide (ITO) conducting glass sheets (8-10Ω/square, Delta Technologies Limited) were used as substrates for TiO₂ film coating. All chemicals were of analytical grade and purchased from Sigma-Aldrich unless otherwise stated. All solutions were prepared using high purity deionised water (Millipore Corp., 18MΩcm). PA solution was prepared by dissolving potassium hydrogen phthalate (KHP) into 0.1M NaNO₃ solution and adjusting the solution pH to 4.0 with HNO₃.

#### 4.2.2. Preparation of the nanoporous TiO₂ film electrode.

Aqueous TiO₂ colloid was prepared by hydrolysis of titanium butoxide according to the method described by Nazeeruddin *et al.*\(^2\) The TiO₂ nanoparticles were
immobilised on the ITO surface using dip coating technique. The coated electrodes were dried in air, and then calcined in a muffle furnace at 700 °C temperature for 16 h in air. The thickness of TiO₂ porous films was ca. 500 nm as measured with a surface profilometer (Alpha-step 200, Tencor Instrument). The details of fabrication procedures and characterization information were described in previous works.²³,²⁴

All photoelectrochemical experiments were carried out in a three-electrode electrochemical cell with a quartz window for illumination.²⁴ The immobilised TiO₂ electrode was used as the working electrode with Ag/AgCl as a reference electrode and a Pt net as a counter electrode respectively. A 0.1 M NaNO₃ solution with a pH of 4.0 was chosen as the supporting electrolyte throughout all the experiments. The working electrode surface area exposed to the solution and UV light which was constrained to a circle with a diameter of 10 mm. Illumination was achieved with a 150W xenon arc lamp light source (Trusttech, Beijing, China). To minimise the heating of the TiO₂ electrode from the infrared fraction of the xenon light, the xenon light beam was passed through an UV-band pass filter (UG-5, Schott) prior to illuminating on the electrode surface. Light intensity at the electrode surface was 6.6mW/cm² unless otherwise stated. An optical shutter with an aperture of 20mm (Copal Co, Japan) was used as optical switch to reproducibly control the ON and OFF of the UV illumination.

4.3 Results and Discussion

The TiO₂ thin-film electrode used in this study was a mixed-phase electrode, containing 96.8% of anatase and 3.2% of rutile. The structural characteristics of the electrode were reported in details in our recent work.²⁴ Under sufficient UV illumination, different organic compounds in a low concentration range, despite their
difference in chemical entities, can be stoichiometrically mineralised at the mixed-phase TiO$_2$ electrode under diffusion-controlled conditions due to the synergetic effect of the rutile and anatase phase.$^{24}$ The general equation for mineralisation can be summarised as follows:

\[
C_yH_mO_jN_kX_q + (2y - j)H_2O \rightarrow \\
yCO_2 + qX^- + kNH_3 + (4y - 2j + m - 3k)H^+ \\
+ (4y - 2j + m - 3k - q)e^-
\]  

(4.1)

where the elements in the equation are represented by their atomic symbols and $X$ represents a halogen element. The stoichiometric ratio of elements in the organic compound is represented by the coefficients $y$, $m$, $j$, $k$ and $q$. The number of electron transfer ($n$) in the complete oxidation process is equal to $4y - 2j + m - 3k - q$. Our previous adsorption study using *ex-situ* photoelectrocatalytic method had demonstrated that the oxidation of adsorbed species follows the same principle as described by Equation. (4.1).

### 4.3.1. The photoelectrochemical property of the TiO$_2$ electrode

The electron transfer process of Equation (4.1) during the photoelectrocatalytic reaction was well established.$^{3,23}$ Generally, organic compounds are more readily oxidised than water by the photoanode.$^{25}$ The oxidation of water and organic compounds takes place at the TiO$_2$ surface under the UV illumination, and the role of the applied potential bias was mainly used to collect electrons generated from the above processes.$^{26}$ The photoelectrochemical behaviour of the TiO$_2$ electrode was firstly investigated using linear sweeping voltammetry (LSV) in PA solution. The photocurrent-potential characteristics of the electrodes were obtained in the presence and absence of PA by LSV at a scanning rate of 10 mV/s between $-0.40$ and $0.60$V vs
Chapter 4: Study of Strong Adsorbate – Phthalic Acid

Ag/AgCl. (Figure 4.1). In the dark (with no UV illumination), no significant current was observed for the blank (i.e., 0.1 M NaNO₃) and PA solution.

**Figure 4.1:** Linear sweeping voltammetry (LSV) in PA solution

LSVs at a light intensity of 6.6mW/cm² and a sweeping rate of 10mV/s: (a) the LSVs of the mixed-phase electrode at various PA concentrations; (b) the LSVs after the subtraction of the background LSV (0 µM PA),
This suggests that no typical electrochemical oxidation of water and PA occurs between −0.40 and 0.60V in the above scenarios.

As shown in Figure 4.1(a), under UV illumination, the photocurrent increases dramatically with the potential bias in a low potential region (i.e., -0.4 to -0.1V) and then levels off with a very small slope in a high potential region (i.e., -0.1 to +0.6V). It was observed that the LSV curves at different concentration (from 2.5 to 125µM PA) share almost identical slope with the LSV curve of the blank in the high potential region. The LSV curve for the blank (with 0 µM PA) involves mainly the oxidation of water and some minor resistance effect between TiO₂ nanoparticles and ITO glass.²⁷ The LSV curves of different PA concentration in Figure 4.1(b) were obtained by subtracting the corresponding LSV values of the blank, which removes the above effects of the blank. Therefore, the i-E curves of Figure 4.1(b) can be considered as a result from the oxidation of different PA concentration. Typical saturated photocurrents at different PA concentration could be observed when the sweeping potential was greater than 0.0V. This suggests that, for a given PA concentration, the photocurrents were independent to the potential in this potential range, which was similar to the photocurrent–potential relationship obtained from a pure anatase TiO₂ electrode in a PA solution as discussed in our previous work.⁸ Such photocurrent–potential relationship may be explained as follows. For a given light intensity, the concentration of photo-generated electron–hole pairs (or the production rate of electron–hole pair) is constant. The magnitude of the photocurrent, i.e., the actual rate of electrons reaching the back contact, depends on two factors: the electron transport in the film and the photohole capture process at the TiO₂–solution interface. Before the photocurrent reaches saturation with respect to potential (i.e., from -0.4V to 0.0V), the electron transport across the film is the rate-determining step. As a result, a
monotone increase LSV curve is obtained. When the rate of the electron transport is not increased by increasing the applied potential (i.e., from 0.0V to +0.5V), the rate of reduction of the photo-generated hole becomes the limiting factor resulting in photocurrent saturation. The saturation suggests that the electrons due to the photoelectrochemical oxidation of PA were collected and transferred to the counter electrodes completely which is evidenced in Figure 4.1(b). In this study, a +0.30V potential bias was selected for all subsequent experiments. This was chosen such that the potential bias was sufficient to suppress the recombination of photo-induced electron–hole pairs but not so positive to electrochemically oxidise water and PA at the ITO surface, which complicates the adsorption investigation.

4.3.2. In-situ transient photocurrent response

Under a constant applied potential bias, a photocurrent spike can be observed from a TiO$_2$ porous film electrode when the UV light is illuminated on the electrode surface. Figure 4.2 shows the transient photocurrent responses obtained at +0.30V applied potential with different dark time duration in a 5 µM PA (pH 4.0) solution containing 0.10 M NaNO$_3$. A sharp photocurrent spike was observed immediately after the light was switched on, the photocurrent then decayed gradually to a steady photocurrent. This phenomenon has been reported in an investigation of photoelectrochemical oxidation of oxalate at TiO$_2$ porous film electrodes.$^3$ The peak current in Figure 4.2 is considered as the photoelectrochemical consumption of adsorbed organic compound rather than a double layer charging and discharging process.$^3$ The magnitude and area of the photocurrent spike increased as the time of the dark period increased. Such a transient response of photocurrent has long been observed and studied.$^{3,8}$
Figure 4.2: Photocurrent–time profile

A typical in-situ transient photocurrent–time profile for various pre-adsorption time (i.e., dark time), in a solution of 5 µM PA at pH 4.0.

The transient response is mainly due to Faradic photoelectrochemical degradation of adsorbed PA. This is because the time domain of the transient observed was much longer than the normal capacitance response of space charge layer and electric double layer, and the area under the current spike was found to be dependent on the non-illumination time length and the PA concentration, which are not the characteristics of charging and discharging current.

The steady-state photocurrent was independent of the length of the dark period, which is another characteristic of the transient photocurrent profiles. According to the semi-empirical treatment of the steady state mass transfer method, under the diffusion control condition, the limiting photocurrent \( i_L \) can be given by:

\[
i_L = \frac{nFAD C}{\delta}
\]  \hspace{1cm} (4.2)
where, $n$ is the number of electrons transferred in the complete mineralization of organic compounds (see Equation (4.1)), $F$ is the Faraday constant, $A$ is the apparent surface area of the electrode, $D$ and $\delta$ refer to the diffusion coefficient of the organic compound and the thickness of the effective diffusion layer respectively, and $C$ is the bulk concentration of the organic compound.

Figure 4.3(a) depicts typical photocurrent responses of TiO$_2$ thin-film electrode in blank and PA solutions under UV illumination. The steady state photocurrent ($i_{ss}$) is the aggregate current resulted from the oxidation of water (steady state photocurrent $i_{blank}$) and oxidation of PA limited by a diffusion control process (steady state current $i_L$).

In practise, the $i_L$ is the difference of $i_{ss}$ and $i_{blank}$, i.e.:

$$i_L = i_{ss} - i_{blank} \quad (4.3)$$

Figure 4.3(b) shows the plot of PA concentration against the net photocurrents ($i_L$) that were calculated using Equation (4.3). The excellent linearity between $i_L$ and the PA concentration was observed at low PA concentrations (<300 µM PA), which suggests that, within the low PA concentration range, the mass transport of PA from the bulk solution to the electrode surface was the rate-limiting step among the interfacial processes, which supports Equation (4.2). This phenomenon was observed for other organic compounds as well.$^{24}$ Our previous work demonstrated that under the diffusion control conditions, all the organic molecules diffused to the electrode surface could completely be mineralised.$^{24}$
Theoretically, photo holes cause three competitive processes at the TiO$_2$ surface: the oxidation of water, the oxidation of PA, and electron-hole surface recombination. Though PA is more preferentially oxidised than water, the competition for photo holes between PA and water is significant at high PA concentrations. In the case of low PA concentrations (i.e., in the range of µMs), the competition for photo holes between low concentration of PA (i.e., µM of PA) and extremely high concentration of water molecules (i.e., 56 M water) can be neglected. Therefore, the current result from the oxidation of water can be considered to be relatively constant and the increase of $i_L$ is more likely due to the decrease of surface carrier recombination that in turn was beneficial from the availability of PA. This analysis is evidenced by the fact that $i_L$ is directly proportional to the PA concentrations at low concentration range while it is levelled off at higher concentrations (see Figure 4.3(b)).

The effect of light intensity on the photo currents under a constant potential was investigated. It is observed that the increase of the light intensity will increase the total current ($i_{ss}$) and $i_{blank}$, which is obviously due to the increase of photo holes resulting from the injection of more photons. $i_L$ at different light intensity are subsequently plotted against PA concentration in Figure 4.3(b). Interestingly, the increase of the light intensity does not increase the sensitivity to PA (i.e., the slope in Figure 3b), but it extends the linear range of the calibration curve. This is because this increase in $i_{ss}$ was mainly contributed by the increase of the blank photocurrent ($i_{blank}$) generated from water oxidation. The excess of photo holes are consumed by water due to the concentration of water (56 M) is dramatically higher than the organic compound concentration.
**Figure 4.3:** Limiting current and PA concentration

(a) The determination of the limiting current ($i_L$); (b) the relationships between the limiting currents and PA concentrations at UV light intensities of 8.1, 6.6, 4.5 mW/cm$^2$, respectively.
The fact that the $i_L$ is independent of the illumination intensity at low PA concentrations (< 100 µM PA under all indicated light intensity) again suggests that the competition for photo holes between water and PA is negligible. More importantly, this confirms that the $i_L$ is under the diffusion control of PA.

### 4.3.3. The Principle of in-situ adsorption measurement

The diffusion-controlled photocurrent in Figure 4.3(b) also implies that, at the time when steady-state current is attained, the PA concentration and water concentration at the TiO$_2$ electrode surface can be assumed to be zero. In other words, a perfectly clean surface (i.e., un-adsorbed surface) of TiO$_2$ can be obtained at the steady state. This is of importance as this characteristic is an excellent indication of the completion of consumption of adsorbates, i.e., pre-adsorbed organic compounds and water during the dark time. Also, a completely clean surface is an ideal starting point for adsorption reaction study. This allows the in-situ measurement of adsorption amount and forms the theoretical base for the proposed in-situ method. The attainment of the diffusion-controlled photocurrent is essential for the proposed adsorption measurement method.

The solid line in Figure 4.4 is a typical photocurrent profile upon the UV illumination and the dash line is an integration reference line. As aforementioned, the steady-state photocurrent is the overall current originated from the photoelectrocatalytic oxidation of organic compounds and water molecules. The photoelectrocatalytic oxidation of organic compounds was under the diffusion control of the organic species, e.g., PA., while the oxidation rate of water is constant due to the invariable water concentration (i.e., 56 M). In contrast, the photocurrent of the spike consists of the oxidation current of the adsorbates (including adsorbed organic compounds and adsorbed water molecules) and the steady-state current. The attainment of steady-state current
indicates the mass transport at the electrode surface is under the control of the diffusion, and suggests that the adsorbates on TiO₂ surface have been mineralized completely. Based on the above observation and hypothesis, we can conclude that the net photocurrent \( i_{\text{net}} \) of the spike photocurrent \( i \) and the steady state current \( i_{\text{ss}} \) is the photocurrent originated from oxidation of adsorbates. i.e., \( i_{\text{net}} = i - i_{\text{ss}} \). By integrating this net current using the integration reference line in Figure 4.4 and Equation (4.4), we obtain the charge \( Q_{\text{net}} \), i.e., the shaded area shown in Figure 4.4.

\[
Q_{\text{net}} = \int_{t_L} i dt = \int (i - i_{\text{ss}}) dt
\]  

(4.4)

Though it is possible that the water can be adsorbed in the presence of organic compounds, the contribution from the water adsorption can be neglected because the adsorption kinetics of water is slow. More importantly, organic adsorbates can compete adsorption sites with adsorbed water molecules. Nevertheless, the adsorption of strong adsorbates, such as PA, is the dominant process in aqueous solution.

For a specific organic compound, the number of electron transfer \( n \) during the mineralization process can be calculated according to Equation (4.1), e.g., \( n = 30 \) for PA. Once the number of electrons (i.e., \( Q_{\text{net}} \)) oxidized at the TiO₂ surface is determined, according to Faraday’s Law, we can quantify the amount of adsorbed molecule using Equation (4.5). Therefore \( Q_{\text{net}} \) can be considered as a measure of the amount of adsorbates on TiO₂ surface.

\[
\text{moles} = \frac{Q_{\text{net}}}{(nF)}
\]  

(4.5)
4.3.4. Effect of PA Concentration

The relationships between the net charge ($Q_{\text{net}}$) and the in-situ pre-adsorption time at different PA concentrations at a long time scale (i.e., 30 min) and a short time scales (i.e., 30 s) were obtained using Equation (4.4) as shown in Figure 4.5(a) and Figure 4.5(b), respectively. Figure 4.5 indicates that $Q_{\text{net}}$ increased dramatically for the first 30 s, and then increased slowly and subsequently levelled off, which suggests that adsorption equilibrium was attained. Figure 4.5(a) shows that the $Q_{\text{net}}$ increased with the increase of adsorbate concentration and time, and that it took less time for high adsorbate concentration to reach adsorption equilibrium state. For example, the adsorption equilibrium could be attained in <20 min at a relatively high concentration of PA (i.e., 25 µM). In contrast, at a low adsorbate concentration (e.g., 2.5 µM), the net charge increased much slower with pre-adsorption time than that at a high
adsorbate concentration. This was similar to the observation at the anatase phase TiO$_2$ electrode using ex-situ method.$^8$

With conventional chemical analytical technique, it is very difficult to investigate the fast adsorption process (e.g., the first 30 s) in an accurate and reproducible manner. This is mainly due to the lack of an effective method to accurately quantify the adsorption reaction time. In this experiment, the accurate control of UV-light shut-off time provides a definite reference point to quantify the adsorption reaction time and a perfect zero adsorption point to quantify the adsorption amount. Figure 4.5(b) shows the adsorption behaviour in the short time scale, which was obtained by using the proposed in-situ method. As shown in Figure 4.5(b), $Q_{net}$ increased linearly with adsorption time for a given PA concentration in the first 30 s. This demonstrates that the PA diffusion prevails over other steps of the adsorption process during the first 30s, which verifies our previous hypothesis.

For further quantitative analysis, linear regression was conducted for the $Q_{net}$ at different PA concentrations with the adsorption in Figure 4.5(b), respectively. The slopes and intercepts on the $y$ axis of the trendline equations for the different PA concentrations were obtained and listed in Table 4.1. Table 4.1 indicates that the slope increased with the PA concentration increase while the intercept values are all positive and relatively constant.
Figure 4.5: \( Q_{net} \) - time.
The relationship between \( Q_{net} \) obtained from the in-situ adsorption measurement (a) in a long time scale and (b) in a short time scale.

The slopes in Table 1 represent the adsorption rates at different PA concentrations. In order to quantitatively investigate the relationship between adsorption rate and PA concentration, the slope values were plotted against PA concentration (see Figure
4.6. Excellent linearity ($R^2 = 0.9988$) could be observed between the adsorption reaction rates and PA concentrations. This linear relationship between the adsorption rate and PA concentration here is a direct reflection of Fick’s law of diffusion (Equation (4.2)). As aforementioned, when a steady-state current is reached, the mass transport of PA from bulk solution to the TiO$_2$ electrode surface is limited by the PA concentration. In other words, at this time, the PA concentration at the TiO$_2$ electrode surface can be considered as zero. When UV light is switched off, the photoelectrocatalytic degradation reaction (Equation (4.1)) stops, and the net adsorption reaction of PA starts on the TiO$_2$ surface.

Interestingly, slopes of PA diffusion-limiting oxidation current, as indicated in Figure 4.3(b), is almost identical to the PA diffusion-limiting adsorption rate (see Figure 4.6), sharing with the same value and unit (i.e., $\mu$A/$\mu$M=$\mu$C$^{-1}$/M). This is because both the adsorption in the dark and the photoelectrocatalytic oxidation processes under UV illumination were controlled by the diffusion of PA. This can be considered as a significant evidence to support our hypothesis. This can be explained by the Fick’s law, i.e., the adsorption amount was proportional to a given adsorption time when the adsorption reaction rate is limited by the mass transport of the adsorbate (See Figure 4.5(b)). It is to note that this is only valid in low adsorbate concentration range and at the time of low surface coverage of the adsorption surface (i.e., sufficient adsorption reaction sites). The former condition assures that the mass transport is sufficiently slow because of the small concentration gradient, while the latter one guarantees an adequately fast adsorption reaction rate. The common slopes of Figure 4.3(b) and Figure 4.6 also suggest that the PA diffusion limiting net current can be used to estimate the maximum adsorption amount, which is simple and straightforward. This is because the adsorption process can never exceed the mass transport of adsorbate. In
a longer time domain, the adsorption rate decreased with the increase of the surface coverage of the interface (see Figure 4.5(a)). In this case, the adsorption rate will be limited by the availability of unadsorbed sites rather than the mass transport of the adsorbates.

**Table 4.1: List of slopes and intercepts in Figure 4.5(b).**

The slopes and intercepts obtained by linear regression using data from in-situ adsorption measurement in a short time scale

<table>
<thead>
<tr>
<th>[PA] µM</th>
<th>slope (µC/s)</th>
<th>intercept (µC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>6.9474</td>
<td>30.358</td>
</tr>
<tr>
<td>20</td>
<td>5.864</td>
<td>30.943</td>
</tr>
<tr>
<td>15</td>
<td>4.5163</td>
<td>25.64</td>
</tr>
<tr>
<td>10</td>
<td>3.3583</td>
<td>26.112</td>
</tr>
<tr>
<td>5</td>
<td>1.9325</td>
<td>29.851</td>
</tr>
<tr>
<td>2.5</td>
<td>1.4053</td>
<td>25.879</td>
</tr>
</tbody>
</table>

The positive small intercepts shown in Table 4.1 is very likely due to the water adsorption. This is because the water concentration (i.e., 56 M) was predominantly higher than the PA concentrations and inevitably contributed a small amount of charge to $Q_{net}$, despite of the weak water adsorption nature of TiO$_2$ surface in the presence of strong adsorbates. Nevertheless, the contribution of water adsorption to $Q_{net}$ was insignificant in comparison to that of strong organic adsorbates (e.g., PA).

Table 1 also shows that the intercept values did not change much with the variation of PA concentrations ranging from 25-31 µC. This variation can be attributed to the fact that the water concentrations were relatively constant (e.g., 56 M) at different PA concentrations.
Figure 4.6: Adsorption rate and PA concentrations

The slopes (adsorption reaction rate) obtained from Table 4.1 were dependent on the PA concentrations.

4.4 Adsorption Thermodynamics

In-situ adsorption measurement of PA illustrated in Figure 4.5(a) also indicates that after a period of 20 min, the adsorption process has reached equilibrium for all concentrations from 2.5 µM to 25 µM. It took slightly less time to reach the adsorption equilibrium for this mixed-phase electrode than that for the anatase electrode in the ex-situ study (ca. 30 min), which is very likely due to the TiO₂ film thickness for the mixed-phase electrode (i.e., 500 nm) is significantly thinner than that for the anatase electrode (i.e., 1 µm). Thinner TiO₂ film apparently facilitates faster mass transport of adsorbate from film surface to the film inside.

Adsorption behaviour of organic compounds on TiO₂ surfaces commonly follows Langmuir adsorption model. Assuming monolayer adsorption, the surface
coverage, $\theta$, can be defined as the amount ratio of occupied sites to the total adsorption sites. Because the amount of occupied sites is directly proportional to the charge, i.e., $Q$, $\theta$ can be expressed by the ratio of the measured net charge ($Q_{\text{net}}$) to the maximum net charge ($Q_{\text{max}}$) at 100% surface coverage, i.e.,

$$\theta = \frac{Q_{\text{net}}}{Q_{\text{max}}}$$ (4.6)

Because of the large ratio of solution volume (i.e., 100ml) to the electrode geometric area (0.75cm$^2$) in our adsorption study setup, there was no significant change in the bulk adsorbate concentration ($C$) during the adsorption and photoelectrochemical measurement processes. In other words, our setup meets another assumption of Langmuir isotherm. Assuming $K$ is the adsorption equilibrium constant, Langmuir isotherm equation can be then written as

$$\frac{C}{Q_{\text{net}}} = \frac{1}{Q_{\text{max}}} C + \frac{1}{Q_{\text{max}} K}$$ (4.7)

The net charges $Q_{\text{net}}$, obtained from Figure 4.5 after 20 minutes of adsorption time, and the corresponding PA concentrations are treated to fit the Langmuir model (i.e., Equation (4.7)) by plotting $C/Q_{\text{net}}$ against $C$ to obtain a straight trendline as indicated in Figure 4.7. The linear relationship ($R^2 = 0.9829$) suggests the adsorption behaviour of PA on TiO$_2$ electrode surface being in good agreement with the Langmuir model, and the adsorbate molecules form a monolayer coverage on the TiO$_2$ surface.
Chapter 4: Study of Strong Adsorbate – Phthalic Acid

According to Equation (4.7), from the gradient and the intercept of the best-fit trendline, $Q_{\text{max}}$ and $K$ of the mixed phase electrode are calculated to be 1.12 mC and $1.7 \times 10^5$ M$^{-1}$, respectively. The $Q_{\text{max}}$ of the single phase (i.e., anatase film) by ex-situ method (i.e., 4.19 mC)\(^8\) was three times higher than that of the mixed phase electrode. This can be explained by the fact that the anatase TiO$_2$ electrode (treated at 450 °C) has a larger thickness (1 µm)\(^8\) and higher porosity than the mixed phase electrode (500 nm) that was treated at 700 °C.\(^{24}\) In comparison of the resulting $K$ value of the mixed phase TiO$_2$ electrode measured by this in-situ method to the result of the anatase phase TiO$_2$ electrode from the ex-situ study (i.e., $4.0 \times 10^4$ M$^{-1}$), the mixed-phase $K$ value is approximately 5 times greater than that obtained from the single-phase electrode. The greater $K$ value of the rutile-anatase mixed-phase coincides with its synergetic effect that bestows the mixed-phase electrodes with an

![Figure 4.7: The fitting of the isotherm to Langmuir adsorption model.](image-url)
exceptional ability to mineralise organic compounds.\textsuperscript{24} This is in strong contrast with the single anatase phase TiO\textsubscript{2} that is readily poisoned by KHP.

### 4.5 Conclusions

The adsorption amount of adsorbates on titania surface can be determined by the proposed \textit{in-situ} photoelectrochemical technique. The proposed method can directly quantify the amount of adsorbates at titania surface in a sensitive, reproducible and accurate manner, hence provides a powerful tool for the adsorption process study. In a short period time (e.g., less than 30 s) and in low adsorbate concentration range, the adsorption reaction rate was found to be equal to the degradation rate, which provides a strong support for the proposed adsorption measurement method. This proposed method may be used to investigate the adsorption behaviour of weak adsorbates, where the weak adsorbates on the TiO\textsubscript{2} may be removed (partly or completely) by the post-adsorption washing process in the \textit{ex-situ} method. Using the obtained data from the \textit{in-situ} measurement, thermodynamic analysis indicated that the adsorption process fits the Langmuir isothermal model.

### 4.6 References


Chapter 5

in-situ Photoelectrochemical Characterisation of Weak Adsorption Behaviour on TiO$_2$ Surface
Chapter 5  \textit{in-situ} Photoelectrochemical Characterisation of Weak Adsorption Behaviour on TiO$_2$ Surface

5.1 Introduction

In Chapter 4, an \textit{in-situ} photoelectrochemical method was proposed and validated by the investigation of adsorption of a strong adsorbate on the TiO$_2$ film surface. In this \textit{in-situ} method, the adsorption process and photocatalytic determination of the adsorbed organic compound were completed in the same photoelectrochemical cell.

The proposed \textit{in-situ} approach in Chapter 4 has several advantages over the photoelectrochemical \textit{ex-situ} method in providing accurate measurement of the adsorption of a given TiO$_2$ thin film photoanode by eliminating the washing step between the pre-adsorption and photocatalytic oxidation processes.$^{1,2}$ Using the \textit{in-situ} technique, the amount of adsorbed compound can be readily quantified by measuring the photocurrent in the photoelectrochemical oxidation process. The measuring principle of the approach is based on the condition that the overall photoelectrochemical oxidation reaction is under diffusion control, and the surface concentration of the organics adsorbed at the TiO$_2$ electrode surface is assumed to be zero after the photocatalytic oxidation reaction has reached the steady state.$^1$

However, for photocatalytic oxidation reactions of a group of organic compounds at the TiO$_2$ surface, such as weak adsorbates, the experimental conditions required for application of this \textit{in-situ} approach may not be applicable. The case may become even more complicated when the surface reactivity of the photocatalyst is affected by intermediates during the photocatalytic process. In this regard, the development of a simple and effective method that can be used to study the adsorption properties of
organic compounds with various adsorption properties at the TiO$_2$ surface has become necessary.

Despite well accumulated knowledge of photocatalytic oxidation of organic compounds by TiO$_2$ photocatalysts, there are several fundamental questions concerning surface reaction mechanisms, even for simple molecules. Several factors may heavily influence the reaction mechanism of a photocatalytic process. These factors include molecular structure of the organic species present in solution, their concentrations, and most importantly, the characteristics of ionic and molecular adsorption at the surface of the TiO$_2$ photocatalyst.$^3$

Methanol photocatalysis by TiO$_2$ has been an active research field for photocatalytic hydrogen production and photocatalyst-based hybrid methanol fuel cells.$^{4-6}$ Because of the high hydrogen/carbon ratio, methanol is one of the most promising sources for hydrogen production by dehydrogenation of methanol at room temperature from an aqueous solution without any detectable formation of carbon monoxide.$^{4,5,7}$

Because methanol is the simplest primary alcohol, is a well-known radical scavenger and is a non-specific adsorbate to TiO$_2$ surfaces, it is often chosen as the representative hydrocarbon species for the investigation of photocatalytic reactions by TiO$_2$. $^8$

The adsorption of methanol on TiO$_2$ surfaces has long been a research interest in photocatalytic processes because of the simplicity of possible photo-oxidation production as well as the ability for chemisorption to the TiO$_2$ surface.$^{9-12}$ Various techniques have been developed to study the behaviour of methanol adsorption at the TiO$_2$ surface, such as sum frequency generation (SFG) vibrational spectroscopy$^{13}$, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS),$^9$ temperature-
programmed desorption spectra,$^{10}$ and by first principle calculation based on density functional theory (DFT).$^{14}$ To date, the majority of these investigations have been in the gaseous phase, and less information is available on the adsorption properties of aqueous methanol at the TiO$_2$ surface. While computer simulation has provided detailed understanding of the adsorption mechanisms,$^{14}$ it is a challenging task to develop experimental methodologies to study the adsorption behaviour of this type of weak organic adsorbate at the TiO$_2$ surface.

In this chapter, an in-situ photoelectrochemical method was proposed to investigate the adsorption behaviour of organic species at the TiO$_2$ thin film surface. The quantification of the adsorption was determined by the initial photocurrent upon UV illumination. This technique is capable of providing useful information on adsorption properties for both strong and weak adsorbates in a direct, simple and rapid manner.

**5.2 Experimental**

**5.2.1. Materials**

All reagents were analytical grade and purchased from Sigma-Aldrich unless otherwise stated. Solutions were prepared using high purity deionised water from a Milli-Q system (Millipore Corp, 18MΩcm). Indium Tin Oxide (ITO) conducting glass (8 10 Ω/square, Delta Technologies Limited) was used as the supporting substrate for the TiO$_2$ thin film photoanode.

**5.2.2. TiO$_2$ photoanode preparation**

Colloidal TiO$_2$ was prepared by hydrolysis of titanium butoxide according to a published procedure.$^{15}$ A mixture of 16 mL of isopropanol and 50 mL of titanium butoxide were slowly added to 600 mL of Milli-Q water with vigorous stirring. 4.0 mL of 7% nitric acid was added to the solution as a peptising agent, and the resultant
solution was immersed in a hot water bath at temperature of 80 °C for 10 hours to form a white TiO$_2$ colloid.

The resultant TiO$_2$ colloid contained ca. 60 g/dm$^3$ of TiO$_2$ solid with particles sizes of 8-10 nm. 30% (w/w) Carbowax (Supelco) was used to increase the porosity of the TiO$_2$ film.

ITO glass (8 – 10 Ω/sq, delta Technonologies Limited) was used as the supporting substrates for the TiO$_2$ thin film photoanode. A pre-treatment process was performed on the ITO glass. The surfaces of the ITO glass was in turn washed by detergent, water, chromic acid, water and ethanol, then thoroughly rinsed by water.$^2$ A dip-coating method was employed to immobilise the TiO$_2$ colloid onto the conducting ITO glass substrates.

The coated TiO$_2$ electrode was placed in an oven and air dried at 80 °C for 30 minutes. The electrode was then calcined in a furnace for 16 hour in air at 700 °C. This high temperature treatment of the TiO$_2$ thin films resulted in mixed-phase TiO$_2$ of anatase and rutile, resulting in larger photocurrent response due to the longer separation lifetime of photoholes and photoelectrons within the TiO$_2$ thin film.$^{16}$ The thin film electrode made of immobilised TiO$_2$ on ITO glass substrate was mounted on a special holder that left an area of 0.78 cm$^2$ exposed to a quartz window for UV illumination. All photoelectrochemical experiments were carried out at 25 °C in a conventional three electrode cell composed of the TiO$_2$ thin film electrode as the working electrode, a saturated Ag/AgCl electrode as the reference electrode, and a platinum mesh as the auxiliary electrode. A 0.1 M NaNO$_3$ solution with pH = 4.1 was used in the electrochemical measurements as an electrolyte.
A voltammograph (CV – 27 BAS) and an AD converter (MacLab 400, AD Instruments) were used to apply the potential bias and to monitor photocurrent response to UV radiation. The UV light source for the photocatalysis was a 150 W xenon lamp (HFC - 150, TrustTech) with regulated optical output. Undesirable heating was avoided by using a UV-band pass filter (UG – 5, Schott) at the lamp output for infrared and near-infrared radiation absorption.

5.3 Results and Discussion

5.3.1. Effect of potential bias in photocatalytic oxidation of methanol

The effect of applied potential bias and mechanisms of the photocatalytic oxidation of organic compounds have been previous reported.\(^2,17,18\) Figure 5.1 illustrates that the photocurrent initially increased with the applied potential bias, then saturated at higher potential bias. The linear increase of photocurrent corresponded to a reaction process that was limited by the photoelectron transport process inside the TiO\(_2\) thin film photoanode. At higher potential bias range (above +0.1V), the photocurrent saturation suggested that the capture of photogenerated holes at the TiO\(_2\) surface had become a limiting step for the overall photocatalytic oxidation reaction under the given light intensity.\(^17-19\) In the subsequent experiment, a potential bias of +0.3 V vs Ag/AgCl was chosen for the photocatalytic oxidation, as this potential bias was sufficient to suppress the recombination of photo-generated electron-hole pairs without causing direct electrochemical oxidation of water and methanol at the ITO substrate surface. Under this potential bias, the measured data should reflect the kinetics of the interfacial process and not be affected by the removal and transport of electrons across the TiO\(_2\) thin film photoanode.
Figure 5.1: Voltammograms of TiO$_2$ thin film photoanode
Methanol concentrations are 0, 0.1, 0.2, 0.3 and 0.4 mM (from a to e) in 0.1 M NaNO$_3$ as the supporting electrolyte.

5.3.2. Photocatalytic oxidation of methanol at TiO$_2$ thin film photoanode

Methanol is a common substrate molecule for photocatalytic performance evaluation, which can be used as the model compound in the study of photocatalysis reaction mechanisms.$^{4,20,21}$ Under UV radiation, photo-generated holes migrate to the TiO$_2$ surface to oxidise the adsorbed water or the surface OH group to produce •OH radicals that are highly active in the oxidation of organic molecules. The methanol molecules can react with either the surface photo holes or the hydroxyl radicals to produce various forms of intermediates that were to be completely mineralised to produce water and carbon dioxide.$^{22,23}$

The intermediate methoxy radicals, such as •CH$_2$OH, CH$_2$O, CHO•, HCOOH, HCOO•, CO, etc$^{20,21}$ can further inject electrons into the conduction band to increase
photocurrent generation. This phenomenon is known as the doubling current effect observed in photoelectrochemical oxidation of organic compounds by TiO$_2$ photocatalysts.$^{24,25}$

**The transient photocurrent response:** Under a constant applied potential bias of +0.3 V vs Ag/AgCl, a photocurrent response can be observed by UV illumination on the TiO$_2$ electrode surface. Figure 5.2 shows the transient photocurrent measured in a 0.2 mM methanol solution in 0.1 mM of NaNO$_3$ supporting electrolyte under light intensity of 7.0 mW/cm$^2$.

![Fig 5.2: Effect of on-off illumination on photocurrent](image)

Immediately upon UV radiation of the photoanode surface, a sharp spike of initial photocurrent ($i_0$) was observed (Figure 5.2). The photocurrent decreases with time to reach a minimum then slightly increases before reaching a steady level which was dependent on methanol concentration and incident light intensity. The current spike shown in Figure 5.2 has been reported in investigations of photoelectrochemical...
oxidation of organic compounds by TiO$_2$ thin film photoanodes.\textsuperscript{1,26} The sharp initial photocurrent spike was considered to be the photocatalytic oxidation of water and the organic compound that had been pre-adsorbed before the UV illumination, rather than a result of a double layer charging process.\textsuperscript{1} Figure 5.2 shows that under constant methanol concentration and the light intensity, the height of the initial photocurrent increases with pre-adsorption time.

During the light “on” and “off” cycle, the total photocurrent generated from the photocatalytic oxidation of methanol consists of two steps: the first is the instantaneous generation of a significant amount of photocurrent from the scavenging of photo-generated holes by the adsorbed methanol at the TiO$_2$ thin film surface, and the current component that is due to the interaction and electron transfer of methoxy radicals formed in the first step of the UV illumination of the photoanode, (the double current effect).\textsuperscript{21}

5.3.3. The in-situ measuring principle

For photocatalytic oxidation of methanol in aqueous solution, the photocurrent in Figure 5.2 consists of two components originating from the photocatalytic oxidation of water and the photocatalytic oxidation of methanol.

It has been widely accepted that in photocatalytic oxidation of organic compounds, the photo-generated hole-electron pairs at the TiO$_2$ surface cause three competitive processes: (a) the oxidation of pre-adsorbed water, (b) the oxidation of the adsorbed organic compounds, and (c) electron-hole surface recombination.\textsuperscript{1} In solutions with low methanol concentration, the competition for photo holes from the methanol is insignificant compared to that from water, which has an overwhelmingly high concentration in the solution (i.e., 56 M). Therefore, for a given pre-adsorption time,
the photocurrent component from water oxidation can be considered to be a constant at various concentrations of methanol.$^1$

During the light “on – off” cycle as demonstrated in Figure 5.2, the net initial photocurrent ($i_{0,\text{net}}$) generated from the photocatalytic oxidation of the pre-adsorbed methanol can be calculated by subtracting the initial peak photocurrent originated from the photo oxidation of water in a blank solution ($i_{0,w}$) from the total initial peak photocurrent ($i_{0,\text{total}}$):

$$i_{0,\text{net}} = i_{0,\text{total}} - i_{0,w}$$  \hspace{1cm} (5.1)

**Figure 5.3:** Photocurrent from photocatalytic oxidation of water ($i_{0,w}$) and from photocatalytic oxidation of methanol ($i_{0,total}$).

Figure 5.3 depicts the typical photocurrent from photocatalytic oxidation of water and methanol solution.
Kinetics of photocatalytic oxidation of methanol at TiO$_2$ film surface: In kinetic theory of a heterogeneous photocatalytic reaction, it has been well recognised that the reaction rate should follow a first-order reaction with respect to both surface coverage of organic adsorbates and the photo hole concentration at the surface of the photocatalyst.$^{17,27}$ Studies of kinetics of photocatalytic oxidation of organic compounds by TiO$_2$ photocatalysts have demonstrated that for many organic compounds, the photocatalytic oxidation reaction often followed first-order reaction rates, or a pseudo-first-order reaction model in low reactant concentrations.$^{28-32}$

Assuming that the initial photocatalytic oxidation of adsorbed methanol upon UV illumination obeys a Langmuir-Hinshelwood mechanism where the reaction rate is proportional to the surface coverage$^{33,34}$:

$$ Rate = k \theta $$  \hspace{1cm} (5.2)

where $k$ is the rate constant for reaction, and $\theta$ is the surface coverage defined by the fraction of the number of adsorption sites occupied and the maximum number of adsorption sites available:$^{33,35}$

$$ \theta = \frac{C_s}{C_{s,max}} $$  \hspace{1cm} (5.3)

For a given TiO$_2$ thin film photoanode, the maximum number of available sites is a constant. In this regard, the apparent degradation reaction rate at the TiO$_2$ thin film photoanode surface is therefore directly proportional to the surface concentration of adsorbate:

$$ Rate = \frac{dC_s}{dt} = k_s C_s $$  \hspace{1cm} (5.4)
where \( k_1 = \frac{k}{C_{s,max}} \) is the apparent rate constant under the given experimental conditions of the photocatalytic process.

Upon UV illumination, the observed photocurrent represents the flow rate of electric charge carried by moving electrons generated from the photocatalytic oxidation of the adsorbed methanol at the surface of the TiO\(_2\) thin film photoanode. If we assume that the electrons generated from the photoelectrochemical oxidation of methanol at the TiO\(_2\) thin film electrode are completely collected and transferred to the counter electrode through the external circuit, the photocurrent should reflect the photocatalytic reaction rate under UV illumination.

Therefore, Equation (5.4) can be expressed by the initial photocurrent \((i_{0,\text{net}})\) to represent the initial reaction rate upon UV illumination:

\[
Rate = \frac{dC_s}{dt} = \frac{i_{0,\text{net}}}{nF} = k_1 C_s
\]

\[
i_{0,\text{net}} = nFk_1 C_s
\]  

Equation (5.5) indicates that the initial photocurrent is proportional to the pre-adsorbed methanol concentration at the TiO\(_2\) surface \((C_s)\).\(^{34}\)

5.3.4. Adsorption thermodynamics

**Quantification of the surface coverage:** Assuming monolayer adsorption, the Langmuir adsorption model has been commonly employed to study the adsorption-desorption of organic compounds at the solid/liquid interface on the TiO\(_2\) surface.\(^{2,36,37}\) The Langmuir adsorption isotherm can be expressed as:
\[ \frac{C_s}{C_{s,max}} = \frac{KC}{1 + KC} \]  \hspace{1cm} (5.6)

where \( C \) is the concentration of the adsorbate in the bulk solution and the \( K \) is the equilibrium constant. Combining Equation (5.3) and Equation (5.5), the surface coverage can be written as:

\[ \theta = \frac{i_{0,net}}{i_{0,net,max}} \]  \hspace{1cm} (5.7)

where \( i_{0,net} \) is the net initial photocurrent generated from the photocatalytic oxidation of the adsorbed methanol at the TiO\(_2\) thin film surface, and the \( i_{0,net,max} \) is the maximum net photocurrent generated from the photocatalytic oxidation of methanol at 100% coverage. In this regard, the Langmuir adsorption isotherm can be expressed as:

\[ \frac{C}{i_{0,net}} = \frac{1}{i_{0,net,max}} C + \frac{1}{i_{0,net,max}} \frac{1}{K} \]  \hspace{1cm} (5.8)

In this study, due to the large solution volume/electrode area ratio, the bulk solution methanol concentration and pH can be regarded as a constant during the adsorption process and the photocatalytic oxidation reaction.

To validate Equation (5.8) for the adsorption of organic compounds by the TiO\(_2\) thin film surface, the photocurrents of photocatalytic oxidation of phthalic acid in Chapter 4 were re-analysed.

**Adsorption of phthalic acid:** The net initial currents of photocatalytic oxidation of phthalic acid can be obtained by Equation (5.1). Figure 5.4 displays the net initial
photocurrent of the photocatalytic oxidation of phthalic acid after 20 minutes of pre-adsorption time under solution concentrations ranging from 2.5-25 µM.

![Graph](image)

**Figure 5.4:** The net initial photocurrent of oxidation of phthalic acid after 20 minutes of pre-adsorption.

The net initial photocurrent obtained from Figure 5.4 and the corresponding concentrations are treated according to the Langmuir adsorption model by plotting $C/i_{0,\text{net}}$ against $C$ to obtain a straight line, as indicated in Figure 5.5. The linear relationship of $C/i_{0,\text{net}}$ vs $C$ ($R^2 = 0.9519$) indicates that the adsorption behaviour of the phthalic acid is in agreement with the Langmuir adsorption model (Equation 5.8). From the gradient and y-intercept in Figure 5.5, the resulting values of $i_{0,\text{net,max}}$ and the adsorption equilibrium constant $K$ are calculated to be $1.9 \times 10^{-4}$ $A$ and $2.1 \times 10^5$ $M^{-1}$, respectively. The $K$ value calculated by Equation (5.8) is in good agreement with the value determined by using net charge from the photocurrent during the in-situ
photocatalytic oxidation of the adsorbed phthalic acid (Figure 4.7 in Chapter 4, \( K = 1.7 \times 10^5 \, M^{-1} \)).

---

**Figure 5.5: The fitting of Langmuir isotherm for adsorption of phthalic acid**

**Adsorption of methanol:** In order to measure the adsorption isotherm of methanol at the TiO\(_2\) thin film photocatalyst, the time required for methanol adsorption to reach equilibrium under various concentrations was first investigated. Figure 5.6 shows the relationship between the net initial photocurrent and the pre-adsorption time for methanol solutions of 0.05 mM and 0.1 mM. Figure 5.6 indicates that the net initial photocurrent initially increases with time, then the photocurrent levels off in less than 2 minutes. The results in Figure 5.6 demonstrate that the adsorption equilibrium can be reached in less than 5 minutes of *in-situ* pre-adsorption for all concentrations investigated in this study.
In order to insure that the adsorption reached equilibrium, the pre-adsorption time for methanol adsorption in this study was chosen to be 5 minutes before photocatalytic oxidation under UV illumination. Figure 5.7 illustrates the photocurrent profile of photocatalytic oxidation of methanol solutions with concentrations from 0.05-0.7 mM. Under UV illumination, photocurrent from the photocatalytic oxidation of methanol in low concentration solution rapidly reaches the steady current state. For photocatalytic oxidation of methanol in high concentration ($C > 0.3$ mM), the photocurrents display a small increase before reaching the steady state photocurrent. This can be attributed to the double current effect resulting from the electron transfer of methoxy radicals formed in the first step of photocatalytic reaction.

The net initial photocurrent in Figure 5.7 from the photocatalytic oxidation of methanol in different concentrations can be determined by Equation (5.1).
Figure 5.7: $i_{ph}$ and time

Photocurrent from the oxidation of pre-adsorbed methanol solutions. Pre-adsorption time is 5 minutes for all solutions with concentrations ranging from 0.05-0.7 mM.

Figure 5.8 shows that the net initial photocurrent obtained initially increases with the methanol concentration, then levels off at higher concentrations.

The net initial photocurrent and methanol concentration in Figure 5.8 are treated to fit the Langmuir adsorption model (i.e. Equation 5.8) by plotting $C/i_{0,n,net}$ against $C$ to obtain a straight line ($R^2 = 0.98912$).

The linear relationship between $C/i_{0,n,net}$ and $C$ (Figure 5.9) suggests that the adsorption of methanol at the TiO$_2$ thin film surface agrees well with the Langmuir model. The maximum net initial photocurrent, $i_{0,n,net,max} = 50 \mu A$ was obtained from the gradient of the curve fit in Figure 5.9. The adsorption equilibrium constant, $K = 2.7 \times 10^3 \ M^{-1}$, for methanol at TiO$_2$ thin film is determined from the y-intercept of the straight line in Figure 5.9.
Figure 5.8: Net initial photocurrent and methanol concentration

Figure 5.9: Plot of the Langmuir adsorption isotherm for methanol adsorption at the TiO₂ thin film surface.
5.4 Conclusions

In this work, an in-situ method based on the photoelectrochemical oxidation principle to study the adsorption behaviour of organic compounds at the TiO$_2$ thin film surface was proposed and validated. The coverage of the TiO$_2$ thin film surface was determined by the net initial photocurrent originating from the photocatalytic oxidation of pre-adsorbed organic compounds at the TiO$_2$ surface. Studies of phthalic acid and methanol adsorption indicate that the method is a simple and effective tool in investigating adsorption behaviour for both weak and strong adsorbates at the surface of TiO$_2$ thin film.

5.5 References


Chapter 6

Photoelectrochemical Study of Water Adsorption Behaviour on TiO$_2$ Surfaces
Chapter 6 Photoelectrochemical Study of Water Adsorption Behaviour on TiO₂ Surfaces

6.1 Introduction

Photocatalysis by TiO₂ semiconductors has been intensively studied in recent years due to its potential applications in solar energy conversion\textsuperscript{1,2} and environmental remediation such as the removal of organic pollutants from waste water treatment.\textsuperscript{3,4} In Chapters 4 and 5, the adsorption behaviour of organic compounds were investigated using the \textit{in-situ} photoelectrochemical method to provide important thermodynamic and kinetic information necessary for the development of plausible photocatalytic process mechanisms.

As most TiO₂ photocatalysis applications involve aqueous media, the surface properties of TiO₂ towards water play an important role. Because the interaction of water with the TiO₂ surface has a strong influence on the catalytic activity,\textsuperscript{5-7} this interaction is therefore currently an object of extensive experimental and theoretical research.\textsuperscript{8-11}

In general, theoretical calculations by first-principle studies and computer simulations have focused on the water interaction at a particular surface of a TiO₂ polymorph.\textsuperscript{6,7,12} Theoretical calculations appear to provide the possibility of achieving atomic-level insight into the properties of the water/TiO₂ interaction.\textsuperscript{13}

A variety of experimental techniques have been developed and employed to study the interaction of water at the TiO₂ surface at the molecular level, in particular, the interaction of Ti–OH groups with photo-generated electrons and holes. These techniques include temperature-programmed desorption (TPD),\textsuperscript{9,14} ultraviolet
photoelectron spectroscopy (UPS),\textsuperscript{15} scanning tunneling microscopy (STM),\textsuperscript{10,16} X-ray photoelectron spectroscopy (XPS),\textsuperscript{11} density functional theory (DFT) calculation,\textsuperscript{17} surface-enhanced IR absorption spectroscopy (SEIRAS),\textsuperscript{18} FTIR,\textsuperscript{19} and visible-infrared sum frequency generation (SFG) spectroscopy.\textsuperscript{20}

Some important information about water adsorption on TiO\textsubscript{2} surfaces has been obtained with these techniques, particularly with IR spectroscopy due to its effectiveness in distinguishing molecular species. Interest in studying the behaviour of surface Ti–OH groups by spectroscopy has increased since Fujishima and co-workers reported the photo-generation of a highly amphiphilic TiO\textsubscript{2} surface.\textsuperscript{19,21} This observation was interpreted in terms of UV-induced changes in the concentration and structure of surface OH groups.\textsuperscript{22}

Despite increased understanding of the structure of the hydrated surface, the mechanism of water adsorption onto the TiO\textsubscript{2} surface is still a matter of debate. Two viewpoints are commonly accepted: water may bind molecularly to the TiO\textsubscript{2} surface or it may dissociate to form surface hydroxyl groups.\textsuperscript{8,23} Surface hydroxyl groups on TiO\textsubscript{2}, which may participate directly in the reaction mechanism by trapping photogenerated holes that reach the catalyst surface producing very reactive surface HO\textsubscript{·} radicals, are now recognized as playing a key role in the photo-oxidative process.\textsuperscript{8}

Photoelectrochemical methods of studying adsorption of organic compounds at the TiO\textsubscript{2} surface have proven useful and effective in obtaining thermodynamic and kinetic information about the photocatalytic process.\textsuperscript{24} In our previous study, \textit{in-situ} and \textit{ex-situ} photoelectrochemical methods were employed to obtain the characteristics of the photocatalytic degradation of different organic compounds at TiO\textsubscript{2} thin film electrodes.\textsuperscript{25,26} The proposed \textit{ex-situ} technique involves a two-step measurement
procedure in which an adsorption step is carried out before the photoelectrochemical measurement. To study organic adsorption over a short time scale (i.e., in seconds), an in-situ method was recently proposed and utilized to determine the adsorption of phthalic acid on the TiO$_2$ surface.$^{26}$ Both in-situ and ex-situ methods have significantly simplified the experimental system and procedures and revealed new insights into the photocatalytic oxidation mechanisms of organic matter.

In this chapter, an in-situ photoelectrochemical method was developed to study water adsorption on the surface of nanoparticulate TiO$_2$ thin film photoanodes. At a given illumination light intensity, when a suitable potential bias is applied to ensure that the overall rate of reaction is not controlled by the electron transport across the TiO$_2$ thin film or by the electron removal at the electrode/solution interface, the photocurrent obtained should reflect important information including the amount of the adsorbed water and adsorption rate.

### 6.2 Experimental

#### 6.2.1. Materials

Indium Tin Oxide (ITO) conducting glass sheets (8-10 Ω/square, Delta Technologies Limited) were used as substrates for TiO$_2$ film coating. All chemicals used in this work were of analytical grade and purchased from Sigma-Aldrich unless otherwise stated. All solutions were prepared using high purity deionised water (Millipore Corp., 18 MΩcm).

#### 6.2.2. Preparation of the TiO$_2$ thin film photoanode

Aqueous TiO$_2$ colloid was prepared by the hydrolysis of titanium butoxide according to the method reported by Nazeerddin et al.$^{27}$ Electrode supporting substrate ITO slides were treated before the resultant colloidal TiO$_2$ nanoparticles were immobilised
by the dip-coating technique. The coated electrodes were ambient dried, and then calcined in a muffle furnace at 700°C temperature for 16 h in air. Detailed fabrication procedures and characterization information can be found in our previous works.\textsuperscript{28,29}

6.2.3. Apparatus and methods

All experiments were performed in a conventional three-electrode electrochemical cell with a quartz window for UV illumination. A TiO_2 thin film photoanode was employed as the working electrode, and was mounted onto a specially made electrode holder with a 0.78 cm\textsuperscript{2} area left unsealed to be exposed to UV illumination. A saturated Ag/AgCl electrode and a platinum mesh were used as the reference and the auxiliary electrodes, respectively. To minimise the influence of solution resistance and the effect of migration, 0.1 M NaNO\textsubscript{3} was chosen as the supporting electrolyte. A voltammograph (CV-27, BAS) was used for the application of potential bias in the experiments and for linear potential sweep experiments. Potential and current signals were recorded through a Maclab 400 interface (AD Instruments). The UV light source was provided by a 150 W xenon arc lamp with focusing lenses (HF-200w-95, Beijing Optical Instruments). Light intensity was measured with a UV irradiance meter (UVA, Instruments of Beijing Normal University). To avoid the sample solution being heated by the infrared component, the light beam was passed through a UV-band pass filter (UG 5, Avotronics Pty. Limited).

All experiments were carried at ca. 23 °C. The pH of the solution was adjusted with nitric acid or sodium hydroxide solution and was closely monitored during the experiment with a pH meter.
Chapter 6: Study of water adsorption

6.3 Results and Discussion

6.3.1. Photoelectrochemical properties of the TiO$_2$ photoanode

The effect of applied potential bias on the photoelectrochemical oxidation of water at the TiO$_2$ photoanode was first investigated by linear sweeping voltammetry (LSV). A set of typical voltammograms under different light intensities were obtained at pH 5.6 with a scanning rate of 10 mV/s. The applied potential bias for the voltammetry was between $-0.30$ and $+0.40$ V versus Ag/AgCl reference electrode. Voltammograms under varying light intensities revealed similar photocurrent/potential ($i/E$) characteristics: the photocurrent initially increases linearly with the applied potential bias and then levels off to reach the saturated photocurrent at higher applied potential bias range (Figure 6.1). Similar results have been reported in studies of photocatalytic oxidation of other organic compounds.$^{25,26,30}$

In the photocatalytic process, electron transport in the TiO$_2$ thin film and the photohole capture process at the TiO$_2$-solution interface may be the limiting factors for the overall photocatalytic reaction.$^{25,31}$ It was previously reported that the applied potential bias could change the rate-determining steps of photocatalytic reactions at the surface of this type of TiO$_2$ thin film photoanode.$^{32,33}$

The photocurrent-potential behaviour in Figure 6.1 may be explained as follows: the linear increase of photocurrent before saturation is limited by the photoelectron transport inside the TiO$_2$ semiconductor thin film.$^{31}$ As a result, a linear photocurrent-potential relationship is obtained. As the potential increases, the photocurrent reaches a saturated level and electron transport is no longer the limiting factor for the overall photocatalytic process. The saturated photocurrent under higher potential indicates
that the overall photocatalytic reaction is controlled by the photo hole capture process at the TiO$_2$ surface.$^{1,24,31}$

![Voltammograms of the TiO$_2$ photoanode](image)

**Figure 6.1:** Voltammograms of the TiO$_2$ photoanode

*Voltammograms of the nanoparticulate TiO$_2$ electrode in 0.1M NaNO$_3$ solution of water at pH 5.6 under light intensity of 5, 7 and 9 mW/cm$^2$ and a scan rate of 10 mV/s.*

For photocatalytic oxidation of organic compounds in low concentrations, mass transfer processes (i.e. diffusion) may be the limiting step of the photohole capture process that in turn controlled the rate of the overall reaction.$^{26}$ However, for the photocatalytic oxidation of water, it is extremely unlikely that the surface reaction is limited by the mass transfer process under the given experimental conditions due to the overwhelmingly high concentration of water (56 M). Assuming water adsorption at the TiO$_2$ coated electrode surface is the limiting step that controls the surface photohole capture reaction at the higher applied potential range, the saturated
Chapter 6: Study of water adsorption

photocurrent in Figure 6.1 should reflect the rate of photocatalytic oxidation of water at the surface of the TiO$_2$ thin film photoanode.

In this study, a +0.30 V potential bias was selected for all subsequent experiments. This potential bias under the given light intensity was sufficient to suppress photogenerated electron and hole recombination, but not positive enough to cause direct electrochemical oxidation of water at the ITO substrate. Most importantly, at this potential bias, photocatalytic oxidation of water is controlled by the photo-hole capture process at the TiO$_2$ surface, rather than by the electron transport within the semiconductor film.

6.3.2. Transient photocurrent response

For the measurement of photocurrent originating from the photocatalytic oxidation of adsorbed water at the electrode surface, the TiO$_2$ thin film electrode was immersed in the prepared solution without UV illumination for a given pre-adsorption period (the dark time period indicated in Figure 6.2). Upon UV illumination, a sharp photocurrent spike can be observed from the TiO$_2$ thin film photoanode, followed by a photocurrent decay to a steady state ($i_s$). It was found that the steady photocurrent was independent of the pre-adsorption period length. Because the time scale observed in the photocurrent response was much longer than the charging/discharging of the capacitance of the space charge layer and the electric double layer, the transient photocurrent is regarded as a Faradaic photoelectrochemical oxidation process for adsorbed species (water in this case) at the TiO$_2$ electrode surface, as previously reported in studies of photocatalytic degradation of organic compounds.$^{25,26,34}$ When the UV illumination was turned off, the current reduced to a negligible level indicating that the observed photocurrents were a result of the photocatalytic reaction
under the UV illumination, and there was no significant contribution from the direct 
electrochemical oxidation of water under the given applied potential bias.

![Photocurrent-time profile](image)

**Figure 6.2: Photocurrent-time profile**

The transient photocurrent–time profile for different pre-adsorption times, in 
water solution with 0.1M NaNO$_3$ at pH 5.6, 23 °C. $i_s$ is the steady state 
photocurrent.

### 6.3.3. Quantification of charge from the photocurrent

Two methods have been used to quantify the charge generated from the photocatalytic 
oxidation of the pre-adsorbed water: (i) directly measured from the recorded 
photocurrent, and (ii) calculated by computer curve fitting.

**By direct measurement:** Figure 6.3 is a typical photocurrent decay of photocatalytic 
oxidation of adsorbed water with a pre-adsorption time of 90 seconds at pH 5.6. 
Contributions to this photocurrent are twofold: (i) photocurrent from oxidation of the 
pre-adsorbed water during the dark-time period and (ii) oxidation of water from
continuous adsorption during the photocatalytic oxidation reaction under UV illumination.

![Graph showing photocurrent decay profile and double exponential fitting curve.](image)

**Figure 6.3: Photocurrent - time**

The photocurrent decay profile (●) and double exponential fitting curve (---) for the photocatalytic oxidation of water adsorbed onto TiO$_2$ with pre-adsorption time of 90s in 0.1M NaNO$_3$ at pH 5.6. $i_s$ indicates the steady state photocurrent.

The shaded area in Figure 6.3 between the recorded photocurrent ($i_{ph}$) and the steady state photocurrent ($i_s$) represents the collected charges generated by the photocatalytic oxidation of the pre-adsorbed water complexes at the TiO$_2$ photoanode. The charge then can be directly measured by the calculation of the area defined by the photocurrent difference between $i_{ph}$ and $i_s$:

$$Q^0_m = \int (i_{ph} - i_s)dt$$  \hspace{1cm} (6.1)

Equation (6.1) is used to measure the charges $Q^0_m$ from the photocatalytic oxidation of the pre-adsorbed water at the TiO$_2$ photoanode.
**Computer curve fitting:** In studies of the photocatalytic oxidation of organic compounds by TiO$_2$ photocatalysts, it has been previously reported that heterogeneous photocatalytic reactions should follow an exponential decay in regards to both surface coverage and photohole concentration.$^{33,35,36}$ The observed overall photocurrent was a result of the sum of the current components corresponding to the photocatalytic oxidation of different adsorbed surface complexes. The characteristics of different types of adsorbed surface complexes have been studied by photoelectrochemical method$^{33}$ and by an in-situ FTIR spectroscopic technique$^5$ in the investigation of the adsorption of oxalic acid at the TiO$_2$ surface. Assuming the observed overall photocurrent in the photocatalytic oxidation of water is the sum of the individual photocatalytic processes of each type of surface complex, then the total photocurrent $i_{ph}$ in Figure 6.3 can be expressed as the sum of the individual photocurrent components:

$$i_{ph} = \sum_{j=1}^{n} i_{phj}$$  \hspace{1cm} (6.2)

where $i_{phj}$ represents photocurrent generated from the photocatalytic oxidation of the $j$ type surface complex adsorbed at the surface of the TiO$_2$ photoanode.

If we assume that a first order rate law with respect to surface coverage can be applied to each individual photocatalytic oxidation of water at the TiO$_2$ surface, the oxidation of each type of adsorbed surface complex should follow an exponential function with respect to time,$^{33}$ Equation (6.2) can be given as

$$i_{ph} = \sum_{j=1}^{n} a_j e^{-k_j t}$$  \hspace{1cm} (6.3)

where $a_j$ represents the instantaneous initial photocurrent of component $j$, and $k_j$ is the exponential decay constant for component $j$.  

160
Computer curve fitting has found that the observed photocurrents generated from photocatalytic oxidation of adsorbed water at the TiO$_2$ photoanode can be fitted into a double exponential expression:

$$i_{ph} = i_s + a_1 e^{-k_s t} + a_2 e^{-k_f t} \quad (6.4)$$

where $i_s$ is the steady state photocurrent corresponding to the continuous photocatalytic oxidation of water under UV illumination.

Figure 6.3 shows the curve-fitting result of Equation (6.4) into the observed photocurrent. It can be seen that the photocurrent fits well with Equation (6.4) indicating that the surface adsorbed complexes were simultaneously oxidized by two different first-order kinetic processes.

The total charges generated from the photocatalytic oxidation of the adsorbed water can be calculated by Equation (6.4). The calculated charge from the curve fitting, $Q_{fit}^0$, was obtained by a definite integration of Equation (6.4):

$$Q_{fit}^0 = \int_0^\infty (i_{ph} - i_s) dt = \int_0^\infty (a_1 e^{-k_s t} + a_2 e^{-k_f t}) dt = \frac{a_1}{k_s} + \frac{a_2}{k_f} = Q_s^0 + Q_f^0 \quad (6.5)$$

$Q_{fit}^0$ consists of two charge components, $Q_s^0$ and $Q_f^0$, that have different exponential decay constants $k_s$ and $k_f$.

The two charge components in Equation (6.5) $Q_s^0$ and $Q_f^0$, characterized by their distinguished kinetic parameters $k_s$ and $k_f$, represented the charges that were generated through a slow ($k_s$) and a fast ($k_f$) oxidation process, respectively during the photocatalytic oxidation of water under UV illumination.
6.3.4. Kinetics of photocatalytic oxidation of water

The fast and slow kinetic processes in Equation (6.5) can be explained by a multisite complexation model that demonstrates two types of surface complexes formed at the TiO$_2$ photoanode surface due to the structural properties of the TiO$_2$ crystallinity. Studies of organic acid adsorption at the TiO$_2$ surface have shown the different forms of surface bound complexes caused by the heterogeneity of the TiO$_2$ surface.$^{5,33,37,38}$ According to Regazzoni, one form of adsorption site was produced by dissociative water adsorbed on the most stable, perfectly cleaved, (001) and (011) crystal faces of anatase with penta-coordinated surface O$^{2-}$ ions to complete the coordination sphere by binding OH$^-$. Such adsorption site types have been reported to be responsible for the majority of the total adsorptions for a group of organic acids on TiO$_2$ surface.$^{33}$ The minor portion of adsorption sites, with high affinity for adsorbing ligands, was the surface titanium ions at edges and corners with fewer coordination positions occupied by O$^{2-}$. Experimental observation has revealed that the charge generated from the slow process, $Q^0_s$, has dominantly contributed to the total charge (Figure 6.4), and the ratio of the two charge components, $Q^0_s/Q^0_f$, varied from about 5 to 50 fold in solution pH ranging from 3 to 11. Figure 6.4 demonstrates that the ratio $Q^0_s/Q^0_f$ increases with the solution pH up to pH 9. This suggests that the adsorption of dissociate water at the TiO$_2$ surface may largely contribute to the slow component $Q^0_s$ and the molecularly bound water is responsible for the fast component $Q^0_f$. 

---

Chapter 6: Study of water adsorption

---

162
Figure 6.4: Relationship between $Q^0_s/Q^0_f$ and solution pH.

Figure 6.5 shows the charges calculated by Equation (6.5), $Q^0_{fit}$, and the charge $Q^0_m$ calculated by Equation (6.1). Figure 6.5 (a), (b), (c) (d) and (e) demonstrate that the two variables were in good agreement at low charge range, but deviated noticeably at higher ranges. The discrepancy of the charges $Q^0_{fit}$ and $Q^0_m$ at higher adsorption may be attributed to the formation of a second layer adsorption complex on the fully hydrated surface at high adsorption coverage of the TiO$_2$ surface.\textsuperscript{6,39,40} Multi-layer adsorption may result in photocurrent departing from the double-exponential function of Equation (6.4).
Figure 6.5: $Q^0_{fit}$ and $Q^0_m$

(a) (b): Evaluation of the two methods used to calculate overall charge generated from the photocatalytic oxidation of adsorbed water at TiO$_2$ surface for (a) pH 3.1 and (b) pH 5.6. $Q^0_m$ is the measured charge by calculated the shadowed area in Figure 6.3 by Equation (6.1), and $Q^0_{fit}$ is the charge calculated by using Equation (6.5).
Figure 6.5 (c) (d): Evaluation of the two methods used to calculate overall charge generated from the photocatalytic oxidation of adsorbed water at TiO$_2$ surface for (c) pH 7.5 and (d) pH 9.1. $Q^0_m$ is the measured charge by calculated the shadowed area in Figure 6.3 by Equation (6.1), and $Q^0_{fit}$ is the charge calculated by using Equation (6.5).
6.3.5. \( i_s \) and water adsorption under UV illumination

The steady state photocurrent \( i_s \) indicated in Figure 6.3 can be attributed to the continuous oxidation of water under UV illumination at the TiO\(_2\) coated electrode surface. The steady state photocurrent is unaffected by the pre-adsorption time, but is dependent on solution pH (Figure 6.6a) and light intensity (Figure 6.6b).

For a given photoanode, the concentration of total adsorption sites is a constant. Under UV illumination with constant light intensity, the photocatalytic oxidation reaction rate is proportional to the surface coverage of the adsorbed amount of water species. During photocatalytic oxidation under UV illumination, the consumption of pre-adsorbed water at the photoanode surface by photocatalytic oxidation results in

---

\[ Y = 1.0372X + 3.1639 \]
\[ R^2 = 0.9965 \]

**Figure 6.5 (e):** Evaluation of the two methods used to calculate overall charge generated from the photocatalytic oxidation of adsorbed water at TiO\(_2\) surface for (e) pH 11.1. \( Q_{m}^0 \) is the measured charge by calculating the shadowed area in Figure 6.3 by Equation (6.1), and \( Q_{fit}^0 \) is the charge calculated by using Equation (6.5).
the depletion of the occupied sites, which in turn act as free sites for further adsorption.

Figure 6.6: Relationship between steady photocurrent and pH condition
(a) steady photocurrent and pH under light intensity 7mW/cm$^2$ and (b) steady photocurrent and pH under different light intensities.
However, the increase in concentration of free sites causes an increase of water adsorption into the TiO$_2$ photoanode surface. Therefore, the decline of the reaction rate of the oxidation of adsorbed water and the increase of water adsorption into the photoanode surface finally reach a dynamic equilibrium where the surface concentrations of occupied sites and free sites are no longer changing with time, as evidenced by the establishment of the steady state photocurrent $i_s$.

As discussed in section 6.3.1, under the selected potential bias (+0.3 V vs Ag/AgCl), the surface photohole capture process, rather than electron transport inside the electrode thin film, is the limiting step that controls the overall photocatalytic reaction. For the surface photohole capture process, it is highly unlikely that water diffusion is the limiting step owing to its high concentration. Therefore, assuming surface adsorption is the limiting step for the surface reaction, the steady state photocurrent ($i_s$) can be considered as the water adsorption rate under UV illumination. Figure 6.6 shows that $i_s$ increases with the pH value. The change of gradient at pH 7 may be attributed to the change of surface speciation distribution of TiO$_2$ surface groups (Figure 6.10) where the concentration of TiO$^-\text{O}$ rapidly increases with solution pH.

The value of point of zero charge ($pzc$) is a useful indicator of the surface charge of the TiO$_2$, which is an important parameter to characterise the ionisation behaviours at the solid surface. The knowledge of the $pzc$ can help, in principle, to predict whether the ion exchange to a specific component to the oxide system is favoured.$^{41-43}$

When the solid TiO$_2$ is immersed in water, the H$^+$ and OH$^-$ from water will react with the hydroxylated TiO$_2$ surface, adsorption of OH$^-$ in the solution will tend to produce for net negative charge on the surface, while adsorption of H$^+$ in the solution for
positive charged surface. Clearly, the pH of the solution will determine the net charge of the solid surface.\textsuperscript{35} Therefore, the \textit{pzc} of the metal oxide therefore is the value of pH required to give zero net surface charge.

Mass titration method has been widely used in determining the \textit{pzc} of metal oxide colloid particles at different ionic strength. In the mass titration method, the subsequent portions of a metal oxide powder are added to an aqueous electrolyte solution, and the pH of the equilibrated dispersion is measured. The pH of the system approaches a constant value, which equal to the point of zero charge pH if the metal oxide is free of impurities.\textsuperscript{41} The value of \textit{pzc} for TiO$_2$ colloid was reported as 6.5 - 6.9.\textsuperscript{44-47}

The change of gradient of adsorption rate at the TiO$_2$ surface at pH range greater than the \textit{pzc} in Figure 6.6 indicates that negatively charged surface favours the adsorption rate at the TiO$_2$ surface under uv illumination.

To investigate the effect of light intensity on the photocatalytic oxidation of water, the steady state photocurrents were plotted against light intensities for varying solution pH values (Figure 6.7). It was found that the steady state photocurrent linearly increased with light intensity for all solution pH. As the surface photohole concentration for a given TiO$_2$ photoanode is proportional to light intensity,\textsuperscript{31} the observation of the linear increase of $i_s$ with light intensity indicates that the overall photocatalytic oxidation of adsorbed water at the TiO$_2$ photoanode surface is an first-order reaction with respect to the photohole concentration, which is in agreement with our previous work.\textsuperscript{31}
6.3.6. Adsorption rate of water at TiO₂ surface

In order to study the adsorption rate of water at the TiO₂ photoanode surface, the charge $Q_{fr}$ calculated from Equation (6.1) was plotted against the adsorption time under pH conditions ranging from 3.1 to 11.1 (Figure 6.8).

For all pH conditions tested it was found that the amount of charge initially linearly increased with adsorption time. The linearity can be attributed to the low surface coverage of adsorption at the TiO₂ electrode surface. Under these adsorption conditions, the rate of water adsorption on the photoanode surface was a constant that was determined by the slope of the best-fitting linear equations for the initial part of the adsorption curves (insert in Figure 6.8, and Table 6.1).
For longer adsorption times, the charge increase deviated from the initial trend line, indicating the change in adsorption rate. The change in adsorption rate may be due to the water adsorption process approaching the saturation of the first monolayer on the TiO$_2$ photoanode surface or the formation of the second layer, or from a combined effect of first and the second layer adsorption, as reported by Zhang et al.$^{40}$ and Liu$^{39}$ in studies of multilayer water adsorption on TiO$_2$ surface by vibrational spectra.

**Table 6.1:** Equations for charge vs time in Figure 6.8, and adsorption rate.

<table>
<thead>
<tr>
<th>pH</th>
<th>Ads. Rate (μC/s)</th>
<th>Equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 11.1</td>
<td>13.007</td>
<td>$y = 13.007x - 80.938$</td>
<td>0.99592</td>
</tr>
<tr>
<td>pH = 9.1</td>
<td>0.4816</td>
<td>$y = 0.4816x + 3.5612$</td>
<td>0.97897</td>
</tr>
<tr>
<td>pH = 7.5</td>
<td>0.4173</td>
<td>$y = 0.4173x + 5.9796$</td>
<td>0.95796</td>
</tr>
<tr>
<td>pH = 5.6</td>
<td>0.4255</td>
<td>$y = 0.4255x + 3.8053$</td>
<td>0.97867</td>
</tr>
<tr>
<td>pH = 3.2</td>
<td>0.3529</td>
<td>$y = 0.3529x + 2.5578$</td>
<td>0.9664</td>
</tr>
</tbody>
</table>
6.3.7. **Influence of pH on the adsorption rate**

It is widely recognised that solution pH greatly affects adsorption processes of organic compounds at TiO$_2$ surfaces, and particularly for the group of compounds whose speciation is pH dependent. The speciation of the adsorbent due to protonation/deprotonation and the electrostatic interaction between the charged TiO$_2$ surface and adsorbent have been previously reported.$^{25,37,48,49}$ The TiO$_2$ functional group speciation in the presence of water has been calculated from the surface acid-base equilibrium by Kormann et al.$^{49}$ (redrawn in Figure 6.10). In the present work, water adsorption was investigated under a broad range of pH conditions from highly acidic pH 3.1 to basic pH 11.1.

Results of the adsorption rate vs solution pH are shown in Figure 6.9. The insert of Figure 6.9 shows the adsorption rate at lower pH ranges. It was found that adsorption rate slightly increased for lower pH ranging from 3.2 to 9.1, but displayed a dramatic surge at solution pH 11.1. The slight increase of adsorption rate vs pH ranging from 3-9 may be due to the increase of OH$^-$ species concentration and the increase of TiOH at the electrode surface.

From pH 9.1-11.1, adsorption rates displayed a significant upsurge (Figure 6.9), which coincides with the rapid increase of TiO$^-$ distribution at the TiO$_2$ electrode surface (Figure 6.10). By assuming water adsorption is largely contributed to dissociated water (OH$^-$) at low surface coverage,$^6$ the increase of TiO$^-$ concentration favouring the adsorption rate implies that electrostatic charge repulsion has negligible effects on the adsorption process.
Figure 6.9: The relationship between adsorption rate and pH.

The upsurge of the water adsorption rate at high pH illustrated in Figure 6.9 may be attributed to the adsorption of OH\(^-\) at the surface according to a model proposed by Menetrey and Clatayud\(^{50,51}\) in which the strong interaction between the adsorbate and the surface is in favour for the dissociative adsorption. The dissociative water is adsorbed via its O end filling oxygen vacancies, with the remaining H\(^+\) ion bonding to a lattice O ion and forming a second type of OH\(^-\) species.\(^{52}\) In electron spectroscopy studies of water adsorption on the TiO\(_2\) surface with varied stoichiometry, Lo et al.\(^{53}\) reported that the presence of Ti\(^{3+}\) sites on defective surfaces is of particular importance for strong, dissociative adsorption of water. The upsurge of the adsorption rate may be attributed to the O\(_2\) and H\(_2\)O adsorption causing changes of the Ti\(^{3+}\) to a different oxidation state that lead to an increased ability of water adsorption at the TiO\(_2\) surface.
Figure 6.10: Surface speciation distribution

Surface speciation distribution of TiO$_2$ surface groups (redrawn from Kormann et al.$^{49}$) and water self ionization species for various solution pH.

6.4 Conclusions

An *in-situ* photoelectrochemical technique was developed in this work to study the water adsorption behaviour at TiO$_2$ surfaces and the kinetics of heterogeneous photocatalytic oxidation of water at TiO$_2$ surface. Computer curve fitting to the photocurrent has indicated two photocurrent components suggesting two types of adsorbed surface complexes at the TiO$_2$ thin film photoanode.

Studies of water adsorption rates have revealed that the charge $Q_{fit}^0$ initially increased linearly with time, indicating the adsorption followed a monolayer adsorption model. The deviation of the charge from the straight trend line for longer adsorption times suggested saturation of the first adsorption monolayer and the formation of the second layer.
The *in-situ* method employed in this work has proven to be effective in providing useful insights into the water adsorption process at the TiO$_2$ surface.

### 6.5 Reference

(23) Diebold, U. *Surface Science Reports* 2003, 48, 53
(44) Ling, C.; Mohamed, A.; Bhatia, S. *Jurnal Teknologi* 2004, 40(F) Jun, 91.


Chapter 7

**Photoelectrochemical Quantification of Photoelectron Transport inside Nanoparticulate TiO$_2$ Thin film Photoanodes**
Chapter 7: Study of Electron Transport

Chapter 7 Photoelectrochemical Quantification of Photoelectron Transport inside Nanoparticulate TiO$_2$

Thin film Photoanodes

7.1 Introduction

In order to improve photocatalytic efficiency at TiO$_2$ surfaces for the oxidative degradation of organic compounds in solution, much effort has been focused on the reaction mechanism of the photocatalytic process.$^{1-5}$ Among a variety of techniques developed for studying photocatalytic processes, the photoelectrochemical method has proven to be useful and effective for photocatalysis investigation.

Surface adsorption is an important step for photocatalysis, because the interfacial electron transfer is kinetically competitive with the photo hole/electron recombination only when the relevant reactant is pre-adsorbed before photocatalysis.$^6$ In Chapter 4 and Chapter 5, the surface adsorption of organic compounds was studied using the proposed in-situ photoelectrochemical method for strong and weak adsorbates at the TiO$_2$ thin film surface. Water adsorption at the TiO$_2$ surface has a great influence on the efficiency of overall photocatalysis. Chapter 6 presented a study of water adsorption at the TiO$_2$ surface by the developed in-situ photoelectrochemical approach.

High photocatalytic efficiency is the ultimate goal pursued by researchers in the field of photocatalysis. To maintain effective charge separation, one of the charge carriers must be removed from the semiconductor film to compete against the process of charge recombination. For photocatalysis by immobilised TiO$_2$ thin film
photocatalyst, electrons are removed through a external circuit under a potential bias applied to the TiO\textsubscript{2} thin film photoanode\textsuperscript{3,7}.

In general, the conductivity of nanostructured TiO\textsubscript{2} thin-film is low under ‘dark’ conditions (i.e. $< 10^{-7}$ S, measured by the four-point technique under dry nitrogen\textsuperscript{8}). Its conductivity is significantly increased under UV illumination (i.e. in an order of $10^{-3}$ S, reported by Jiang \textit{et al.}\textsuperscript{7}). This is attributed to the lowering of the conductivity activity energy and the upward shifting of the Fermi level\textsuperscript{9}. These results suggest that low conductivity in the dark is due to the low electron concentration in the conduction band rather than the poor electrical conductivity of the TiO\textsubscript{2} particles\textsuperscript{3,9}.

A substantial effort has been devoted to understanding the charge transport process inside the TiO\textsubscript{2} photocatalyst using different experimental techniques\textsuperscript{10-12}. Charge transport and recombination kinetics of nanoparticulate and ordered nanotube TiO\textsubscript{2} photocatalysts have been investigated using intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS)\textsuperscript{13,14}. Charge transport and recombination are the two competitive processes that directly affect the overall efficiency of the photocatalytic system. It has been reported that while both nanoparticulate and nanotube thin film display comparable transport times, recombination occurs at slower rate for nanotube films, leading to significantly higher charge-collection efficiency for nanotube TiO\textsubscript{2} films than for the nanoparticulate film\textsuperscript{13}.

In studies of a photocatalytic process by photoelectrochemical method in which TiO\textsubscript{2} nanoparticles are immobilised onto a conducting substrate to form a thin film photoanode, a potential bias is often applied to the TiO\textsubscript{2} photoanode to remove the photoelectrons in order to suppress the recombination process. The rapid removal of
the photoelectron is an important factor that results in improvement of the photocatalytic oxidation process efficiency.\textsuperscript{6,7,15,16} The observed photocurrent from the photo-induced oxidation is affected by many factors including the incident light intensity, the concentration of the photohole scavenger in the solution and the magnitude of the applied potential bias. Depending on the given experimental conditions, these factors can be the rate-limiting step of the overall photocatalytic reaction. Jiang and others have proposed a model to characterise the charge transport of TiO\textsubscript{2} film photoanodes. By using glucose as a model photohole scavenger, analysis of the photocurrent response to the applied potential bias revealed that the total reaction resistance during the photocatalytic reaction consisted of two components:\textsuperscript{7}

(i) the component reaction resistance that was affected by reaction conditions such as light intensity and surface concentration of the photohole scavenger. This was attributed to the nature of the surface photocatalytic reaction that generated photoelectrons.

(ii) the intrinsic resistance of the photoanode resulting from the TiO\textsubscript{2} crystal boundary resistances and from the contact resistances at the conducting substrate/TiO\textsubscript{2} interface.

This chapter aims to investigate the electron transport properties inside TiO\textsubscript{2} thin film photocatalysts. Because photocatalyst film thickness has a significant influence on electron transport efficiency within the film, a photoelectrochemical approach was employed to study how film resistance was affected by photoanode thickness in the photocatalytic oxidation of organic compounds. In this study, glucose was chosen as the model compound, and the overall photocatalytic reaction was manipulated by
altering the applied potential bias to study the photocatalytic reaction controlled by different limiting steps. By measuring the photocurrent response to the applied potential bias for various glucose concentrations and incident light intensities, the total resistance of a given TiO$_2$ thin film photoanode is quantified.

### 7.2 Experimental

#### 7.2.1. Materials

Indium tin oxide (ITO, 8 Ω/square) conducting glass slides were purchased from Delta Technologies Limited (USA). Titanium butoxide (97%, Aldrich), D-glucose (AnalaR, BDH) and sodium nitrate (99%, BDH) were used as received without further purification. All other chemicals were of analytical grade unless otherwise stated and all solutions were prepared using high purity deionised water (Millipore Corp. 18 MΩ cm).

#### 7.2.2. Fabrication of TiO$_2$ thin film photoanodes

The TiO$_2$ colloid was prepared by the hydrolysis of titanium butoxide according to a procedure described by Nazeeruddin et al. The resultant colloidal solution contains ca. 60 g dm$^{-3}$ of TiO$_2$ solid. 30% (w/w) of Carbowax (Supelco) was added to increase the porosity of the final TiO$_2$ film. ITO glass slides were used as the electrode substrate.

In this work, the inkjet-printing technique was chosen for TiO$_2$ colloid immobilisation onto conducting glass substrates to fabricate reproducible and uniform thin film photoanodes. Compared to various techniques that have been developed for the immobilisation of TiO$_2$ photocatalysts, such as sol-gel dip-coating, spin-coating, sputtering and chemical vapour deposition, inkjet printing has proven to be more effective in controlling the thickness of the resultant thin films with more
reproducible results.\textsuperscript{23} For these reasons, the inkjet-printing technique has been employed for large-scale production of solar cells.\textsuperscript{24-26}

A commercially available Epson R290 inkjet printer was for print coating of the TiO\textsubscript{2} colloid onto ITO glass substrates where a uniform thin film was formed after each print. The thickness of the photoanode was controlled by repeating the printing procedure so new layers of small TiO\textsubscript{2} colloidal grains were added onto the ITO glass substrate for each print. The coated substrates were placed on a level platform for 30 minutes to air dry, then subjected to calcination in a muffle furnace at 700°C in air for 16 h to remove the carbowax and improve film adhesion and crystallinity. The surface structure and thickness of the thin film photoanode were measured by field emission scanning electron microscope (FESEM, Tokyo, Japan).

### 7.2.3. Photoelectrochemical measurement

The experiment setup for the photoelectrochemical measurements is schematically illustrated in Figure 2.4 in Chapter 2. All experiments were carried out at 25°C in a three-electrode photoelectrochemical cell with a quartz window for UV illumination.\textsuperscript{7,27,28} The TiO\textsubscript{2} thin film working-electrode was mounted onto an electrode holder with a 0.78 cm\textsuperscript{2} area for UV exposure and in contact with the solution for photoelectrochemical reactions. A saturated Ag/AgCl electrode and a platinum mesh were used as the reference and auxiliary electrodes, respectively. The UV illumination was provided by a 150 W Xenon arc lamp light source with focusing lenses (HF-200w-95, Beijing Optical Instruments). Light intensity was measured with a UV irradiance meter (UVA, Instruments of Beijing Normal University). The light intensity was carefully controlled and measured at wavelength of 365 nm. To avoid the electrolyte being heated by the infrared component of the light source, the
light beam passed a UV-band-pass filter (UG5, Avotronics Pty. Ltd) before illuminating the surface of the TiO$_2$ thin film photoanode. To minimise the influence of solution resistance and the electrolyte migration effect, 0.1 M NaNO$_3$ was chosen as the supporting electrolyte. A voltammograph (CV-27, BAS) was used for application of potential bias for the linear sweep voltammetry (LSV). The applied potential and photocurrent signals were recorded through a Maclab 400 interface (AD Instruments).

### 7.3 Results and Discussion

#### 7.3.1. Structural and phase compositional characteristics of the photoanodes

Field emission scanning electron microscope (FESEM) analysis was carried out to measure the actual particle size and distribution of the crystallites (Chapter 2). Images of the film surface shown in Figure 2.3 appeared to be rough and porous, which is a characteristic phenomenon of TiO$_2$ nanoparticles prepared by this method.$^{29}$

The values of the thicknesses in different parts of the cross-section SEM image were averaged to represent the thickness of the TiO$_2$ thin film. In this work, four photoanodes with different thickness were prepared for photoelectrochemical characterisation. The film thicknesses of the photoanodes were calculated from the cross-section SEM images (Figure 7.1 and Figure 7.2) and are listed in Table 7.1.

**Table 7.1: Film thickness for each photoanode**

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>Film thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T$_{0.2}$</td>
<td>0.2 ± 0.01</td>
</tr>
<tr>
<td>T$_{0.4}$</td>
<td>0.4 ± 0.03</td>
</tr>
<tr>
<td>T$_{1.0}$</td>
<td>1.0 ± 0.05</td>
</tr>
<tr>
<td>T$_{1.5}$</td>
<td>1.5 ± 0.1</td>
</tr>
</tbody>
</table>
Chapter 7: Study of Electron Transport

It has been reported that pure anatase phase TiO$_2$ thin film is prepared by sintering TiO$_2$ colloid at 500°C, and formation of mixed anatase/rutile phases were obtained by calcination at higher temperature above 700°C.$^{30,31}$ X-ray diffraction (XRD) analysis was performed to determine the morphological structure of the prepared
photoanodes. Figure 7.3 illustrates the XRD patterns of a TiO$_2$ photoanode to show the relative intensity of diffraction peaks in the pattern corresponding to the anatase and rutile phases of the TiO$_2$ sample prepared by calcination at 700°C.

![XRD analysis patterns](image)

**Figure 7.3: XRD analysis patterns.**

*The photoanode was prepared by calcination in a muffle furnace at 700°C for 16h in air.*

The composition of the prepared TiO$_2$ thin film was calculated by the peak intensity ratio of $I_A/I_R$ according to the procedure developed by Spurr and Myers. The results of phase composition for the TiO$_2$ film prepared under the experimental conditions were discussed in Chapter 2.

### 7.3.2. Effect of potential bias, light intensity and glucose concentration

**Effect of potential bias:** The role that the applied potential bias plays in a photocatalytical process, in particular, electron transport within the TiO$_2$ semiconductor photocatalyst has been previously investigated and reported. In contrast to bulk semiconductors, a nanoparticulate TiO$_2$ thin film photoanode has no
band bending within the TiO$_2$ particles. Because both photo-generated electrons and holes reside on the TiO$_2$ surface, one of the charge carriers must be rapidly removed from the surface to maintain an effective charge separation in order to compete with the charge recombination process. Electron transport within the TiO$_2$ thin film occurs by migration under the electric field of the applied potential bias.\textsuperscript{7}

To characterise the effect of applied potential bias on the photocatalytic oxidation of glucose at the surface of TiO$_2$ thin film photoanodes, Linear Sweep Voltammetry (LSV) was used to determine the photocurrent response to the applied potential bias under varying light intensities and glucose concentrations.

It is well known that the kinetic characteristics of a photocatalytic oxidation reaction can be largely influenced by the applied potential bias.\textsuperscript{36} Figure 7.4 displays a typical photocurrent response to the applied potential. The photocurrent shows a linear increase with the potential ranging from -0.3 to -0.1 V, then the photocurrent reaches a saturated level at a higher potential bias. The photocurrent response is in agreement with the results from previous measurements that were conducted under similar experimental conditions.\textsuperscript{7} The observed linear increase and the saturated photocurrent may be explained by the different rate-limiting steps that control the overall photocatalytic reaction. In the linear photocurrent range under applied potential between -0.3 to -0.1V, electron transport within the TiO$_2$ film is the rate limiting process. In such situation, the photo-generated electron at the TiO$_2$ particle surface is surplus to the applied potential bias and is the decisive factor for the overall reaction rate. The applied potential bias serves as an external driving force to remove the photo-generated electron from the TiO$_2$ conduction band to the conducting substrate. Under these circumstances, the photocurrent and the potential bias behaviour in the
photocatalytic system are similar to a pure resistance defined by Ohm’s law. In the photocatalytic oxidation reaction, the total resistance, $R$, is defined by the ratio of the change of applied potential bias to the change of photocurrent.

$$R = \frac{\Delta E}{\Delta i_{ph}}$$  \hspace{1cm} (7.1)

**Figure 7.4:** Linear increase of photocurrent with the applied potential.

The gradient ($\Delta i_{ph}/\Delta E$) of the curve is calculated by the best-fit linear equation. The total resistance in Equation (7.1) is obtained from the reciprocal of the calculated gradient.

Total resistance values were calculated from the linear range of the photocurrent by the best-fitting linear equation (Figure 7.4).

The photocurrent in Figure 7.4 reaches the saturation level at higher applied potential bias where the overall photocatalytic reaction is limited either by the interfacial reaction step or by the mass transfer process in the solution. Therefore, the saturated
photocurrent, \( i_{ph} \), at higher potential range represents the maximum reaction rate for the photocatalytic oxidation reaction under the given experimental conditions.\(^7\)

A slight increase in saturated photocurrent was observed, and may be attributed to the oxidation of water whose concentration is overwhelmingly high (ca. 56 M, details of the influence of water oxidation by TiO\(_2\) thin films in a photocatalytic process have been discussed in Chapter 3).

**Effect of light intensity and glucose concentration:** Figure 7.5 shows the photocurrents of photocatalytic oxidation of glucose for different concentrations and light intensity. In both cases, photocurrent response to the applied potential bias displays two stages indicating that the overall reaction being controlled by different limiting steps. The magnitude of the saturated photocurrent increases with both the glucose concentration (Figure 7.5a) and the incident light intensity (Figure 7.5b).

---

**Figure 7.5:** Voltammograms of TiO\(_2\) thin film photoanode \( T_{0.4} \).

---
Photocurrent response to the applied potential bias was obtained under (a) concentrations of 5, 2, 1, 0.5, 0.2, 0.1 and 0 mM glucose from top to bottom under light intensity of 5 mW/cm$^2$, and (b) light intensities of 7, 6, 5, 4, and 3 mW/cm$^2$ from top to bottom with glucose concentration of 0.2 mM.

Figure 7.6 shows the relationship of the saturated photocurrent $i_{sph}$ with the glucose concentration for electrode $T_{0.4}$ and $T_{1.5}$. Figure 7.6 reveals that the saturated photocurrent increases linearly with the glucose concentration at low concentration range up to 0.3 mM. In this concentration range, the overall photocatalytic reaction is limited by the mass transfer process of the glucose from the bulk solution to the TiO$_2$ photoanode surface. At higher glucose concentration, mass transfer is no longer the limiting step, and the saturated photocurrents deviate from the linear range. The interfacial reaction at the photoanode surface is controlling step for the overall photocatalytic process.\footnote{7}
Figure 7.6: Relationship between saturated photocurrent and glucose concentration for photoanode $T_{0.4}$ and $T_{1.5}$ under UV light intensity of 5mW/cm$^2$.

At the applied potential region where the photocurrent reaches the saturated level, the rate-determining step was the interfacial reaction rather than the electron transport process within the TiO$_2$ thin film. The linear relationship in Figure 7.7 indicates that the interfacial reaction rate is first order with respect to the concentration of surface bound photoholes which is determined by the incident radiation.$^{2,7}$ The first order relationship with light intensity is an interesting feature of the immobilised TiO$_2$ photocatalyst in contrast to TiO$_2$ colloidal suspension where a half-order relationship between reaction rate and light intensity was reported.$^2$
The results presented in Figure 7.6 and Figure 7.7 suggest that the saturated photocurrent (i.e. the maximum interfacial reaction rate) is first order with respect to both surface photohole concentration and surface glucose concentration, and the saturated photocurrent can be expressed as:

$$i_{sph} = k_i \times C_{s, \text{glucose}} \times C_{s, \text{photohole}}$$  \hspace{1cm} (7.2)

where $C_{s, \text{glucose}}$ is the surface concentration of the glucose, $C_{s, \text{photohole}}$ is the surface photohole concentration, and $k_i$ is the rate constant for the surface reaction.

### 7.3.3. Effect of film thickness and the saturated photocurrent

Figure 7.8 illustrates the relationship between the saturated photocurrent and the film thickness. Under the experimental conditions, the saturated photocurrent increases with film thickness, but levels off for photoanodes of high film thickness (i.e., 1.0 µm and 1.5 µm, Figure 7.8).
Figure 7.8: Relationship between saturated photocurrent and film thickness.

The total resistance defined by Equation 7.1 is calculated from the linear increasing section of the photocurrent in the voltammograms. Total resistance decreased with film thickness, but levelled off in the higher film range (Figure 7.9).

Figure 7.9: Relationship between total resistance and film thickness at a light intensity of 5.0 mW/cm².
The effect of film thickness on the saturated photocurrent and the total resistance may be attributed to the porous nature of the TiO$_2$ film photoanode and the properties of UV absorption by the film.

Figure 7.10 schematically presents a model that may explain the effect of photoanode film thickness on the saturated photocurrent of a photocatalytic process. By immersing the TiO$_2$ porous photoanode into the electrolyte solution, the electrolytes percolate the whole TiO$_2$ thin film to reach the surface of the conducting substrate. Under UV illumination, photohole and electron pairs are generated at the surface of TiO$_2$ particles near the TiO$_2$/electrolyte interface, much like the situation in a normal colloidal system. The photoholes migrate to the TiO$_2$ particle surface where an electron from a donor species (i.e., glucose) can combine with the surface photoholes. However, the electrons must pass several crystallites before reaching the conducting substrate to be collected as photocurrent. The probability of the electron recombining with the photohole depends on the length of the path starting from the photo-excited particle to the conducting substrate.

For very thin film photoanodes, UV radiation penetrates the whole depth of the film. Under the constant light intensity, the photocurrent increases with film thickness because of the increase in the total photo-generated electron/hole pairs within the TiO$_2$ thin film. However, as the film thickness increases, surface electrons need to travel a longer distance before reaching the conducting substrate. The increase in the probability of photo hole/electron recombination may contribute to the results in which the saturated photocurrents levelled off for film thicknesses between 1.0 – 1.5 µm in Figure 7.7.
Figure 7.10: A model of charge transport in TiO$_2$ thin film photoanodes with different film thicknesses.
Chapter 7: Study of Electron Transport

Figure 7.9 illustrates the relationship between the total resistance of the TiO$_2$ thin film photoanode and film thickness. The total resistance, calculated from the reciprocal of the gradient of linear part of photocurrent (Equation (7.1)), decreases with film thickness. However, the total resistance reaches a constant value for photoanodes with increasing film thickness which is in agreement with the assumption described in the model in Figure 7.10.

7.3.4. Quantification of resistance

The total resistance defined in Equation (7.1) was photoelectrochemically determined from the linear photocurrent increase section of the voltammograms (Figure 7.4). Analysis of the relationship between total resistance, $R$, and the saturated photocurrent, $i_{sph}$, revealed that the total resistance for the photocatalytic process is reciprocally proportional to the saturated photocurrent, and can be represented by a linear equation:  

$$ R = \frac{k}{i_{sph}} + R_0 $$

(7.3)

where $k$ is a proportional constant and $R_0$ is the $y$-intercept of the $R$ axis. Figure 7.11 illustrates the relationship between the total resistance $R$ and $1/i_{sph}$ for four photoanodes. Table 7.2 summarises the values of $k$, $R_0$ and film thickness of the four photoanodes tested in this investigation.

**Table 7.2:** Film thickness and values of $k$ and $R_0$ for the four photoanodes tested.

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>Film thickness</th>
<th>$k$ (V)</th>
<th>$R_0$ (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T$_{0.2}$</td>
<td>0.2 ± 0.01</td>
<td>0.3944</td>
<td>0.07271</td>
</tr>
<tr>
<td>T$_{0.4}$</td>
<td>0.4 ± 0.03</td>
<td>0.3255</td>
<td>0.13469</td>
</tr>
<tr>
<td>T$_{1.0}$</td>
<td>1.0 ± 0.05</td>
<td>0.3102</td>
<td>0.28774</td>
</tr>
<tr>
<td>T$_{1.5}$</td>
<td>1.5 ± 0.1</td>
<td>0.2966</td>
<td>0.34549</td>
</tr>
</tbody>
</table>

198
Chapter 7: Study of Electron Transport

**Figure 7.11**: Resistance and inversed saturated photocurrent

(a) photoanode $T_{0.2}$ and (b) photoanode $T_{0.4}$. The total resistance was plotted against $1/i_{sph}$ to fit Equation 7.3. Values of $k$ and $R_0$ are summarised in Table 7.2.
Figure 7.12: Resistance and inversed saturated photocurrent

(c) photoanode $T_{1.0}$ and (d) photoanode $T_{1.5}$. The total resistance was plotted against $1/i_{sph}$ to fit Equation 7.3. Values of k and $R_0$ are summarised in Table 7.2.
The first term in Equation (7.3), \( k/i_{ph} \), is the reaction resistance for the photocatalytic system. It is a variable component depending on the experimental conditions of the photocatalytic process. As shown in Figure 7.6 and Figure 7.7, the saturated photocurrent represents the maximum reaction rate of the photocatalytic reaction, and it is a function of both glucose concentration and incident light intensity.

The parameter \( k \) in Equation (7.3) can be calculated from the gradient of the curve shown in Figure 7.11. The \( k \) value represents the minimum applied potential bias required to completely remove the photo-generated electrons from the thin film photoanode (i.e., the saturated photocurrent). For a given light intensity and glucose concentration, the saturated photocurrent is determined by the thickness of the film photoanode. The thicker the film, the higher photocurrent produced from photo oxidation of glucose (Figure 7.8), and the lower the total resistance (i.e., requiring lower potential to produce a given level of photocurrent, Figure 7.9). For this reason, \( k \) decreases with film thickness, as illustrated in Figure 7.12.

The second term in Equation (7.3), \( R_0 \), is the invariable part of the total resistance for a given TiO\(_2\) film photoanode, regardless of experimental conditions. \( R_0 \) can be interpreted as an intrinsic property of the TiO\(_2\) thin film photoanode, and is the collective result of the resistance between the grain crystalline boundaries and the contact resistance between the TiO\(_2\) particle and the conducting substrate.

The fact that \( R_0 \) linearly increases with film thickness supports the assumption that \( R_0 \) represents the collective results of the resistance between the grain crystalline boundaries that the electrons must pass to reach the conducting substrate (Figure 7.13).
Chapter 7: Study of Electron Transport

Figure 7.13: Relationship between $k$ values and film thickness.

Figure 7.14: Relationship between $R_0$ and film thickness
Chapter 7: Study of Electron Transport

7.4 Conclusions

A photoelectrochemical method was proposed to investigate the electron transport process within TiO₂ thin films. Glucose was chosen as the model compound for studying the photocatalytic oxidation reaction by the TiO₂ semiconductor photocatalyst. The photocurrent response to the applied potential bias can be classified into two stages that were controlled by different limiting steps. The linear increase in photocurrent with applied potential bias is controlled by electron transport within the TiO₂ thin film. The saturated photocurrent, representing the maximum reaction rate, is dependent on both surface glucose concentration and the incident light intensity. Linear increase of the saturated photocurrent with light intensity and surface glucose concentration suggests that the reaction rate is first order to both variables. The total resistance for a thin film photoanode was defined by the ratio of change in applied potential bias to the change in photocurrent. Analysis of the photocurrent obtained from the photocatalytic oxidation of glucose revealed that the total resistance consists of two components. The variable component is reciprocally proportional to the saturated photocurrent, which is subject to the experimental conditions. The invariable component is an intrinsic property for a given photoanode whose value increases with TiO₂ film thickness.

7.5 Reference


Chapter 8

General Conclusions
Chapter 8 General Conclusions

8.1 Summary

For the past two decades, a great deal of effort has focused on searching for new energy sources and environmentally friendly decontamination technologies. TiO$_2$ is a semiconductor material with significant application potential in environmental remediation and solar energy conversion, due to its superior photoactivity and high resistance to photo-corrosion.

This thesis presents a series of investigations into the properties of photocatalytic oxidation of organic compounds by immobilised TiO$_2$ photocatalysts. Its aim was to develop new methodologies that can systematically evaluate the performance of the TiO$_2$ photocatalyst with respect to the three major consecutive steps in a photocatalytic process.

8.2 Conclusions

Mass transfer in a photocatalytic process was first studied by the proposed *in-situ* photoelectrochemical method, and the effective diffusion coefficients of a group of organic compounds were determined.

The measurement of diffusion coefficients of organic compounds is based on a photoelectrochemical principle that when a photocatalytic process is in diffusion control, the diffusion coefficient is directly proportional to the limiting current according to Fick’s law. This simple and effective method can be a useful tool in providing information for studying mass transfer processes in a photoelectrocatalytic process. The diffusion coefficient calculated by this method should directly reflect the characteristics of the mass transfer process in the given photocatalytic system.
Studies of interfacial reactions of a photocatalytic process have focused on surface adsorption and desorption of reactants at the TiO$_2$ surface. In this work, the adsorption properties of a strong adsorbate (phthalic acid), and a weak adsorbate (methanol) at the TiO$_2$ thin film surface were investigated by a proposed $in$-$situ$ photoelectrochemical method. In this $in$-$situ$ method, both adsorption and the measurement processes occur in the same electrochemical cell containing a solution of the organic compound and supporting electrolytes. By this technique, the electrode washing step between the two processes, as required in the $ex$-$situ$ method, can be avoided and accurate adsorption measurement for short time scale has become possible.

In the study of phthalic acid adsorption, when the photocatalytic reaction was under diffusion control, the surface coverage could be directly quantified from the observed photocatalytic oxidation current. For the study of methanol adsorption, due to the weak adsorption nature and the doubling current effect from the photocatalytic oxidation of methanol, the magnitude of the initial photocurrent spike, rather than the current decay, was used to quantify the surface coverage of the organic compound. It was found that in both cases, the adsorption isotherm followed a Langmuir adsorption model. The adsorption equilibrium constants for phthalic acid and methanol at the TiO$_2$ thin film were determined by employing this $in$-$situ$ photoelectrochemical method. In summary, a simple approach for studying the adsorption of organic compounds was proposed and validated, and has great potential for the investigation and characterisation of both strong and weak organic adsorbates for TiO$_2$ photocatalytic systems.
Water adsorption properties at the TiO\textsubscript{2} surface were studied using an *in-situ* photoelectrochemical method. For a process of photocatalytic oxidation of adsorbed water at the TiO\textsubscript{2} surface, photocurrent decay was analysed by computer curve fitting based on the assumption that the photocatalytic oxidation of the adsorbed water followed a first order rate reaction, and the overall photocurrent was the sum of the individual components. The result of computer curve fitting revealed the existence of two types of adsorbed surface complexes at the TiO\textsubscript{2} thin film electrode. Adsorption rate at the TiO\textsubscript{2} surface was also investigated. The initial linear increase of adsorption with time can be explained by the monolayer adsorption model, and the subsequent deviation from the linearity indicates the saturation of the first adsorption monolayer, and the formation of the second adsorption layer.

In the last chapter of this thesis, a photoelectrochemical method was proposed to study the properties of electron transport within TiO\textsubscript{2} thin films. In general, the low conductivity of nanoparticulate TiO\textsubscript{2} photocatalysts under dark conditions is due to low electron concentration in the conduction band, rather than poor electrical conductivity in the contact of TiO\textsubscript{2} particles. In this study, photocurrent of voltammograms in photocatalytic oxidation of glucose under UV illumination revealed the existence of two stages of the photo oxidation reaction that were controlled by different limiting steps. The linear increase of photocurrent with applied potential bias suggests that electron transport within the TiO\textsubscript{2} film is the limiting step, and the electric property of the TiO\textsubscript{2} photoanode at this stage is similar to that of a pure resistance in regards to its current response to the potential change. At higher potential bias ranges, the photocurrent reaches a saturated level that represents the maximum reaction rate for the photocatalytic oxidation of glucose. The
saturated photocurrent is dependent on the incident light intensity and glucose concentration.

The total resistance for a given TiO$_2$ thin film photoanode was defined by the rate of changing applied potential bias over the change of photocurrent. Analysis of the observed photocurrent from the voltammograms revealed that the total resistance consists of two components. The reaction resistance, the variable component of the total resistance, is reciprocally proportional to the saturated photocurrent, and is subject to experimental conditions. The invariable component $R_0$ is an intrinsic property for a given photoanode whose value increases with the TiO$_2$ film thickness.

8.3 Suggestions for future work

Several research interests in the field of TiO$_2$ photocatalysts appear promising.

The improvement of TiO$_2$ photocatalysis efficiency is largely dependent on overcoming the electron-hole recombination within the photocatalyst. Mixed phase TiO$_2$ based composite material has shown higher photo-activity in comparison to pure phase TiO$_2$ in photocatalysis due to the fact that the solid-solid interfaces enable rapid electron transfer from rutile to anatase. Efforts to combine TiO$_2$ with active carbon or carbon nanotube in simple mixtures have been reported in an attempt to reduce electron-hole recombination. The photoelectrochemical method proposed in Chapter 7 could be considered a simple and effective way in characterising electron transport within the photocatalyst. The intrinsic resistance measured by the photocurrent response to applied potential bias would be interesting in revealing the electric resistance of interfaces.
The *in-situ* method in determining diffusion coefficient may be useful in other photocatalytically oxidisable species including both organic and inorganic compounds.

To demonstrate economic feasibility for large scaled applications in photocatalysis, researchers need to design reactors and to study kinetics of the heterogeneous photocatalytic process on immobilised semiconductor catalyst in order to increase the efficiencies of photocatalytic degradation to mineralise a host of water contaminants. The photocatalytic processes include destruction of toxic organics in wastewater, oxidation of liquid hydrocarbons, and transformation of toxic inorganic ions into less harmful species.

Scale-up or reconfiguration of photocatalyst systems requires understanding of the mass transfer process in order to investigate the experimental conditions for newly designed reactors in photocatalytic degradation of contaminants.

The measuring principle of the proposed *in-situ* method can be applied for quick evaluation of the mass transfer in a photocatalytic process in a particular reactor geometry under the given experimental configuration. Knowledge of mass transfer of the compound in the photocatalytic process would be useful in design of reactors and optimisation of experimental condition.

Understanding the effects of water adsorption at the TiO$_2$ surface in a photocatalytic process is of uttermost importance as most TiO$_2$ photocatalytic applications involve aqueous media. In order to get structural information of the surface atoms, great effort has been directed to the determination of the nature of the surface reactive groups. The mechanism of water adsorption onto the TiO$_2$ surface is still a matter of debate because of the two adsorption models of water that interact with the TiO$_2$
surface. The *in-situ* photoelectrochemical method proposed in this thesis may provide a useful tool in understanding the adsorption mechanisms from the photocatalytic oxidation of the adsorbed water at the TiO$_2$ surface, and knowledge of water adsorption at the TiO$_2$ surface can be beneficial in searching of anti-fogging and self-cleaning materials by exploiting the UV radiation induced hydrophilicity of the surface coated TiO$_2$, also in the field of biosensors by adsorption of proteins on TiO$_2$ and in study of dye-sensitised solar cell.