STUDIES OF PHOTOCATALYTIC PROCESSES AT NANOPOROUS TiO₂ FILM ELECTRODES BY PHOTOELECTROCHEMICAL TECHNIQUES AND DEVELOPMENT OF A NOVEL METHODOLOGY FOR RAPID DETERMINATION OF CHEMICAL OXYGEN DEMAND

A thesis submitted in fulfillment of the requirement for the award of the degree

DOCTOR OF PHILOSOPHY

From Griffith University

by

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School of Environmental and Applied Sciences

JUNE 2004
DECLARATION

I hereby declare that the work presented in this thesis is original and was carried out by the candidate in the School of Environmental and Applied Sciences, Griffith University; and has not been submitted for any degree at any other university or institution.

Signature of Candidate
ACKNOWLEDGEMENTS

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Huijun Zhao, Dianlu Jiang, Richard John, Novel photoelectrochemical oxygen demand assay, Australian Provisional Patent 2003901589, 2003

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Shanqing Zhang, Huijun Zhao, Dianlu Jiang, Richard John, Photoelectrochemical Determination of Chemical Oxygen Demand Based on an Exhaustive Degradation Model in a Thin-layer Cell, Analytica Chimica Acta, in press.


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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>A</td>
<td>Apparent surface Area of Electrodes</td>
</tr>
<tr>
<td>Ag/AgCl</td>
<td>Silver/Silver Chloride Reference Electrode</td>
</tr>
<tr>
<td>BOD</td>
<td>Biochemical Oxygen Demand</td>
</tr>
<tr>
<td>C</td>
<td>Molar Concentration</td>
</tr>
<tr>
<td>C&lt;sub&gt;eq&lt;/sub&gt;</td>
<td>Equivalent Concentration</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td>C&lt;sub&gt;S&lt;/sub&gt;glu</td>
<td>Surface Concentration of Glucose</td>
</tr>
<tr>
<td>C&lt;sub&gt;S&lt;/sub&gt;h</td>
<td>Surface concentration of photoholes</td>
</tr>
<tr>
<td>D</td>
<td>Diffusion Coefficient</td>
</tr>
<tr>
<td>E</td>
<td>Electrode Potential with Reference to Ag/AgCl Electrode</td>
</tr>
<tr>
<td>e</td>
<td>Electron</td>
</tr>
<tr>
<td>E&lt;sub&gt;c&lt;/sub&gt;</td>
<td>Conduction Band Position of Semiconductor</td>
</tr>
<tr>
<td>E&lt;sub&gt;cs&lt;/sub&gt;</td>
<td>Conduction Band Position at the Interface</td>
</tr>
<tr>
<td>E&lt;sub&gt;F&lt;/sub&gt;</td>
<td>Fermi Level</td>
</tr>
<tr>
<td>E&lt;sub&gt;flat&lt;/sub&gt;</td>
<td>Flatband Potential</td>
</tr>
<tr>
<td>E&lt;sub&gt;g&lt;/sub&gt;</td>
<td>Band Gap of Semiconductor</td>
</tr>
<tr>
<td>eq</td>
<td>Equivalent Mole</td>
</tr>
<tr>
<td>E&lt;sub&gt;on-set&lt;/sub&gt;</td>
<td>Potential at Which Anodic Photocurrent Starts to Flow</td>
</tr>
<tr>
<td>E&lt;sub&gt;v&lt;/sub&gt;</td>
<td>Valence Band Position of Semiconductor</td>
</tr>
<tr>
<td>E&lt;sub&gt;vs&lt;/sub&gt;</td>
<td>Valence Band Position at the Interface</td>
</tr>
<tr>
<td>F</td>
<td>Faraday Constant</td>
</tr>
<tr>
<td>fs</td>
<td>Femtosecond</td>
</tr>
<tr>
<td>hν</td>
<td>Photons</td>
</tr>
<tr>
<td>h&lt;sup&gt;+&lt;/sup&gt;</td>
<td>Photohole</td>
</tr>
<tr>
<td>I&lt;sub&gt;blank&lt;/sub&gt;</td>
<td>Steady State Photocurrent for Blank Solution</td>
</tr>
<tr>
<td>I&lt;sub&gt;ph&lt;/sub&gt;</td>
<td>Photocurrent</td>
</tr>
<tr>
<td>I&lt;sub&gt;sph&lt;/sub&gt;</td>
<td>Saturation Photocurrent with Respect to Potential</td>
</tr>
<tr>
<td>I&lt;sub&gt;sph&lt;/sub&gt;</td>
<td>Steady State Photocurrent</td>
</tr>
<tr>
<td>I&lt;sub&gt;phM&lt;/sub&gt;</td>
<td>Maximum Steady State Photocurrent with Respect to Concentration</td>
</tr>
<tr>
<td>K</td>
<td>Adsorption Equilibrium Constant</td>
</tr>
<tr>
<td>k</td>
<td>Boltzmann Constant</td>
</tr>
<tr>
<td>k&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Reaction Rate Constant</td>
</tr>
<tr>
<td>KHP</td>
<td>Potassium Hydrogen Phthalate</td>
</tr>
<tr>
<td>k&lt;sub&gt;L,H&lt;/sub&gt;</td>
<td>Rate Constant Base on Langmuir-Hinshelwood Kinetic Model</td>
</tr>
<tr>
<td>L&lt;sub&gt;D&lt;/sub&gt;</td>
<td>Debye Length</td>
</tr>
<tr>
<td>LH</td>
<td>Langmuir-Hinshelwood</td>
</tr>
<tr>
<td>mC</td>
<td>Milli-coulomb</td>
</tr>
<tr>
<td>mM</td>
<td>Millimolar</td>
</tr>
<tr>
<td>ms</td>
<td>Millisecond</td>
</tr>
<tr>
<td>N&lt;sub&gt;D&lt;/sub&gt;</td>
<td>Dopant Concentration</td>
</tr>
<tr>
<td>N&lt;sub&gt;e&lt;/sub&gt;</td>
<td>Number of Electrons Collected</td>
</tr>
<tr>
<td>N&lt;sub&gt;max&lt;/sub&gt;</td>
<td>The Maximum Number of Free Electrons</td>
</tr>
<tr>
<td>ns</td>
<td>Nanosecond</td>
</tr>
<tr>
<td>Ox</td>
<td>Oxidized Form</td>
</tr>
<tr>
<td>OD</td>
<td>Oxygen Demand</td>
</tr>
<tr>
<td>pH&lt;sub&gt;zpc&lt;/sub&gt;</td>
<td>Zero Charge Potential pH</td>
</tr>
<tr>
<td>pK&lt;sub&gt;a&lt;/sub&gt;</td>
<td>Acid Constant</td>
</tr>
<tr>
<td>ps</td>
<td>Picosecond</td>
</tr>
<tr>
<td>Q</td>
<td>Faraday Electrolytic Charges</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$Q_{\text{max}}$</td>
<td>Maximum Faraday Electrolytic Charges Corresponding to the Maximum Adorption Quantity</td>
</tr>
<tr>
<td>$r$</td>
<td>Distance from Surface to the Inside of Semiconductor</td>
</tr>
<tr>
<td>$R$</td>
<td>Resistance</td>
</tr>
<tr>
<td>$R_0$</td>
<td>Constant Component of the Resistance</td>
</tr>
<tr>
<td>$r_0$</td>
<td>Radius of Semiconductor Particle</td>
</tr>
<tr>
<td>Red</td>
<td>Reduced Form</td>
</tr>
<tr>
<td>$R_I$</td>
<td>Variant Component of the Resistance</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>t</td>
<td>Time elapsed</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>W</td>
<td>Width of Space Charge Layer</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Electron Collection Coefficient</td>
</tr>
<tr>
<td>$\beta$</td>
<td>True Half-peak Width of XRD peaks</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Thickness of Effective Diffusion Layer</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>Potential Difference between the Applied Potential and the Zero Current Potential or On-set Potential</td>
</tr>
<tr>
<td>$\Delta \Phi_{\text{sc}}$</td>
<td>Potential Difference Across the Space Charge Layer</td>
</tr>
<tr>
<td>$\Delta \Phi$</td>
<td>Potential Difference at the Surface and Inside of the Semiconductor</td>
</tr>
<tr>
<td>$\Delta I_{\text{sph}}$</td>
<td>$I_{\text{sph}} - I_{\text{blank}}$</td>
</tr>
<tr>
<td>$\Delta I_{\text{sphM}}$</td>
<td>$I_{\text{sphM}} - I_{\text{blank}}$</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Light Intensity</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Surface Coverage</td>
</tr>
<tr>
<td>$\theta$</td>
<td>The angle of the XRD Peak</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Dielectric Constant of the Semiconductor</td>
</tr>
<tr>
<td>$\epsilon_0$</td>
<td>Permittivity of the vacuum</td>
</tr>
<tr>
<td>$&gt;\text{TiO}^+$</td>
<td>Surface Species of TiO$_2$</td>
</tr>
<tr>
<td>$&gt;\text{TiOH}_2^+$</td>
<td>Surface Species of TiO$_2$</td>
</tr>
<tr>
<td>$&gt;\text{TiOH}$</td>
<td>“Titanol” Moiety of TiO$_2$ Surface</td>
</tr>
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</table>
ABSTRACT

In this work, a series of simple, rapid and effective photoelectrochemical methodologies have been developed and successfully applied to the study of kinetic and thermodynamic characteristics of photocatalytic oxidation processes at TiO$_2$ nanoparticulate films. As an application of the systematic studies of photocatalytic processes by photoelectrochemical techniques, a rapid, direct, absolute, environmental-friendly and accurate COD analysis method was successfully developed.

In this work, the TiO$_2$ nanoparticles colloid was prepared by the sol-gel method. The TiO$_2$ nanoparticles were immobilized onto ITO conducting glass slides by dip-coating method. Thermal treatment was carried out to obtain nanoporous TiO$_2$ films of different structures. At low calcination temperature (below 600 °C), nanoporous TiO$_2$ films of pure anatase phase were prepared. At high calcination temperature (above 600 °C), nanoporous TiO$_2$ films of mixed anatase and rutile phases were obtained. At these film electrodes, the work was carried out.

By employing steady state photocurrent method and choosing phthalic acid as the model compound, the photocatalytic activity of the TiO$_2$ nanoporous films calcined at various temperatures and for different lengths of time was evaluated. It was found that the films with mixed anatase and rutile phases calcined at high temperature exhibited high photocatalytic activity. Based on semiconductor band theory, a model was proposed, which explained well this finding.

By employing linear sweep voltammetry (under illumination) and choosing glucose (an effective photohole scavenger) as a model compound, the characteristics of the photocatalytic processes at nanoparticulate semiconductor electrodes were investigated. Characteristics of the nanoporous semiconductor electrodes markedly different from bulk semiconductor electrodes were observed. That is, within a large range of electrode
potentials above the flat band potential the electrodes behaved as a pure resistance instead of exhibiting variable resistance expected for bulk semiconductor electrodes. The magnitude of the resistance was dependent on the properties of the electrodes and the maximum photocatalytic oxidation rate at TiO$_2$ surface determined by the light intensity and substrate concentration. A model was proposed, which explained well the special characteristics of particulate semiconductor electrodes (nanoporous semiconductor electrodes). This is the first clear description of the overall photocatalytic process at nanoparticulate semiconductor electrodes. The investigation set a theoretical foundation for employing photoelectrochemical techniques to study photocatalytic processes.

By using the transient technique (illumination step method analogous to potential step method in conventional electrochemistry), the adsorption of a number of strong adsorbates on both low temperature and high temperature calcined TiO$_2$ nanoporous films was investigated. Similar adsorption characteristics for different adsorbates on different films were observed. In all the cases, three different surface bound complexes were identified, which was attributed to the heterogeneity of TiO$_2$ surface. The photocatalytic degradation kinetics of the pre-adsorbed organic compounds of different chemical nature was also studied by processing the photocurrent-time profiles. Two different photocatalytic processes, exhibiting different rate characteristics, were observed. This was, again, attributed to the heterogeneity of the TiO$_2$ surface corresponding to heterogeneous adsorption characteristics. The catalytic first order rate constants of both fast and slow processes were obtained for different organic compounds. It was found that for different adsorbates of different chemical nature the magnitudes of rate constant for the slow kinetic process were very similar, while the magnitudes of rate constant for the fast process were significantly affected by the photohole demand characteristics of different adsorbates. Photohole demand distribution that depends on the size and structure of the adsorbed molecules was believed to be responsible for the difference.
By employing steady state photocurrent method, the photocatalytic degradation kinetic characteristics of both strong adsorbates and weak adsorbates of different chemical structures were compared at pure anatase TiO$_2$ nanoporous TiO$_2$ films as well as at anatase/rutile mixed phase TiO$_2$ nanoporous film electrodes. At the former electrodes for all the different organic compounds studied, the photocatalytic reaction rate increased linearly with concentration at low concentrations. Under such conditions, it was demonstrated that the overall photocatalytic process was controlled by diffusion and was independent of the chemical nature of organic compounds. However, the linear concentration range and the maximum photocatalytic reaction rate at high concentrations were significantly dependent on the chemical nature of the substrates. This was explained by the difference in the interaction of different organic compounds with TiO$_2$ surface, the difference in their photohole demand distributions at the TiO$_2$ surface and the difference in their nature of intermediates formed during their photocatalytic mineralization. In contrast, at the latter electrodes for the photocatalytic oxidation of different organic compounds the linear ranges (diffusion control concentration range) and the maximum reaction rates at high concentration were much larger than at the former electrodes and much less dependent on the chemical nature of the organic compounds. The spatial separation of photoelectrons and photoholes (due to the coexistence of rutile phase and anatase phase) and the increase in the lifetime of photoelectrons and photoholes are responsible for the excellent photocatalytic activity of the electrodes.

By employing the thin-layer photoelectrochemical technique (analogous to the thin-layer exhaustive electrolytic technique), the photocatalytic oxidation of different organic compounds at the mixed phase TiO$_2$ nanoporous electrodes were investigated in a thin layer photoelectrochemical cell. It was found that the charge derived from exhaustive oxidation agreed well with theoretical charge expected for the mineralisation of a specific organic compound. This finding was true for all the compounds investigated and was also
true for mixtures of different organic compounds. The photocatalytic degradation kinetics of different organic compounds of different chemical identities in the thin layer cell was also investigated by the photoelectrochemical method. Two kinetic processes of different decay time constants were identified, which were attributed to the degradation of preadsorbed compounds and the degradation of compounds in solution. For the degradation of compounds in solution, a change in the overall control step from substrate diffusion to heterogeneous surface reaction was observed. For different organic compounds, the variation of the rate constant was determined by the photohole demand rather than by the chemical identities of substrates. The kinetics of the fast kinetic process, on the other hand, was greatly affected by the adsorption properties of the substrates. For the strong adsorbates, the rate was much larger than for weak adsorbates. However, the rate constant of the process was independent of the chemical identities of the substrates and the variation of the constant was also determined by the photohole demand.

Based on the principles of exhaustive photoelectrocatalytic degradation of organic matter in a thin layer cell, a novel, rapid, direct, environmental-friendly and absolute COD analysis method was developed. The method was tested on synthetic samples as well as real wastewater samples from a variety of industries. For synthetic samples with given compositions the COD values measured by my method agree very well with theoretical COD value. For real samples and synthetic samples the COD values measured by my method correlated very well with those measured by standard dichromate COD analysis method.
1.1 INTRODUCTION

Illuminated TiO$_2$ is one of the most powerful oxidants due to the high oxidizing potential of holes in the valence band formed by photoexcitation $^{1-4}$. Owing to its outstanding photocatalytic activity, excellent chemical and photochemical stability, and superior oxidation ability, TiO$_2$ based photocatalysts have been used for water purification/sterilisation $^{5-7}$ and wastewater treatment $^2, 3$.

Although notable progress has been made, the quantum efficiency has been reported to be very low $^{1-3}$ and many fundamental aspects involved in the photocatalytic oxidation process still remain unclear. To date, most of the published research articles in these fields have focused on the study of photocatalytic properties of one or more types of organic compounds. The photocatalytic properties of different compounds may have been studied, but often under different conditions or by different methods. This makes it very difficult to draw conclusive information from these reports that can be used as a general guide for improving the performance of existing photocatalytic systems or to develop new photocatalytic systems due to the incomparability of the reported data. This is especially true for studies carried out in a TiO$_2$ suspension/slurry system, where the complexity involved makes it impossible to control the experiment under desired conditions $^{8-11}$. This situation can be attributed to the lack of an appropriate study methodology. At present, there is no systematic methodology available that can be used to objectively evaluate the performance of a photocatalyst for a specific application.

The aims of this study are two-fold. The primary aim is to develop a series of photoelectrochemical methodologies that can be used for systematic characterisation of kinetic and thermodynamic properties of photocatalytic oxidation processes at TiO$_2$ nanoparticle surfaces. A secondary aim is to take advantage of the strong oxidising power
of TiO$_2$ nanoparticles to develop a rapid, accurate, environmental-friendly and cost effective method for the determination of aggregate properties of water or wastewater samples such as chemical oxygen demand.

The nature of this study necessitates a multidisciplinary approach incorporating aspects of electrochemistry, photochemistry, semiconductor physics, colloid chemistry and analytical chemistry. This chapter reviews the present status of relevant research developments and the fundamental theories involved.

### 1.2 SOME IMPORTANT TERMINOLOGIES

This project is a multi-disciplinary project, involving areas such as semiconductor physics, electrochemistry and photoelectrochemistry. In this section, some important terminologies are defined for the convenience in discussing experimental results.

**Band Model:** In order to describe electron transfer to or from a semiconductor, it is desirable to utilize the concepts of band model. The band model of a solid stems directly from the statistic distribution of atomic energy levels. As described by the Pauli exclusion principle, the energy levels of identical overlapping electronic orbitals cannot be equal. Analysis shows that the discrete energy levels of the atoms forming the solid broaden when the orbitals overlap, forming bands of energy levels with about $2 \times 10^{22}$ levels in each band when there are the order of $10^{22}$ atoms in the crystal. Bands are a large number of orbitals with different energy levels.

**Valence Band:** The aggregate of orbitals occupied by valence electrons is called the valence band of the solid.

**Conduction Band:** The band associated with the first excited state, normally unoccupied by electrons, is called the conduction band of the solid.
**Bandgap:** The energy gap between conduction band and valence band of a solid is called the bandgap of the solid.

**Hole:** A hole is an empty level in the valence band or a valence bond with an electron missing.

**Fermi Level** ($E_f$): The Fermi Level and the Fermi distribution describe the distribution of electrons and holes among the available energy levels in a solid. To a first approximation, all the energy levels below the Fermi level are occupied by electrons, while all the energy levels above Fermi are unoccupied by electrons. From a statistical point of view, Fermi level is the average energy of electrons and electrons moving from the solid to ions in solution originate with a free energy of $E_f$. From a chemical point of view, the Fermi Level is the electrochemical potential of electrons in the solid.

**Space Charge Layer:** When semiconductors are brought into contact with liquid, due to the difference in Fermi levels of the two phases, charged planes or space charge layer almost inevitably form at the interface to reach an equilibrium. A schematic diagram of this interface is shown in Figure 1.1.

*Figure 1.1*  *Schematic diagram of the semiconductor/liquid interface*. 
As shown in Figure 1.1, the Band Edges $E_{cs}$ and $E_{vs}$, are the energy levels of the conduction band bottom and the valence band top at the interface. The Band Bending is the energy or potential difference between the interface and inside the semiconductors. The physical region in which the band bending occurs is called the Space Charge Layer, or the Depletion Layer.

**Flatband Potential:** The Fermi level of a semiconductor can be controlled by an applied external potential bias. The flatband potential is the applied potential, when the bands of the semiconductor are flat. In other words, there is no band bending on the semiconductor side of the interface. By measuring the flat band potential, the band edge of semiconductor can be determined. For most oxide semiconductors their flatband potentials have a Nernstian-type pH dependence in aqueous media.

**On-set Potential:** For a n-type semiconductor electrode, when the applied potential is below the conduction band edge (or below the flatband potential), there would be no electrons withdrawn from the semiconductor. As a result there is no anodic current observed even if there are large amount of electrons under illumination. The On-set Potential in this work refers to the potential at which anodic photocurrent starts to be measured. In ideal cases the On-set potential approximates the flatband potential.

### 1.3 CLASSIFICATION OF PHOTON/SEMICONDUCTOR SYSTEMS

The bonding and electron distribution in a solid material is often described by the band theory. When many atoms interact, as in a metal, a large number of resultant electronic orbitals become closely spaced, forming a continuum of energy levels, a so-called continuous band. In metals, due to the continuum of energy levels, valence electrons can be thermally excited freely from filled valence orbitals to the unfilled orbitals. Therefore, valence electrons can move freely at normal temperatures, resulting in high electronic conductivity. In contrast, semiconductors can be characterised by two types of energy
bands – a filled low energy valence band and an empty high energy conduction band. Between these two bands, an energy gap, the bandgap, exists. In semiconductors, the valence electrons have little chance of being thermally excited and only a small portion of electrons with high kinetic energy can reach the conduction band resulting in low electrical conductivity. When the two bands of a solid material are further separated to larger than 3 eV, similarly the free electron concentration is further lowered and such material is regarded as insulator. However, this definition is not rigid, since, for example TiO$_2$ is still considered to be semiconductor even though it has a band gap of 3.2 eV.

Light excitation of a semiconductor promotes electrons from the valence band to the conduction band. In metals, where there is a continuum of energy states, the light generated electrons deactivates easily and the lifetime of the electron/hole pair is so short that they cannot be harvested. The existence of band gap in semiconductors prevents rapid deactivation of the excited electron/hole pairs, which can be deactivated only by recombination. This assures that an electron/hole pair lifetime is sufficiently long to participate in interfacial electron transfer$^1$.

Depending on the methods of harnessing the light generated electron/hole pairs and the purpose of the applications, a few areas of studies have emerged from photon/semiconductor interactions. According to the types of semiconductors involved, the areas of studies can be classified into bulk semiconductor systems and particulate semiconductor systems (see Figure 1.2). When the size of semiconductors is down to nanometer scale or submicrometer scale they display a number of properties different to those of the macro-size semiconductors. The former systems are defined as particulate semiconductor systems and the latter are defined as bulk semiconductor systems. In history, the early research focused mainly on the bulk semiconductors. The bulk
semiconductor theory has been well established and various applications have been extensively studied\textsuperscript{4,12}.

The particulate semiconductors refer to semiconductors with particle sizes ranging from nanometre to submicrometer. Driven by potential applications of TiO\textsubscript{2} nanoparticle photocatalysts for the total destruction of organic compounds in polluted air and wastewater, the TiO\textsubscript{2} nanoparticle heterogeneous photocatalysis has become one of the most active research areas in the past two decades\textsuperscript{13-15}. Since the successful application of nanoparticulate TiO\textsubscript{2} film electrode in the Dye Sensitised Solar Cell\textsuperscript{16}, a large amount of research has been devoted to understanding the fundamentals of nanoporous particulate semiconductor electrodes\textsuperscript{17-27}. This project aims to study the fundamentals of photocatalytic degradation of organic compounds at TiO\textsubscript{2} nanoparticulate film electrodes by photoelectrochemical methods. These studies fall into the description of photoelectrocatalytic systems in the classification shown in Figure 1.2.

\textbf{Figure 1.2} Classification of Photon/Semiconductor Systems.
1.4 ENERGETICS AND REDOX POWER OF SEMICONDUCTORS

Semiconductors can absorb light with energy higher than certain energy thresholds that is determined by the bandgaps (E\textsubscript{g}) of semiconductors. Once photons are absorbed, photoelectrons and photoholes are formed. The photogenerated electrons and holes quickly relax to the bottom of the conduction band and the top of the valence band respectively by dissipating their kinetic energy. These electrons and holes can be used to drive a redox reaction. Thermodynamically, the energy level of the conduction band edge (E\textsubscript{cs}) is a measure of the reduction strength of electrons in the semiconductor, whereas that of valence band edge (E\textsubscript{vs}) is a measure of the oxidation power of holes in the semiconductor\textsuperscript{3}. Figure 1.3 shows the band edge energy levels of common semiconductors that are in contact with aqueous media at pH 0.0\textsuperscript{1}.

![Energy-level diagram for various semiconductors indication the energy positions of valence band and conduction band edges in aqueous media at pH 0.0.](image)

\textit{Figure 1.3} Energy-level diagram for various semiconductors indication the energy positions of valence band and conduction band edges in aqueous media at pH 0.0.
Different semiconductors possess different band edge energies. The higher the valence band edge potential, the higher oxidising power its holes have. For a semiconductor to have ‘universal’ photocatalytic reactivity toward different organic compounds, thermodynamically its valence band edge must sit at a relatively high potential. Small band-gap semiconductors have a better absorption spectrum match with solar emission spectrum. From a utilisation of solar energy point of view, the small band gap semiconductors would be a better choice. However, small band gap semiconductors normally do not have high valence band potential. Compounding this problem is that many semiconductors, particularly, the small band gap semiconductors suffer from serious chemical corrosion and photocorrosion when used as photocatalysts. Therefore, the selection of semiconductor photocatalysts, depending on the application, often involves the compromise between a number of factors, such as high oxidising power, good solar spectrum coverage, and chemical/photochemical stability. TiO$_2$ is among the few semiconductors that have good chemical/photochemical stabilities and high oxidation power (E=3.1V vs SHE). Its poor solar spectrum coverage is traded off for these excellent properties to be used as a photocatalyst.

1.5 TiO$_2$ PARTICULATE PHOTOCATALYTIC SYSTEM

The interaction between light and semiconductor has led to a broad range of applications. This work mainly deals with photocatalytic degradation of organic matter using a TiO$_2$ particulate system. In the following sections some fundamentals and developments in this research area are discussed and reviewed.

Over the past two decades there has been a tremendous scientific and engineering interest in the application of semiconductor photocatalysis. TiO$_2$ nanoparticle either in slurry or in immobilised film, in particular, has been the primary focus due to its excellent chemical/photochemical stabilities and excellent photocatalytic reactivity towards a wide
spectrum of organic compounds. Photocatalytic destruction of organic matter, either in particle slurry system or at immobilised nanoporous film, shares many common features in that the semiconductors in both cases can be treated as particulate semiconductors. This type of particulate semiconductor has many distinct features, which are quite different in comparison to the conventional bulk semiconductors.

1.5.1 Nanoparticles and Bulk TiO$_2$ Semiconductors

Nanoparticulate and bulk TiO$_2$ semiconductors are both made of the same material. The particle size of the material distinguishes the nanoparticulate semiconductor from bulk TiO$_2$ semiconductors. The nanoparticulate semiconductor consists of extremely small size of TiO$_2$ particles. The extremely small particle size renders this type of semiconductor with many special properties. It possesses extremely large surface area, but is thermodynamically unstable. More importantly, its electronic properties at the solution/particle interfaces differ remarkably from those of bulk type semiconductors.

When a bulk semiconductor is in contact with an aqueous medium, the semiconductor band edges are fixed. Due to the Fermi level differences between the semiconductor and aqueous medium, the major charge carrier of the semiconductor is moved to the surface and minor charge carrier is moved into the inside of the semiconductor. A space charge layer, similar to a P-N junction in semiconductor physics, can therefore be formed within this type of semiconductor (see Figure 1.1). This space charge layer is also called depletion layer and within this layer an inner electric field is formed. The potential difference between the surface and the inside of the semiconductor is known as band bending. Whenever there are excess electrons and holes in the space charge region, they will move according to the direction of the electric field. As a result, the inner electric field separates the photogenerated electrons from holes by driving them in different
directions. It is this spatial separation that further increases the lifetime of photoelectrons and photoholes generated upon illumination of bulk semiconductors.

The scenario is very different for a semiconductor formed with small particles (particulate semiconductor). The difference in electronic property between bulk semiconductor and nanoparticle semiconductor can be described by the potential distribution at the interface on the semiconductor side. This potential distribution has been derived by Albery and co-workers using a linearized Poisson-Boltzmann equation\textsuperscript{28}. The potential difference between the centre of a semiconductor particle \((r=\theta)\) and a distance \(r\) is given by:

\[
\Delta \Phi_{sc} = \frac{kT}{6e} \left( r - \left( \frac{v_0 - W}{L_D} \right) \right)^2 \left( 1 + \frac{2(v_0 - W)}{r} \right)
\]  

(1.1)

where \(\Delta \Phi_{sc}\) is the potential drop within the layer, \(k\) is the Boltzmann constant, \(r\) is the distance starting from the centre of the particle, \(T\) is the temperature, \(e\) is the charge of an electron, \(N_D\) is the dopant concentration, \(L_D = (\epsilon_0 \epsilon kT/2e^2 N_D)^{0.5}\) is the Debye length depending on charge carrier and on the dopant concentration, \(W\) is the width of the space charge layer, \(\epsilon_0\) is the permittivity of the vacuum and \(\epsilon\) is the dielectric constant of the semiconductor.

For very large size semiconductor particles (bulk semiconductor), the potential drop within the particles can be given by\textsuperscript{29}:

\[
\Delta \Phi_{sc} = \frac{kT}{2e} \left( \frac{W}{L_D} \right)^2
\]  

(1.2)

For extremely small size semiconductor particles (nanoparticulate semiconductor) the potential drop within the semiconductor becomes\textsuperscript{29}:
Equation 1.3 suggests that the potential drop within TiO$_2$ semiconductor nanoparticles is negligibly small due to the extremely small $r_0$ of the particle. This makes the nanoparticulate semiconductor behave very differently in comparison with the bulk semiconductor since there is no substantial junction or band bending formed within these extremely small semiconductor particles$^{29}$. In other word, the bands within semiconductor nanoparticles are almost flat. Figure 1.4 shows a diagram of the difference in band bending when a bulk semiconductor and small semiconductor particles are brought into contact with an aqueous solution$^{29}$.

\[ \Delta \Phi = \frac{kT}{6e} \left( \frac{r_0}{L_D} \right)^2 \]  

(1.3)

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{diagram.png}
\caption{Schematic diagram showing the difference of band bending at semiconductor solution interface between n-type bulk semiconductor and small semiconductor particles.}
\end{figure}

Due to the small band bending of semiconductor nanoparticles, the charge separation occurring within the particle is via an electron diffusion mechanism$^{29}$. Upon absorption of light, the electron-hole pairs generated are distributed in a spatially random fashion along the optical path. Based on the random walk model, the average transit time of electrons for semiconductor nanoparticles from the inside of the particle to its surface is in the order
of picoseconds\textsuperscript{29}. This diffusion process is faster than the electron/hole recombination process, but the charge separation has not yet been realised because the photoelectrons and photoholes are still spatially very close. The actual charge separation can only be achieved through the removal (capture) of at least one type of charge carrier upon their arrival at the interface. In this regard, the overall quantum efficiency of photocatalysis relies solely on the interfacial reaction kinetics. These differences impart quite a few special features to particulate semiconductor systems. For example, at a bulk semiconductor electrode, especially a single crystal semiconductor electrode, the applied potential bias not only can regulate its band bending but also can modulate the interfacial reaction kinetics. This means that the photocurrent responses obtained from different organic compounds, and even in the absence of organic compounds (only blank electrolyte solution) are very similar—as have been reported by many researchers\textsuperscript{30-33}. This feature is advantageous to solar energy conversion applications. This property, however, is disadvantageous for photocatalytic mineralization of organic compounds because water oxidation would consume most of the photoholes.

Particulate film semiconductor electrodes are composed of interconnected nanoparticles and can be treated as nanoparticles\textsuperscript{29}. In contrast to the bulk semiconductor electrodes, the applied potential bias in a particulate film electrode is expected to serve totally different functions due to the unique electronic features of nanoparticles. While nanoporous film electrodes (particulate film electrode) have been used in other studies such as in potential assisted photocatalytic degradation of organic compounds\textsuperscript{33-40} and in dye sensitized solar cell applications\textsuperscript{29, 41-48}, the exact nature of the differences between particulate film and bulk semiconductor electrode including the difference in potential bias function has yet to be addressed in any detail in the literature when it comes to photocatalytic oxidation of organics.
It is well known that in the TiO$_2$ nanoparticle slurry system the overall photocatalytic degradation process of organic compounds is controlled by the interfacial photocatalytic reaction. Based on the unique electronic feature of particulate semiconductor electrodes, we anticipate that the applied potential bias only serves as the electromotive force to remove the freed photoelectrons (by the interfacial photohole capture reaction) to the external circuit and then to the auxiliary electrode. The photocurrent response obtained under certain circumstances should reflect the interfacial photocatalytic reaction kinetics, which is dependent on the type of organic compounds involved and on the properties of TiO$_2$ particulate film electrodes employed. This would provide us with a powerful tool to study the photocatalytic oxidation kinetics and thermodynamics of different organic compounds. This would also allow us to quantitatively evaluate the photocatalytic performance of a particulate semiconductor electrode. The information obtained from quantitative evaluation of different TiO$_2$ nanoparticle photocatalysts could then be useful for improving the overall photocatalytic performance or even in the synthesis of high-performance photocatalysts.

1.5.2 General Mechanisms of Semiconductor Photocatalysis

The mechanisms of photocatalytic oxidation of organic compounds at a particulate semiconductor electrode involve multiple processes. These include light/semiconductor interactions, photogenerated electrons/holes interactions with the semiconductor both at the surface and within the semiconductor, photogenerated electrons/holes migration/recombination within the semiconductor and photogenerated electrons/holes capture at the interface. The reaction mechanisms on the solution side of the semiconductor/solution interface depend on the organic compounds involved. On the semiconductor side of the interface, however the mechanisms are basically the same regardless of type of organic compounds involved. Based on laser flash photolysis
measurements, general mechanisms and the time characteristics of various steps involved in the heterogeneous photocatalysis at TiO₂ have been given by Hoffmann ⁵. Table 1.1 outlines the steps and their characteristic times. According to this general mechanism, the overall photocatalytic quantum efficiency is controlled by two critical factors. One is the competition between the recombination of the charge carriers (photoelectrons and photoholes) and the trapping of charge carriers, and the other is the competition between the recombination of the trapped charge carriers and the interfacial charge transfer (capture of charge carriers). Any action that can either increase the lifetime of the charge carriers or interfacial charge transfer would be beneficial to the overall photocatalytic process.

**Table 1.1**  
*General mechanism of semiconductor photocatalysis at TiO₂*

<table>
<thead>
<tr>
<th>Primary process</th>
<th>Characteristic times</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge carrier generation</td>
<td>( \text{TiO}<em>2 + \text{hv} \rightarrow h</em>{vb}^+ + e_{cb}^- ) Fast (fs)</td>
</tr>
<tr>
<td>Charge-carrier trapping</td>
<td>( h_{vb}^+ + &gt;\text{Ti}^\text{IV}OH \rightarrow &gt;\text{Ti}^\text{IV}OH^* ) Slow (100ns)</td>
</tr>
<tr>
<td></td>
<td>( e_{cb}^- + &gt;\text{Ti}^\text{IV}OH \rightarrow &gt;\text{Ti}^\text{III}OH ) Very slow (ms)</td>
</tr>
<tr>
<td>Charge-carrier recombination</td>
<td>( e_{cb}^- + &gt;\text{Ti}^\text{IV}OH^* \rightarrow &gt;\text{Ti}^\text{IV}OH ) Slow (100ns)</td>
</tr>
<tr>
<td>Interfacial charge transfer</td>
<td>( &gt;\text{Ti}^\text{IV}OH^* + \text{Red} \rightarrow &gt;\text{Ti}^\text{IV}OH + \text{Red}^* ) Very slow (ms)</td>
</tr>
</tbody>
</table>

*Note: \( h_{vb}^+ \): photoholes, \( e_{cb}^- \): photoelectrons, >TiOH: TiO₂ surface group, Red: Reductant, Ox: Oxidant.*
Along these lines, a great deal of effort has been devoted to improving the photocatalytic reactivity of TiO₂ photocatalyst. For example, TiO₂ has been doped with transition metals to increase the lifetime of photoelectrons and photoholes. An increase in the quantum efficiency of the photocatalytic reduction of N₂ and of methyl viologen has been demonstrated by employing Fe(III) doped TiO₂ due to inhibited electron-hole recombination. However, in the case of phenol degradation, Fe(III) doped TiO₂ showed a little effect on the photocatalytic efficiency. Karakitsou and Verykios reported that doping TiO₂ with cations of higher valency than that of Ti(IV) resulted in enhanced photoreactivity, while Mu et al. reported that doping with trivalent and pentavalent cations was actually detrimental to the photoreactivity of TiO₂. Surface treatment by some inorganic ions has been reported to enhance the photoreactivity of TiO₂. Thermal treatment of oxide catalyst is a routine technique to change catalyst surface properties in the hope to improve the catalytic reactivity. Various ways of thermal treatment of TiO₂ photocatalyst have been reported to be effective in improving the photocatalytic activity. It is well known that the particle size, surface area, crystallinity and crystalline forms of TiO₂ nanoparticles can be changed during a thermal treatment process. However, in practice, it is difficult to change one of these parameters without changing the others. Hence, it is difficult to identify whether the overall photocatalytic reactivity change is due to the change of a specific parameter. Because of this, to date, it is still a challenge to quantitatively relate the photocatalytic reactivity with various parameters. Due, largely, to the complexity of the photocatalytic degradation process and the lack of consistent assessment criteria, no quantitative correlations between the photocatalytic activity and electrode parameters have been given - this is despite reports of new TiO₂ photocatalysts that have superior photocatalytic activity toward one or one type of organic compounds. As a consequence, the conclusions of these reports are only applicable
to those specific conditions and cannot be used as a general guideline for circumstances other than those reported.

TiO$_2$ usually exists in three common crystal structures: rutile, brookite and anatase. Of the three forms, brookite is the most unstable form and is very difficult to prepare $^{65}$. Probably out of these reasons, brookite form is rarely used in photocatalytic studies. Most studies in TiO$_2$ photocatalysis have been carried out using either pure anatase form or pure rutile form or a mixture of the two as photocatalysts $^{65}$. Often the anatase form of TiO$_2$ is believed to be more photocatalytically active than rutile form $^{66-70}$. Interestingly, P25, a commercial TiO$_2$ catalyst containing a mixture of rutile and anatase crystalline forms, is the most widely used photocatalyst and has proven to be the best photocatalyst towards a broad range of organic pollutants $^{71, 72}$. Unfortunately, the mechanisms for this still remain unclear. With the special advantages of photoelectrochemical method (will be discussed in later sections), I believe that employing a photoelectrochemical method in combination with other characterisation methods can identify these mechanisms.

1.5.3 Kinetics of TiO$_2$ Photocatalytic Degradation

The quantum efficiency in a photocatalysis process is one of the most critical factors that determine whether a photocatalytic technique will be of any practical significance. At a certain light intensity, the photocatalytic degradation kinetics of organic matter is directly related to the light utilization efficiency. Kinetic studies are of paramount importance to the design of practical photocatalytic degradation reactors as well as to the understanding of the photocatalytic degradation processes, the optimization of photocatalysts, and ultimately to the efficient utilization of light.
1.5.3.1  Kinetic Studies by Traditional Approach

Traditional approaches to photocatalytic kinetic studies employ a TiO₂ particle suspension system or an immobilized TiO₂ photocatalyst system and monitor the concentration change of an organic compound in bulk solution. In many cases, the macroscopic kinetics of photocatalytic degradation of organic compounds follow the Langmuir-Hinshelwood kinetic expression, namely the double reciprocal linear relationship between reaction rate and the substrate concentration. In early studies, this kind of kinetic behaviour was always taken as the kinetic feature for complying with Langmuir-Hinshelwood reaction model or reaction mechanism. The model assumes that: (i) at equilibrium the number of surface adsorption sites is fixed; (ii) only one substrate may bind at each surface site; (iii) the heat of adsorption by the substrate is identical for each site and is independent of surface coverage; (iv) there is no interaction between adjacent adsorbed species; (v) the rate of surface adsorption is greater than the rate of any subsequent chemical reaction; and (vi) no irreversible blocking of active sites by binding to product or intermediates occurs. Under these assumptions, the surface coverage $\theta$ is related to the initial concentration of the substrate $C$ and the adsorption equilibrium constant $K$. That is:

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

The reaction rate can be expressed as:

$$\text{Rate} = -\frac{dC}{dt} = k_{LH} \theta = \frac{k_{LH} KC}{1 + KC} \quad (1.5)$$

where $k_{LH}$ is the photocatalytic reaction rate constant.
The saturation of reaction rate with respect to reactant concentration is usually taken as an indication of adsorption saturation of reactants. Although the macroscopic photocatalytic degradation kinetics of many organic compounds can be described by Langmuir-Hinshelwood type rate laws, what leads to this type of macroscopic kinetics cannot be attributed solely to the adsorption of reactants\(^2\). As a matter of fact, recent studies have found that many different kinds of reaction mechanisms could lead to this type of kinetic expression\(^3\). In such cases, the derived kinetic parameters represent fundamentally different processes compared with the processes assumed in the Langmuir-Hinshelwood model. Conflicts have also been found between reality and that expected from the simple model. These include the huge difference between the adsorption equilibrium constants extracted from photocatalytic kinetic measurements and the actual adsorption equilibrium constants measured in the dark adsorption experiments\(^4\). In addition, the very poor correlations between the photocatalytic reaction rate and the surface adsorption coverage by reactants have been reported\(^5\). An explanation for the former case is that various equilibrium adsorption constants involved are changed under illumination\(^2\). With respect to the latter issue, Regazzoni and co-workers have attributed the poor correlations between the photocatalytic oxidation rate and the organic compound surface coverage to the surface adsorption heterogeneity\(^6\). They argued that different surface adsorption species were formed on TiO\(_2\) surface and each possessed different photocatalytic reactivity. Therefore, assigning an operational mechanism for reactions taking place in a heterogeneous medium to a Langmuir-Hinshelwood (LH) (or even to an Eley-Rideal (ER) model), on the basis of observed kinetics alone, is questionable.

Despite the problems outlined above, there is no question that the adsorption of reactant does play an important role in the overall photocatalytic reaction process. However, in consideration of the large surface area of TiO\(_2\) nanoparticles, the surface heterogeneity and structural defects are unavoidable. For strong adsorbates in particular, there is likely more
than one type of surface complexes formed on the surface. It has been confirmed by in-situ FTIR technique that different surface complexes of certain strong adsorbates do exist on TiO$_2$ surface and each possess a specific interfacial charge transfer reactivity$^{87,88}$. Given the complexity in the photocatalytic degradation of organic compounds, great caution should be taken in relating the Langmuir-Hinshelwood type macroscopic kinetic behaviour to adsorption of reactants. In multiple-step photocatalytic reactions for example, any step could be the rate-determining step, the influence of original reactant adsorption on the overall photocatalytic degradation may become insignificant.

As for the primary oxidation of organic substrates on an irradiated semiconductor, currently two pathways have been proposed and recognised. One is that the photoholes are trapped first at surface hydroxyl groups, with which then the bimolecular heterogeneous reaction of organic compounds takes place, and so called outer-sphere pathway$^{2,86,89}$. For weak adsorbates or non-adsorbates their photocatalytic oxidation usually take this pathway. The alternative pathway, called inner-sphere electron transfer pathway, involves direct hole transfer to the adsorbates and the photocatalytic oxidation of strong adsorbates is believed to take this pathway$^{2,90}$.

In spite of the complexity of photocatalytic oxidation mechanism for different organic compounds, the general heterogeneous catalytic reaction kinetics should always apply for the primary charge transfer process in a slurry system and an immobilised TiO$_2$ nanoparticle photocatalytic system:

$$\text{Rate}(\text{O}_2\text{ reduction}) = k_r \theta_a \theta_{o_2} \quad (1.5)$$

$$\text{Rate(oxidation)} = \sum k_o \theta_h \theta_{\text{org}} \quad (1.6)$$

where, the $k_r$ is the charge transfer rate constant for O$_2$ reduction by conduction band photoelectrons ($e_{cb}$), and $k_o$ is the charge transfer rate constant for organic compound
oxidation by valence band photoholes \( (h_{vb}^+) \). \( \theta_e, \theta_{O_2}, \theta_h \) and \( \theta_{\text{Org}} \) are the surface coverage for photoelectrons, \( O_2 \), photoholes and organic reactants respectively.

In the case of more than one kind of surface species co-existing on the surface, the total reaction rate should be the sum of the rate of oxidation of all species.

To keep the overall photocatalytic reaction going, the reaction rates of processes expressed by Equations 1.5 and 1.6 must be equal. Whichever is slower will become the control process for the overall photocatalytic reaction. For organic photocatalytic degradation in slurry system and immobilized TiO\(_2\) system, \( O_2 \) is usually used as the photoelectron acceptor. Often, its reduction is the rate-determining step\(^{91-93}\). Measures have been taken to accelerate electron-accepting process, such as modifying TiO\(_2\) surface with noble metal islands\(^91\) or by the addition of a sacrificing electron acceptor to the slurry\(^{58, 94, 95}\).

1.5.3.2 Other Important Experimental Parameters

*Effect of Incident Light Intensity*

The incident light intensity determines the rate of photoelectron and photohole generation and consequently the photoelectron/hole concentrations in an illuminated semiconductor. It influences not only the rate of photocatalytic degradation of organic matter, but also the rate of photoelectron and photohole recombination\(^3, 96-98\). In this regard, the light intensity affects the overall quantum efficiency of photocatalytic degradation. With a slurry system, at very low light intensity, photocatalytic degradation rates (or quantum efficiency) usually increase linearly with the light intensity \(^3\). Nevertheless, at high light intensity, a non-linear dependence (a square root dependence on light intensity \(^97-104\)) for many degradation reactions has been observed. The square root dependence of the reaction rate on the light intensity is often attributed to the enhanced recombination of photoelectrons and photoholes at higher light intensities \(^50, 51, 105\). An alternative
explanation attributes this to the inhibition of active surface sites and competition for photoholes by reaction intermediates \(^{102}\). What causes this kind of rate/light intensity dependence still remains unclear. Partly, it may be attributed to the way such experiments were carried out, where reduction and oxidation reaction take place on the same particles and the reduction reaction could be the control step of the overall photocatalytic process. Partly, it may be caused by the way that the photocatalytic degradation rates are expressed. In such studies, usually, the reaction rates are expressed by the disappearance rates of original substrates. Due to the uncertainty of their degradation degree and the competition for photoholes by intermediates or other photohole acceptors, only considering the part of photoholes consumed by a specific assumed reaction would be impossible to elucidate the underlining cause for this lowered quantum efficiency at higher light intensities.

It has been widely reported that potential bias applied to TiO\(_2\) nanoparticle immobilised electrodes can suppress the photoelectron and photohole recombination \(^{34, 35, 38, 106-110}\). However, the use of photocurrents in expressing the reaction rate to study photocatalytic degradation kinetics and consequently to investigate the cause of the lowered quantum efficiency at higher light intensities has not been reported. Photocurrent directly reflects the photohole capture rate by various photohole acceptors including intermediates. A study of photocurrent dependence on light intensity at different potential bias would offer an insight into the reason for the lowered quantum efficiency of overall photocatalytic process at higher light intensities.

**Effect of pH**

TiO\(_2\), when contacted with aqueous media, is known to be amphoteric. The principal amphoteric surface functionality is the “titanol” moiety, denoted as >TiOH. Hydroxyl groups on the TiO\(_2\) surface are known to undergo the following acid-base equilibria:
\[ >\text{TIOH}^2 \leftrightarrow >\text{TIOH} + H^+ \ (pK_{a1}^s) \quad (1.7) \]

\[ >\text{TIOH} \leftrightarrow >\text{TIO}^- + H^+ \ (pK_{a2}^s) \quad (1.8) \]

The corresponding surface acidity constants have been found to be $pK_{a1}^s = 4.5$ and $pK_{a2}^s = 8.0$, which yield a $pH_{zpc} = 6.25^{111}$. Below this pH the surface is positively charged, while above this pH the surface is negatively charged. Depending on the $pH$ value in the medium the surface concentration of different species will change. Kormann and co-workers have proposed a model to describe the distribution of different surface species with pH as shown in Figure 1.5.

In general, the surface speciation conditions dictate what type of organic species can be adsorbed at a given pH. In particular, for organic compounds that undergo deprotonation/protonation reactions, the pH change will influence not only their adsorption quantity but also the surface complexation modes (ways adsorbates are coordinated to TiO\(_2\) surface). In this regard, the pH would greatly influence the photocatalytic oxidation kinetics of strong adsorbates. However, the complexity involved in the substrate/surface coordination and in the subsequent photocatalytic oxidation steps.

**Figure 1.5** The distributions of TiO\(_2\) surface species with pH, (■) >TIOH, (●) >TIOH\(^+\), (▲) >TIO\(^-\).

In general, the surface speciation conditions dictate what type of organic species can be adsorbed at a given pH. In particular, for organic compounds that undergo deprotonation/protonation reactions, the pH change will influence not only their adsorption quantity but also the surface complexation modes (ways adsorbates are coordinated to TiO\(_2\) surface). In this regard, the pH would greatly influence the photocatalytic oxidation kinetics of strong adsorbates. However, the complexity involved in the substrate/surface coordination and in the subsequent photocatalytic oxidation steps.
make it difficult to identify what effect of the original substrate adsorption has on its 
photocatalytic oxidation kinetics. In addition, the band edge energy or flat band potential 
of TiO$_2$ will change with pH and thermodynamically this change would lead to a change 
in the oxidation power$^1$. Although cases have been presented where the pH greatly 
changed the photocatalytic reaction rates$^3$, in a vast majority of cases, the rate of 
photocatalytic reaction is found to be only weakly dependent on the solution pH$^8, 86, 112-115$. 

Photoelectrochemical methods due to their inherent advantages (will be discussed in later 
sections), when employed to study the effect of substrate adsorption and pH on the overall 
photocatalytic degradation kinetics of substrate, is expected to offer some insight into the 
these issues.

**Effect of Temperature**

The photocatalytic reaction is typically not sensitive to minor variations in temperature. 
For example, the rate of photocatalytic decomposition of aliphatic alcohols has been 
shown to be insensitive to temperature variation$^{116, 117}$. Thus, the potentially temperature-
dependent steps, such as adsorption, desorption, surface migration, and rearrangement do 
not appear to be the rate determining process in these cases$^{82}$. This feature is an advantage 
for practical application of photocatalytic process since controlling temperature is not 
necessary.

**1.5.3.3 Kinetic Studies by Photoelectrochemical Methods**

The photocatalytic degradation of organic compounds in a slurry system has been 
demonstrated having a few serious practical problems such as the difficulty in recycling 
the TiO$_2$ nanoparticle photocatalyst, the need to replenish O$_2$ and the low quantum 
efficiency resulting from slow O$_2$ reduction kinetics$^{109, 118, 119}$. Immobilization of TiO$_2$ 
particles may overcome the problem associated with the recycling of the photocatalyst, but 
other problems still remain. When it comes to the study of photocatalytic kinetics and
thermal dynamics in both slurry and immobilized TiO$_2$ photocatalyst systems by the traditional kinetic approach, more problems arise. These include the complexity caused by oxygen reduction, the difficulty in the determination of instantaneous substrate concentration (especially for strongly adsorbed compounds), the difficulty in controlling the desired experimental conditions and tedious procedures in acquiring kinetic data$^{8, 9, 11, 74, 75}$. In addition, the photocatalytic reaction rate is normally expressed by the disappearance of organic reactants, however, the number of electrons required for photodegradation of different organic compounds may vary substantially from a few to hundreds. The rates are therefore incomparable for different organic compounds and the physical meaning of reaction rate thus obtained for the overall photocatalytic reaction is not clear due to the unknown oxidation extent.

Immobilisation of TiO$_2$ nanoparticles onto conducting substrate forms nanoporous TiO$_2$ film electrodes or particulate semiconductor electrodes. This approach was first introduced by Gratzel and has been widely used in dye sensitised solar cells$^{16, 120}$. This type of semiconductor electrode differs from a bulk semiconductor electrode in that it behaves more like small semiconductor particles$^{29, 41, 121}$. This kind of electrode has also been used in the photocatalytic oxidation of organic compounds$^{34, 35, 38}$. It has been verified that the applied potential bias can greatly suppress the photoelectron-hole recombination and make the dependence of the overall photocatalytic oxidation on oxygen insignificant$^{34, 35, 37-39, 106, 107, 109, 122}$. To my knowledge, the main intention of introducing a potential bias in previous studies was to improve the photocatalytic efficiency - all other useful information made available by the photoelectrochemical system has been ignored.

As previously mentioned, the nanoporous film TiO$_2$ electrodes can be treated as particulate semiconductor electrodes and photocatalytic degradation of organic compounds at this type of electrode shares most of the common steps as for the
photocatalytic degradation on TiO$_2$ particles. This means that the results obtained from photoelectrochemical studies at TiO$_2$ particulate electrodes ought to provide useful information for the understanding of photocatalytic degradation process taking place on TiO$_2$ particle photocatalysts and immobilized TiO$_2$ photocatalysts. Owing to the way photoelectrocatalytic degradation is carried out, studying photocatalytic degradation kinetics and thermodynamics of organic compounds by photoelectrochemical techniques has many advantages over the traditional methods. Firstly, the spatial separation of the oxidation half reaction (which occurs at working electrode) from the reduction half reaction (which occurs at auxiliary electrode) makes the photocatalytic processes independent of oxygen reduction. This greatly simplifies the system and allows the study of the photocatalytic oxidation process without the influence of the reduction half reaction and reduction reaction kinetics. Secondly, the method is a simple, rapid *in situ* method, which is capable of providing instantaneous kinetic information. Thirdly, the desired experimental parameters/conditions can be achieved easily with this photoelectrochemical method and a wide spectrum of organic compounds can be studied under comparable conditions, which makes the systematic evaluation of photocatalytic processes possible. Finally, photocurrent as an expression for the rate of the photocatalytic oxidation has a clear physical meaning since it directly reflects the photohole capture kinetics by organic substrates at the surface under sufficient potential bias.

In summary, I believe that the adoption of the photoelectrochemical method to study the photocatalytic oxidation of organic compounds at particulate semiconductor surface can offer significant advantages over traditional methods for obtaining new kinetic information.
1.6 PREPARATION AND CHARACTERISATION OF TiO$_2$ PHOTOCATALYSTS

Most of the semiconductor materials used for photocatalytic studies are metal oxides, such as TiO$_2$, WO$_3$, ZnO, CdO and In$_2$O$_3$, and metal chalcogenides such as CdS, CdSe, MoS$_2$ and WS$_2$. Among these photocatalysts, TiO$_2$ has drawn most attention due to its excellent chemical/photochemical stability, non-toxicity, high photocatalytic oxidation power and excellent photocatalytic activity towards a wide range of organic compounds. This section reviews the methods used for preparation and characterisation of TiO$_2$ photocatalysts.

1.6.1 Synthesis of TiO$_2$ Colloid

TiO$_2$ can be synthesised by several different methods including (i) inert gas condensation; (ii) flame synthesis by TiCl$_4$ oxidation; (iii) oxidation-hydrothermal synthesis from metallic Ti and (iv) hydrolytic precipitation of Titanium alkoxide or titanium salt (sol-gel method). Of particular interest is the sol-gel approach since it allows compositional and microstructural tailoring through controlling the precursor chemistry and processing conditions. Sol-gel processing also provides excellent chemical homogeneity and the possibility of deriving unique metastable structure at low reaction temperatures. In this study sol-gel method was adopted to synthesize the TiO$_2$ colloid.

1.6.2 Immobilisation of TiO$_2$

To prepare the TiO$_2$ films dry methods and wet methods are both used. Dry methods include chemical vapor deposition, sputtering, etc, and wet methods include sol-gel, Langmuir-Blodgett films, self-assembled monolayers and liquid phase deposition. Among these methods, the so-gel method has been widely used due
to simplicity in equipment, low cost and in particular, the ease of manipulating physical properties of immobilised TiO$_2$.\textsuperscript{120, 121, 130, 136}

Various substrates for immobilisation of TiO$_2$ particles have been reported. These include the non-conductive supports (e.g. glass, silica, etc) and conductive substrates (e.g. indium-doped tin oxide (ITO) coated glass, Ti, and noble metals).\textsuperscript{15, 62, 130, 137-140} Among these substrates non-conductive substrates are not suitable for my study because the application of electrochemical techniques requires conductive substrates. Among the conductive substrates used, Ti substrate seems to be a good choice, but the high-resistance compact TiO$_2$ layer unavoidably formed on Ti surface would complicate the photoelectrochemical response, it is not suitable for my purpose either. Noble metals have good electrocatalytic activity towards water oxidation, water reduction and oxygen reduction. If a porous TiO$_2$ film is immobilised on noble metals, pure electrochemical processes occur at the bare sites. The current response will be the sum of the currents derived from the photocatalytic processes and the pure electrochemical processes, complicating the system. Therefore, noble metals are not suitable as substrates for my study. ITO glass has been demonstrated to be a good substrate for fundamental studies due to its high overpotential for water oxidation/reduction and oxygen reduction, resulting in negligible currents from pure electrochemical processes.\textsuperscript{8} In general, there are two methods in widespread use for immobilisation of TiO$_2$ nanoparticle onto ITO glass. One is spread coating of TiO$_2$ nanoparticle paste,\textsuperscript{121, 131, 141} another is dip-coating.\textsuperscript{59, 60} The former is suitable for making thick film and the latter is suitable for thin film fabrication.

\textbf{1.6.3 Thermal Treatment}

The photocatalytic activity of a photocatalyst for a certain organic compound is heavily dependent on the physical properties of the photocatalyst. Physical properties, such as the bulk crystal structure, porosity, microstructures and surface area, all affect the
photocatalytic activity of TiO\textsubscript{2} photocatalyst\textsuperscript{61, 70}. Thermal treatment is a common and convenient practice used for manipulating the physical properties of a catalyst to improve the activity of the catalyst.

Many studies on the changing TiO\textsubscript{2} physical properties in an attempt to improve the photocatalytic activity of TiO\textsubscript{2} photocatalyst have been reported\textsuperscript{56, 58, 61}. Despite intensive investigation, due largely to the lack of assessment criteria (usually, the arbitrary selection of a specific organic compound against which the activities of photocatalysts were evaluated) and the limitation of the traditional kinetic study method, how the physical properties affect the photocatalytic activity of TiO\textsubscript{2} photocatalyst still remains unclear. This from another aspect reflects on the complexity of relating physical properties to the photocatalytic activity, and the difficulties in acquiring the intended physical parameters of the photocatalyst. In this study, the thermal treatment of immobilized TiO\textsubscript{2} films is adopted to manipulate the physical properties of the films. In addition, the thermal treatment of immobilized TiO\textsubscript{2} films also serves other purposes, including burning away organic pore-creating agent, obtaining better electric connection among TiO\textsubscript{2} particles and between TiO\textsubscript{2} particles and ITO conductive glass\textsuperscript{29}, and achieving good mechanical stability of the films. Overall, thermal treatment of TiO\textsubscript{2} nanoparticles on ITO allows us to investigate the effects of physical parameters of TiO\textsubscript{2} photocatalysts on their photocatalytic activity by photoelectrochemical methods.

1.6.4 Characterisation

1.6.4.1 Physical Characterisation

Many physical parameters influence the performance of TiO\textsubscript{2} photocatalysts\textsuperscript{94, 125, 142-148}. These include crystal structure (anatase or rutile), particle size, crystallinity, porosity, surface area, and surface hydroxyl groups. Generally, it is difficult to control the physical
properties of TiO\textsubscript{2} samples precisely and independently, because some of properties are related to each other and technically it is almost impossible to change one parameter without changing the others\textsuperscript{58}. Despite this, to understand the photocatalytic performance of a specific photocatalyst, a great deal of effort has been put into characterisation of TiO\textsubscript{2} photocatalysts. The following table outlines the characterisation methods commonly used and the information that can be obtained from these characterisation techniques.

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Information</th>
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<tbody>
<tr>
<td>X-ray diffraction (XRD)</td>
<td>Crystalline form</td>
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<tr>
<td>Photo correlation spectroscopy</td>
<td>Particle size distribution</td>
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<tr>
<td>X-ray photoemission spectroscopy</td>
<td>Surface elemental analysis, oxidation state</td>
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<td></td>
<td>information</td>
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<tr>
<td>Nitrogen adsorption-desorption</td>
<td>Pore size distribution</td>
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<tr>
<td>BET adsorption</td>
<td>Surface area</td>
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<tr>
<td>Scanning Electron Microscopy (SEM)</td>
<td>Surface morphology, microstructure</td>
</tr>
<tr>
<td>Transmission Electron Microscopy (TEM)</td>
<td>Surface morphology, crystallinity</td>
</tr>
</tbody>
</table>

1.6.4.2 Characterisation of Photocatalytic Activity

Preparation of photocatalysts of high photocatalytic activity is the ultimate goal for most of studies in the field of photocatalysis. To be of any practical value, a photocatalyst must be subject to photocatalytic activity evaluation. Given the existence of large number of organic compounds with different chemical identities, for a photocatalyst to be useful in various applications, it is imperative that it has reasonable photocatalytic activity toward a wide range of organic compounds. To date, most of the studies on the activity of TiO\textsubscript{2} photocatalysts, both in particle suspended form and immobilized form, are carried out by employing traditional approaches\textsuperscript{58, 62, 94, 149-151}. As pointed out in previous sections, these
traditional approaches have many limitations, which make these methods incapable of evaluating a particular photocatalyst effectively. It is known that the photocatalytic activity of a specific photocatalyst depends heavily on the types of substrates to be photocatalytically degraded\textsuperscript{152}. A highly active photocatalysts, evaluated by arbitrary selection of the photocatalytic degradation of one particular organic compound, does not secure its photocatalytic activity toward the photocatalytic degradation of others. In this regard, the photoelectrochemical approach offers many advantages. The most significant one is its rapidity and simplicity in acquiring kinetic and thermodynamic data under comparable conditions, which allows systematic evaluation of the photocatalytic activity of a particular photocatalyst towards many different organic compounds.

1.7 APPLICATIONS OF TiO$_2$ PHOTOCATALYSIS

Since the discovery by Fujishima and Honda in 1972 that water could be decomposed into hydrogen and oxygen over an illuminated titanium dioxide semiconductor electrode as storable fuel\textsuperscript{153}, the exploration of new applications of this material has been carried out enthusiastically by a generation of research scientists. Owing to its excellent photocatalytic activity, superior oxidation power and cheap production, TiO$_2$ has been applied to various photocatalytic processes in a broad range of application areas. The primary application of TiO$_2$ photocatalysis lies in water treatment (the mineralisation of organic pollutants in water)\textsuperscript{39, 72, 154-166}. Other applications include destruction of air pollutants\textsuperscript{167-169}, photocatalytic splitting of water\textsuperscript{170, 171}, solar energy conversion based on dye sensitization\textsuperscript{16, 29, 121, 131, 172}, self-cleaning window materials\textsuperscript{173, 61, 174}, removal of inorganic pollutants\textsuperscript{175}, destruction of bacteria and virus\textsuperscript{6, 7, 176}, and the photocatalytic reduction of N$_2$ and CO$_2$\textsuperscript{177, 178}. In addition, application of TiO$_2$ photocatalysis has been seen in chemical analysis, such as the indirect use of TiO$_2$ photocatalysis in the analysis of total organic carbon (TOC)\textsuperscript{179}, the use in the HPLC for analysis of organic compounds\textsuperscript{180}.
and indirect use in the analysis of chemical oxygen demand (COD). As part of this study, I propose a novel direct use of photoelectrocatalysis for the analysis of COD in water samples. Since this represents an important practical application of the present study, aspects of oxygen demand (and its analysis) are covered in the following section.

1.8 OXYGEN DEMAND (OD)

1.8.1 OD Index of Water

Nearly all natural, domestic and industrial waters contain organic matter. Even at low concentrations these organic compounds can cause detrimental oxygen depletion in waterways. The analytical determination of organic material in water and wastewater represents one of the most important measurable parameters for water quality. Currently, two standard analytical methodologies are in widespread use for the determination of the oxygen demand of waters and wastewaters. These are Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD). Both methods involve the quantification of oxygen requirement via oxidative degradation of the organic matter present in the sample. When the oxidation is carried out biochemically (with the aid of microorganisms) the methodology is known as BOD. When the oxidation is carried out chemically (via the use of strong oxidant such as dichromate) the methodology is referred to as COD. For BOD, this is done by measuring O\textsubscript{2} consumption over five days; for COD it is done by measuring oxidant depletion.

The current standard method for determining the BOD of wastewaters is the five-day BOD\textsubscript{5} method. The five-day duration is clearly the most serious limitation where rapid feedback is required for environmental monitoring and/or process control. Other problems with the BOD\textsubscript{5} assay include: limited linear working range; complicated and time-consuming procedures; questionable accuracy and poor reproducibility.
1.8.2 Standard COD Analysis Method

The COD method is more accurate and more rapid than BOD method. It is the preferred method for assessing the oxygen demand in heavily polluted water bodies and is the national standard method for organic pollution evaluation in many countries. Depending on the oxidants used, there are two COD standard analysis methods in use. These are the dichromate method and the permanganate method. Of these two, dichromate method is more accurate and reproducible due to its strong oxidation power. It is therefore the preferred COD method. Despite its widespread use and its acceptance as APHA (American Public Health Association) and EPA (Environmental Protection Agency) standard method for COD assay, the method has several drawbacks. These include: requirement of harsh experimental conditions (high temperature, concentrated H\textsubscript{2}SO\textsubscript{4}), long analysis time (2-4h), use of highly toxic reagents (e.g. Hg(II) and Cr(VI)), use of expensive reagents (e.g. Ag\textsubscript{2}SO\textsubscript{4}) and the difficulty to be automated.

1.8.3 Current Status in the Development of New COD Analysis Methods

Due to the limitations of the conventional standard COD analysis methods, many efforts have been made to overcome these problems. Recent advances in method development for COD determination can be classified into two categories. One is, based on the principle of the conventional chemical oxidation methods, simplifying and automating the analytical process. Another is, based on the electrocatalytic oxidation of organic substances, carrying out the COD assay electrochemically. The latter approach, being simple, fast, direct and easily automated, has drawn more attention. LAR GmbH, a German instrument manufacturer, has developed an electrochemical COD instrument using PbO\textsubscript{2} electrodes as anodes, which has been successfully implemented in an automatic online monitoring system. However, obviously there is considerable assay difference between the instrument and the conventional methods, which even led to their
defining a new terminology, Electrochemical Oxygen Demand. Even though such a method is acceptable as an on site monitoring method, its viability as a standard water quality assay methodology is questionable. Karube and co-workers have also published a series of research papers employing composite oxide materials as electrocatalytic anodes. In their work, a copper oxide coated copper electrode was used as the electrocatalytic anode 188, 192. In these studies, the electrodes were only tested on a few fairly easily oxidisable organic substances. Even with organic substances such as carbohydrates and amino acids, a poor correlation was found between their COD method and standard COD method. Another attempt was made by Rossler-Fromme 190, using AgO and CuO composite carbon paste electrode. Unfortunately, the range of the organic compounds that can be oxidized at this electrode is limited.

Several problems exist when employing the conventional electrochemical approaches described above. Firstly, although the oxidising power of the electrode can, theoretically, be adjusted continuously, the high overpotential of electrochemical oxidation of most organic compounds at electrodes makes the rate of water oxidation faster than the speed of oxidation of organic compounds. As a result the electrochemical signal for their oxidation is usually buried in that for water oxidation. This would greatly influence the sensitivity, resolution, reproducibility and accuracy of COD result. Secondly, it is almost impossible to use a normal inert electrode to get meaningful COD value. Researchers typically resort to electrocatalytic electrodes that have high selectivity for the oxidation of organic compounds. The catalytic electrodes investigated so far are all themselves electrochemically active. As a consequence, the reproducibility of the assay suffers. Thirdly, the oxidation power of the electrode is limited by the oxidising power of the electrocatalyst. To date, no electrocatalyst reported has the oxidising power to oxidise a broad spectrum of organic pollutants whilst still being stable in aqueous media. Therefore
the spectrum of organic pollutants, which can be oxidised by such electrode, is limited. This is probably the most serious problem associated with these approaches.

To date, all COD methods based on electrochemical oxidation principles including those used in the commercial instruments are only capable of oxidising a very small fraction of organic compounds in the sample. In other words, these methods obtain the analytical signal from a very small fraction of the analytes in samples and then use it to predict the overall COD of the sample. These analytical results may be meaningful only when the percentage of the detectable components to the rest of sample matrix is fixed. This is obviously impossible to achieve in practice since the matrix of the sample will change from one site to the other and even at the same site, it will change from time to time. Attempts to minimise this matrix effect by employing standard calibration has also failed to bring the analytical results obtained from these methods in-line with the standard COD method. This is because no universal standard can be defined for COD being an aggregate organic parameter. As a result, the COD values obtained by employing these methods are highly questionable. In addition, electrochemical methods for COD analyses suffer from poisoning of the electrode caused by the adsorption of un-oxidisable organic substances or the polymerisation of oxidation intermediates.

More recently, Karube reported a new methodology for COD assay based on photocatalytic oxidation principle\textsuperscript{181, 183}. This approach utilizes TiO\textsubscript{2} particles as photocatalyst to replace the traditional oxidizing agent (e.g. Cr(IV)). In this process, the oxygen concentration change during the photocatalytic degradation is measured as the analytical signal using a pair of oxygen electrodes. This depletion of O\textsubscript{2} is then correlated with standard COD methods. The photocatalytic degradation approach is more promising in comparison with electrocatalytic degradation methods due to the strong oxidation power of illuminated TiO\textsubscript{2} particles. Despite this, the approach suffers several problems.
These include the low fraction of degradation, which is a trade-off for a faster analysis time, low sensitivity caused by the small change in oxygen concentration during degradation, limited dynamic working range due mainly to the low solubility of oxygen in water and the need to control experimental temperature since oxygen concentration measurement by an oxygen electrode is highly temperature dependent. Furthermore, the low degradation efficiency makes the method also matrix dependent, thus requiring the system to be calibrated in order to correct for this influence. As mentioned above, because COD is an aggregate parameter, it is difficult to define an appropriate calibration standard that would be universally applicable to all matrices. This is not just an inconvenience for the system operation but it would also impact on the accuracy and reproducibility of the method. In a later paper they described their method as “neither sensitive nor reproducible”\textsuperscript{183}.

In summary, to date there is still no simple, rapid, accurate and reproducible methodology to replace the conventional COD method.

1.9 SCOPE OF THE THESIS

The primary aim of this study is to develop a series of photoelectrochemical methodologies that can be used for systematic characterisation of kinetic and thermodynamic properties of photocatalysis processes at TiO\textsubscript{2} nanoparticle surfaces.

Generally, an overall photocatalysis process involves three major processes:

(i) Solution process: involving the reactant and product transport to or from the electrode surface. In an aqueous media, this process is determined by the solute properties, which is mainly related to the physical properties of the compound such as molecular size, charge status, solubility, hydrophobicity, diffusion coefficient etc. This process is related to the subsequent interfacial process and may even
become a dominant process for the overall photocatalytic process under certain experimental conditions.

(ii) Interfacial process: involving the interactions between the light and semiconductor, interactions of photoholes/photoelectrons with semiconductor surface groups, the interactions between the semiconductor and the reactant/product, charge carrier recombination and charge transfer processes. This process is determined by the nature of both semiconductor and reactant. Nevertheless, the process may, in some cases, be affected by the experimental conditions. For example, pH of a solution determines the speciation conditions (i.e. functional group, charge status etc) of both electrode surface and the compound in solution, which will greatly affect the adsorption process at the interface. In addition, this process can be influenced by both the above solution process and the subsequent semiconductor physical process.

(iii) Semiconductor physical process: involving the migration, separation, recombination of photoelectrons and photoholes within the semiconductor. This process mainly is determined by the physical properties of the semiconductor (i.e. electrical conductivity, crystalline structure, bandgap/band structure, particle size etc), but can also be strongly influenced by the interfacial process and experimental conditions (e.g applied potential bias).

It is clear that two types of information are required to fully understand the above processes - one is related to the nature of the semiconductor and the other is concerned with the nature of the reactant. It is also obvious that the overall photocatalysis process incorporates the above three processes in an integrative manner, which makes the study of one process in isolation of others very difficult. The complexity of the system makes the traditional research methods for determining meaningful photocatalytic kinetic and
thermodynamic information powerless. As the primary aim of this study, I attempt to develop a new strategy in systematic characterisation of photocatalytic processes occurring at a particulate TiO$_2$ nanoporous electrode with expectation that the findings of this study (and especially the research methodology developed through this study) would be useful in understanding and studying other photocatalysis processes.

The photoelectrochemical methodologies developed in this study for kinetic and thermodynamic characterisation involve the use of TiO$_2$ nanoparticle electrodes. Chapter 2 investigates the fabrication and characterisation of the particulate TiO$_2$ nanoporous electrodes. The physical, electrochemical and photocatalytic characteristics of these electrodes were studied.

In Chapters 3 to 6, the investigations focused on a better understanding of fundamentals involved in TiO$_2$ photocatalytic processes at TiO$_2$ nanoparticulate electrodes. A set of methodologies was developed and used to obtain an insight into photocatalytic processes and TiO$_2$ nanoparticulate electrodes. Due to the extremely large numbers of existing organic compounds, it is impossible to exhaustively investigate the photocatalytic behaviours of each individual compound at the semiconductor surface. Nonetheless, it is feasible to perform detail studies on the photocatalytic behaviour of different categories of model compounds. The classification of organic compounds for this study was based on the significance of the properties of the compounds influence on the photocatalysis processes at TiO$_2$ nanoparticulate electrodes. The adsorptivity of organic compounds and adsorption processes occurring at TiO$_2$ surface have been identified as a primary parameter for the classification. According to this, all organic compounds were classified into two main categories - the weak adsorbates and the strong adsorbates. Model compounds from each category were strategically chosen to represent the general case for that category of compounds.
In Chapter 3, glucose was chosen as a model compound to represent weak adsorbates. A new methodology based on photoelectrochemical technique was proposed. The kinetic behaviour of photocatalytic degradation of glucose at a TiO$_2$ nanoparticulate electrode was extensively characterised by the proposed photoelectrochemical method. The semiconductor physical process of the TiO$_2$ nanoparticulate film electrode focusing on the difference from bulk semiconductor electrodes was also investigated by the proposed method. The mechanisms of photoelectron movement inside of the particulate semiconductor film electrode was proposed and experimentally validated.

In Chapter 4, potassium hydrogen phthalate (KHP) was chosen as a model compound to represent strong adsorbates. A new methodology based on photoelectrochemical technique was developed for characterising the thermodynamic properties of adsorption process at TiO$_2$ nanoparticulate electrodes. The kinetic behaviours of photocatalytic degradation of potassium hydrogen phthalate were studied in detail by this newly developed method in combination with the method developed in Chapter 3. Due to the significant difference in photocatalytic oxidation kinetic behaviour among different strong adsorbates, a series of dicarboxylic acid ranging from the simple to more complicated ones were studied. A kinetic model under interfacial reaction controlled condition was proposed and experimentally proven.

It is anticipated that the classification method used for this study may be too simple and the photocatalytic behaviours of different compounds from the same category may differ from each other. In order to overcome this, the organic compounds from each category were further classified according to their functional groups. In Chapter 5, I investigated photocatalytic kinetic characteristics of large numbers of compounds from each category at a low temperature calcined electrode using the methods developed in Chapters 3 and 4. The kinetic and thermodynamic data obtained from these compounds were analysed and
correlated with their chemical nature. By doing so, the conclusions of Chapters 3 and 4 drawn from single model compound were generalised to large number of compounds.

In realisation of the physical property difference of TiO$_2$ film electrodes calcined at different temperatures – causing different photocatalytic kinetic behaviours, I investigated photocatalytic kinetic characteristics of large number of compounds at a high temperature calcined electrode in Chapter 6. The kinetic characteristics of these compounds at the electrode were compared with those obtained at the low temperature calcined electrode.

In Chapter 7, the aim was to develop a suitable method for studying photocatalytic behaviour in a thin-layer photoelectrochemical cell where exhaustive mineralisation of substrates can be fulfilled. The photocatalytic mineralisation of different categories of compounds at the TiO$_2$ nanoparticulate electrode in a thin-layer photoelectrochemical cell was investigated. The findings of this part of the study were to be used as the foundation for development of a new environmental monitoring technique described in Chapter 8, which was set as a secondary aim for this study.

In Chapter 8, as an example of application, a novel analytical principle for determination of aggregate properties of sample solution such as chemical oxygen demand was proposed and experimentally validated.

The overall summary of this study was given in Chapter 9 with indication of future research directions.
CHAPTER 2  PREPARATION AND CHARACTERISATION OF TiO$_2$ COLLOID AND TiO$_2$ NANOPARTICULATE FILM ELECTRODES
2.1 INTRODUCTION

TiO\textsubscript{2} electrode preparation and characterisation are of paramount importance for the success of this study since the photocatalytic activities of these electrodes depend on the crystalline structure of TiO\textsubscript{2}, microstructure and the immobilisation technique\textsuperscript{2, 58, 61, 70, 82, 193}.

TiO\textsubscript{2} exists in nature in two tetragonal forms, rutile and anatase, and each possesses its own photocatalytic characteristics\textsuperscript{3, 44, 66, 194-196}. The applications of these photocatalysts are typically carried out in two different ways – as a particle suspension and as an immobilised film\textsuperscript{3, 34, 35, 108-110}.

To date, most of reported kinetic studies have been carried out using either TiO\textsubscript{2} nanoparticle slurries or immobilized TiO\textsubscript{2} film by traditional kinetic study methods\textsuperscript{76-78, 111, 118, 155, 179, 197}. However, the reproducibility and accuracy of the methodologies are poor\textsuperscript{8, 9, 11}. More importantly, it is extremely difficult to obtain the real time or instantaneous kinetic information by employing this type of methodology due to the inherent drawbacks involved (see Section 1.5.3.)\textsuperscript{8, 9, 11}.

For photoelectrochemical studies, two different types of semiconductor electrodes: the bulk and the particulate semiconductor electrodes are frequently used. The bulk semiconductor electrodes are unsuitable for studying the photocatalytic oxidation of organic compounds by photoelectrochemical method due to the electronic characteristics at the bulk semiconductor interface. At these electrodes, usually the interfacial charge transfer process is not the control step for the overall photocatalytic process, as a result the photocurrent response obtained from these type of electrodes in solution is insensitive to the presence of organic compounds\textsuperscript{31, 33, 198}. The particulate TiO\textsubscript{2} porous film electrodes possess the characteristics of TiO\textsubscript{2} nanoparticles and the interfacial charge transfer
reaction processes control the overall photocatalytic process, as a result, their photocurrent responses are sensitive to the presence of organic compounds and the variation of experimental conditions. This type of electrodes has been widely used in dye sensitised solar cell applications. They have also been used for the photocatalytic degradation of organic compounds under direct under-band gap light excitation. However, most of these studies focused solely on the effect of the application of potential bias on the photocatalytic degradation efficiency.

The photocatalytic activity of a particulate TiO$_2$ porous film electrode depends on the crystal structure, crystallinity, particle size, surface area and surface hydroxyls, and all of these parameters are dependent on how the electrode is prepared. In this chapter, I investigate the fabrication of particulate TiO$_2$ porous film electrodes with particular focus on the effect of thermal treatment conditions. Structural, surface morphology and photocatalytic properties of the resultant electrodes were characterised. I adopt a well-documented method for the synthesis of TiO$_2$ colloidal particles developed by Gratzel’s group for the preparation of particulate TiO$_2$ porous film electrode. For immobilisation of TiO$_2$ nanoparticles onto conductive substrates a dip-coating method has been adopted for making thin film. In order to achieve better conduction and adhesion, the dip-coated films were subjected to a thermal treatment process. This treatment process serves the purpose of manipulating the physical parameters of the electrodes because the particle size, surface morphology, surface area and crystalline forms of the resultant electrode depend on the calcination conditions. Phthalic acid was chosen as a model organic compound to evaluate the photocatalytic reactivity of electrodes made under different conditions by photoelectrochemical techniques. It is chosen not only because it is an aromatic organic compound (it can represent aromatic organic pollutants in some wastewater) and is the standard organic compound in standard COD analysis method but also during its degradation a lot of
intermediates are involved which could deactivate the photocatalyst. It is relatively hard to be mineralized. The photocatalytic activity of the electrodes for its photocatalytic degradation is presumably a bottleneck issue of my proposed application.

2.2 EXPERIMENTAL

2.2.1 Material and Chemicals

Indium Tin Oxide (ITO) conducting glass slides (8Ω/square) were commercially supplied by Delta Technologies Limited. Titanium butoxide (97%, Aldrich), potassium hydrogen phthalate (AR, Aldrich), isopropyl alcohol (AR, Merck) and carbowax 20M (Supelco) were used as received. All other 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).

2.2.2 TiO₂ Colloid Synthesis and Immobilisation Procedure

The typical synthesis procedure of TiO₂ colloid is similar to that used by Gratzel²⁹, ¹²⁰, ¹³¹. A mixture of 12.5ml titanium butoxide and 4ml isopropyl alcohol were added drop-wise at room temperature to a 150ml 0.1M nitric acid solution under vigorous stirring. Hydrolysis of titanium ions took place instantly, forming nonstoichiometric titanium oxide and hydroxide slurry. After hydrolysis the slurry was heated to 80°C and stirred for 8h to achieve peptization (i.e., destruction of the agglomerates and redispersion into primary particles). The colloid was then filtered to remove the nonpeptized agglomerates.

For better crystallinity of the nano-particles, the colloid was hydrothermally treated in an autoclave at 200°C for 12h. During the autoclaving sedimentation occurred, and after autoclaving the particles were redispersed by sonication. Water was used to adjust the final solid concentration to ca. 6% w/v. To prevent cracking during calcination and to
create porosity within the film, carbowax 20M (Merck) was added to the colloidal suspension in a proportion of 30% of the solid TiO$_2$ weight. The colloid thus obtained was used for the preparation TiO$_2$ nanoporous film electrode.

ITO conducting glass slides were used as the substrate for immobilisation of TiO$_2$ particles. To get a clean surface, the ITO glass slide was pre-treated by washing in turn with detergent, water, chromic acid washing solution, water and ethanol. In order to avoid acidic dissolution of the ITO layer, washing time with the chromic acid was kept to less than 30 seconds. The conductance of the substrate was checked before and after the treatment to ensure no measurable conductivity change was observed. After the pre-treatment, the ITO slide was dip-coated in the colloidal solution and dried in air. The coated slides were then calcined in a muffle furnace in air at different temperatures for different time durations. For X-ray diffraction characterisation silicon wafers were used as the substrate for coating the TiO$_2$ porous film and the coated silicon wafers were subject to the same thermal treatment as coated ITO glass slides.

2.2.3 Apparatus and Methods

The particle size and crystallinity of colloidal TiO$_2$ particles was characterised using transmission electron microscopy (TEM) (Philips CM200). The TiO$_2$ film microstructure was studied using a high resolution scanning electron microscopy (SEM) (JSM-6400F, JEOL). X-ray diffractometry was performed with a Philips PW1050 diffractometer using CuKα radiation. The thickness of the TiO$_2$ coated film was ca. 1µm, measured with a surface profilometer (Alpha-step 200, Tencor Instrument).

All photoelectrochemical experiments were performed at 23°C in a three-electrode electrochemical cell with a quartz window for illumination. The TiO$_2$ film electrode was used as the working electrode and placed in an electrode holder with ca. 0.65cm$^2$ left
unsealed to be exposed to the solution for illumination and photoelectrochemical reaction. Figure 2.1 shows Photographs of the components of electrode holder. Figure 2.1 (a) shows the parts of the holder and Figure 2.1 (b) shows the assembled working electrode.

![Photographs of the electrode holder](image)

**Figure 2.1** Photographs of the electrode holder, unit in Figure 2.1(b) is mm.

A saturated Ag/AgCl electrode and a platinum mesh were used as the reference and auxiliary electrodes respectively. 0.1M NaNO₃ was used as the supporting electrolyte. A voltammograph (CV-27, BAS) was used for application of potential bias in steady state photocurrent measurements and linear potential sweep experiments. Potential and current signals were recorded using a Macintosh computer (7220/200) coupled to a Maclab 400 interface (AD Instruments). Illumination was carried out using a 150W xenon arc lamp light source with focusing lenses (HF-200W-95, Beijjing Optical Instruments). To avoid the sample solution being heated-up by infrared light, the light beam was passed through an UV-band pass filter (UG 5, Avotronics Pty, Limited) prior to illumination of the electrode surface. The experimental set-up for photoelectrochemical experiments is shown in Figure 2.2.
2.3 RESULTS AND DISCUSSION

2.3.1 Characterisation of the TiO₂ Nanoparticles

It is known that amorphous TiO₂ has no photocatalytic reactivity due to severe structural defects that act as electron/hole recombination centres under illumination\(^3, 29, 58, 208\). For electrode fabrication, it is preferable to start with nanoparticles having good crystallinity. Upon the hydrolysis of butoxide, a white precipitate of large agglomerates of primary particles formed immediately. These agglomerates were peptised to obtain mono-dispersed particles (colloids). After this process, the resultant particles may still not be well crystallized due to the existence of excessive hydroxyl groups and non-stoichiometric Ti-O-Ti bridging bonds. To increase the crystallinity of the TiO₂ colloidal particles obtained after hydrolysis and pectisation, the colloidal suspension was subjected to hydrothermal treatment in an autoclave. Figure 2.3 shows the TEM images of the TiO₂ particles before and after autoclaving. Before autoclaving the surfaces of TiO₂ particles are very coarse with particle size ranging from 4nm to 8nm. The particles are not well
crystallized. After autoclaving it shows clearly that the particle surfaces are well defined and nanocrystals are clearly seen with particle sizes ranging from 8nm-10nm. After autoclaving the crystallinity of the particles is improved and the particle also grow larger. This suggests that during the treatment very small amorphous particles are dissolved and re-deposited on larger particles and at the same time the extra hydroxyl groups inside the particles are dehydrated.

Error! Not a valid link.

**Figure 2.3** The TEM images of TiO\textsubscript{2} particles before (left) and after (right) autoclaving.

To further look at their crystallinity, electron diffraction patterns of the colloidal particles before and after autoclaving were taken (Figure 2.4). From the electron diffraction patterns it can be seen that, after autoclaving, the particles give clear diffraction circles that are typical for random-oriented and well-defined polycrystalline particles. The electron diffraction patterns obtained before autoclaving are somewhat “fuzzy”, which is typical for systems containing a mix of crystallinity and amorphous structures. Computer fitting (Intensity Process Diffraction v.1.20) of the electron diffraction pattern intensity demonstrates that the hydrothermal treatment does not change the crystalline forms, and particles before and after autoclaving are mainly composed of anatase phase (99.9%). In both cases, a very small portion of brookite phase of TiO\textsubscript{2} was found.

These results indicate that autoclaving is necessary and desirable for obtaining TiO\textsubscript{2} nanoparticles of high crystallinity.
2.3.2 Crystalline Structure and Surface Morphology of TiO$_2$ Porous Films

The TiO$_2$ nanoparticle coated films were calcined in air at different temperatures and for different durations. The purposes of this treatment on one hand are to obtain better electric contact between the ITO substrate and the nanoparticles (and between TiO$_2$ nanoparticles) and also to improve the adhesion between the substrate and the TiO$_2$ nanoparticles, which will improve the physical stability of the electrode. On the other hand, the photocatalytic performance of the electrode can be improved by thermal treatment due to the changes of crystalline structure and other surface properties. The films were calcined at various temperatures from 500°C to 850°C and were characterised by x-ray diffraction and SEM.

Figure 2.5 shows the x-ray diffraction patterns of TiO$_2$ films calcined at various temperatures. It was found that the intensity of the diffraction peak of the anatase (101) plane increased as the calcination temperature increased suggesting an improvement in crystallinity and growth of particle size. A decrease in the half peak width with increasing
calcination temperature and calcination time was also observed. This implies an improvement in crystallinity and an increase in the degree of aggregation between primary particles (or growth of the particles) due to an increase in calcination temperature and/or calcination time.

![X-ray diffraction patterns of the TiO\(_2\) films calcined at various temperatures and different time lengths](image)

**Figure 2.5** X-ray diffraction patterns of the TiO\(_2\) films calcined at various temperatures and different time lengths, (a) 500°C 0.5h, (b) 600°C 0.5h, (c) 700°C 0.5h, (d) 750°C 0.5h, (e) 700°C 16h, (f) 750°C 8h, (g) 850°C 0.5h.

The crystallite size can be estimated from XRD line broadening according to the Scherer equation\(^\text{56,209}\):

\[
r = \frac{K\lambda}{\beta\cos\theta}
\]  

(2.1)

where \(r\) is the particle size in the film, \(K\) is a constant, \(\lambda\) is the wavelength of X-ray (CuKa = 1.5406 Å), \(\beta\) is the true half-peak width, and \(\theta\) is the half diffraction angle of the centroid of the peak in degree.

The particle size and the phase composition calcined for various calcination temperature treated electrodes is listed in Table 2.1.
<table>
<thead>
<tr>
<th>Calcination temperature and time duration</th>
<th>Particle size (nm)</th>
<th>Phase composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>500°C, 0.5h</td>
<td>7</td>
<td>Anatase (100%), rutile (0.0)</td>
</tr>
<tr>
<td>600°C, 0.5h</td>
<td>10</td>
<td>Anatase (100%), rutile (0.0)</td>
</tr>
<tr>
<td>700°C, 0.5h</td>
<td>18</td>
<td>Anatase (99.9%), rutile (0.1%)</td>
</tr>
<tr>
<td>700°C, 16h</td>
<td>33</td>
<td>Anatase (96.8%), rutile (3.2%)</td>
</tr>
<tr>
<td>750°C, 0.5h</td>
<td>24</td>
<td>Anatase (99.8%), rutile (0.2%)</td>
</tr>
<tr>
<td>750°C, 8h</td>
<td>33</td>
<td>Anatase (96.5%), rutile (3.5%)</td>
</tr>
<tr>
<td>850°C, 0.5h</td>
<td>43(anatase), 45(rutile)</td>
<td>Anatase (81.4%), rutile (18.5%)</td>
</tr>
</tbody>
</table>

The particle size deduced in this way may only serve as a guide to estimate the grain size of primary particles, the particle size of secondary particles and the degree of aggregation among the primary particles in a secondary particle because crystallinity of primary particles and the degree of aggregation between primary particles in a secondary particle affect the intensity of diffraction peaks\textsuperscript{210, 211}. At low calcination temperature (500°C) the deduced particle size is close to the particle size of the colloidal particles, indicating low degree of aggregation of the primary particles. The XRD patterns obtained from the films calcined below 750°C for half hour show mainly the anatase phase of TiO\textsubscript{2} and no rutile diffraction lines were observed. However, with the use of SIROQUANT software fitting the diffraction patterns, small portion of rutile phase was identified for the films calcined at 700°C and 750°C for 0.5h, while for the films calcined at 500°C and 600°C the fitting results show no existence of rutile phase. A significant amount of rutile phase was found for the film calcined at 850°C for 0.5 hours or the films calcined at 700°C and 750°C for longer periods.

The effects of calcination temperatures and time duration on the surface morphology of the resultant films were examined by scanning electron microscopy. Figure 2.6 shows the
SEM images of the films calcined at various temperatures and for various times. A similar surface morphology with highly porous microstructures was observed for those electrodes calcined at temperatures from 500°C to 750°C for 0.5h (see Figure 2.6, (a) to (d)). The shape of primary particles (similar to colloidal particles) can still be observed from these films. The sizes of secondary particles in these films were found to be very similar, ranging from ca. 30nm to 50nm. Interestingly, the sizes deduced from X-ray diffraction fall in between the primary particle size and the secondary particle size. At low calcination temperature, the XRD deduced size is close to the primary particle size while at higher calcination temperature the XRD deduced size is similar to the size of secondary particles shown by the SEM images. Based on the above observations, it can be inferred that the change of particle size deduced from XRD reflects the degree of aggregation and crystallinity between primary particles in the aggregates.

For films calcined at 700°C and 750°C for longer periods (see Figure 2.6, (e) and (f)) the primary particles can no longer be discerned. In these cases, the edges of primary particles in the secondary particles disappeared indicating a high degree of aggregation between primary particles. Still, the particles are very coarse and the films are porous though porosity is greatly decreased. The sizes of secondary particles in these films were from 50nm to 70 nm. For the film calcined at high temperature (850°C) for a short period (0.5h) SEM image shows a much larger secondary particle size though the edges between primary particles can still be seen. The porosity of this film is greatly decreased in comparison with the films calcined at lower temperatures.
Figure 2.6  SEM images of the TiO$_2$ film electrodes calcined at different temperature and time length, (a) 500 °C, 0.5h, (b) 600 °C, 0.5h, (c) 700 °C, 0.5h, (d) 750 °C, 0.5h, (e) 700 °C, 16h, (f) 750 °C, 8h, (g) 850 °C, 0.5h.
The above results indicate that the TiO₂ porous films with different crystal structures and microstructures have been prepared. In the following sections, how these physical properties influence the photocatalytic activity of these films will be investigated.

2.3.3 Effect of Potential Bias

As shown by SEM images, the TiO₂ films are interconnected porous particle networks, through which electrolyte can penetrate the semiconductor film and reaches the substrate. Even though the TiO₂ film itself possesses poor conductivity in the dark (without illumination) and electrochemical reactions are unlikely at the semiconductor film, direct electrochemical reactions may occur at the bare sites of the conducting substrate (ITO glass). Voltammograms obtained from linear potential sweep experiments without illumination were similar for all electrodes regardless of calcination temperature and calcination time. A set of typical voltammograms is shown in Figure 2.7.

![voltammogram](image.png)

*Figure 2.7* The linear potential sweep voltammograms of the electrode calcined at 500°C for 0.5h in air in dark, in blank 0.1M NaNO₃ solution (solid line) and in electrolyte +40µM potassium hydrogen phthalate (dash line), scan rate 5mV/s.
Under such conditions, the voltammograms revealed very little differences in the presence and absence of potassium hydrogen phthalate. The cathodic current observed below –0.2V can be attributed to the direct electrochemical reduction of water and/or oxygen at bare site of the ITO substrate while almost zero current was observed above –0.2V indicating that there is no pure electrochemical oxidation of either water or the organic compound occurs at the bare sites of the ITO substrate within this potential range.

Figure 2.8 shows the linear potential sweep voltammograms of a TiO\textsubscript{2} electrode calcined at 500°C for 0.5h under illumination in a blank solution (containing electrolyte only) and a test solution (containing electrolyte and potassium hydrogen phthalate). It is important note that voltammograms obtained under illumination were similar for all electrodes regardless of calcination temperature and time period.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_8.png}
\caption{Linear potential sweep voltammograms of the electrode calcined at 500°C in air for 0.5h, under illumination in 0.1M NaNO\textsubscript{3} blank solution (dash line) and in blank electrolyte + 40µM potassium hydrogen phthalate (solid line). Scan rate 5mV/s.}
\end{figure}

In contrast to the zero anodic current obtained at high potential in dark, under illumination, almost linear increase in anodic photocurrents was observed in the low
potential range with or without the presence of organic compound. In high potential range, the photocurrents levelled off. In the absence of organic compound, the anodic photocurrent observed can be attributed to the photocatalytic oxidation of water. When organic compound was present, the anodic photocurrent observed was the sum of the oxidation current due to both water and the organic compound. In other words, the photocurrent obtained in the presence of organic compound is superimposed on the photocurrent generated from the oxidation of water. This is the reason for the saturation photocurrent obtained in the presence of potassium hydrogen phthalate is higher than that obtained in the blank electrolyte solution.

For particulate semiconductor electrodes upon illumination, electron-hole pairs are formed and localised on the particles. The overall photocatalytic reaction rate depends on the efficient removal of both charge carriers (photoelectron and hole)\(^3,29\). At a given light intensity and solution composition, the photohole removal rate is constant, which is equivalent to the saturation photocurrent obtained under such conditions. At the same time, the overall photohole capture rate is also related to the removal rate of electrons, which is dependent on the applied potential bias\(^8\). If there is electron build-up on the particles, it will suppress the photohole capture rate and facilitate the photoelectron-hole recombination. As a result the overall photocatalytic oxidation rate will be decreased. The applied potential bias, in effect, acts as an external force to removal the photoelectron by drawing the electron through the external circuit to the auxiliary electrode. This is, in turn, minimises the build-up of electrons on the particles. In the low potential range, the removal rate of the available photoelectron is proportional to the electric field across the film. The degree of the electron build-up decreases with an increase in the potential bias. Therefore, the overall photocatalytic oxidation rate (photocurrent) increases with potential bias. Under these conditions, the overall process is controlled by electron migration in the semiconductor film. When the applied potential bias is sufficiently high, there is no
electron build-up and the overall photocatalytic oxidation rate is solely reliant on the
photohole capture rate at TiO$_2$ particle surface. This is represented by the saturation
photocurrent, with respect to potential bias, observed in the voltammograms. Under such
conditions, the photohole capture rate at the particle surface controls the overall
photocatalytic oxidation process. The role and importance of applied potential bias in the
overall photocatalytic oxidation process will be discussed further in the next chapter.

2.3.4 Photocatalytic Oxidation of Water

Under illumination, the voltammograms obtained from a 0.1M NaNO$_3$ blank solution for
all electrodes calcined with different temperatures exhibit the similar characteristics as the
voltammograms shown in Figure 2.8. The saturation photocurrent ($I_{sph}$) obtained from the
blank electrolyte solution indicates photocatalytic oxidation rate of water. Figure 2.9
shows the plot of $I_{sph}$ against the electrode calcination temperature. It was found that
when the electrodes were calcined with temperatures below 600°C, $I_{sph}$ resulting from
water oxidation remains virtually unchanged with calcination temperature, indicating the
similar photocatalytic activity towards water oxidation. For those electrodes calcined at
temperatures above 600°C, an increase in the electrode calcination temperature results in
an increase in the $I_{sph}$, indicating the photocatalytic efficiency towards water oxidation is
enhanced. As shown in Figure 2.6, the morphology and microstructure of the films at the
calcination temperature up to 750°C are very similar. Also, the particle sizes on the films
(deduced from XRD) were shown monotonously as calcination temperature increases,
which may indicate that the degree of condensation between primary particles is
increased. The increase in $I_{sph}$ for electrodes calcined above 600°C is therefore unlikely to
be due to changes in crystallinity and/or the degree of aggregation between primary
particles. Instead, the change of $I_{sph}$ with calcination temperature appears to coincide with
the change in crystalline form. As shown in Table 2.1, the rutile phase exists when the
electrode is calcined with 700°C (although slightly) for 0.5hr and the percentage of rutile phase increases as the calcination temperature increased. It is known that photocatalytic evolution of oxygen from water oxidation is faster at rutile form than at the anatase form of TiO₂⁶⁶, ¹⁷⁰, ²¹². My result is therefore in agreement with Abe’s result where it was claimed that the rutile form is much more active than the anatase form towards the photocatalytic oxidation of water when a sacrifice electron acceptor is used ¹⁷¹.

![Figure 2.9](image)

**Figure 2.9** The dependence of saturation photocurrent on the calcination temperature of electrodes

The underlying mechanism for this enhancement of water oxidation in my case may be due to the fact that the rutile phase can facilitate the combination of surface bound hydroxyl radicals to form O₂ molecules. The fact that adsorption of oxygen on the anatase form of TiO₂ is easier and the adsorption amount is larger (than on rutile form) supports this argument ⁵⁶. Another possibility, or together with the above, concerns the coexistence of both rutile and anatase forms (with different band gaps) on the same electrodes. Contact between the two can facilitate the temporal and spatial separation of the photogenerated electron/hole pairs and increase the lifetime of the electron/hole pairs. It
has been well documented that coupling semiconductors of different band gaps can improve the photocatalytic reactivity of a photocatalyst by prolonging the lifetime of photoelectron and photohole pairs\textsuperscript{3, 38, 213}. To further test this hypothesis, commercial TiO\textsubscript{2} powder (p25) containing a higher proportion of rutile form was immobilised onto an ITO substrate with approximately the same thickness. This electrode was then calcined at 450°C for half an hour – a temperature at which the phase composition does not change. When the same experiment was performed under same conditions, a much higher photocurrent from water oxidation was observed. This indicated that the presence of both crystalline forms (in high proportions) led to higher rate for photoelectrocatalytic oxidation of water.

2.3.5 Photocatalytic Oxidation of Potassium Hydrogen Phthalate

As shown in Figure 2.8, when potassium hydrogen phthalate was present in the solution, the photocurrent obtained increased with applied potential bias in low potential range, and reached saturation at higher applied potentials. The saturation photocurrent ($I_{sph}$) at higher potentials reflects the maximum photohole capture rate at the TiO\textsubscript{2} surface which, in turn, is determined by the concentration of potassium hydrogen phthalate ($C$) in the solution. The effect of electrodes calcination temperature on the $I_{sph}$ was investigated. Figure 2.10 shows $I_{sph}$ vs $C$ relationships for electrodes calcined at various temperatures. In all cases, $I_{sph}$ increases almost linearly with potassium hydrogen phthalate concentration at low concentration (i.e. < 50 µM). This linear increase in saturation photocurrent can be ascribed to the mass transfer limitation of the organic compound as evidenced by the increase in photocurrent upon stirring the solution. $I_{sph}$ tends to reach saturation at higher potassium hydrogen phthalate concentrations, but in some cases decreases slightly due to an inhibition effect (detail discussions are given in Chapter 4 and 5). The intercepts on photocurrent axis represent the blank saturation photocurrents ($I_{blank}$) generated from the
blank electrolyte solution due to the photooxidation of water. These blank saturation photocurrents remained constant for electrodes that were calcined at temperatures below 600°C and increased for those electrodes calcined at temperatures above 650°C. This is in agreement with the data shown in Figure 2.9.

Interestingly, for electrodes calcined with temperatures below 600°C, though the blank saturation photocurrents stays virtually unchanged, the linear range of \( I_{\text{sph}}-C \) curves is extended as the electrode calcination temperature is increased. Under illumination at the same light intensity, the difference in the maximum saturation photocurrent reflects the difference in the capture of photoholes by water and potassium hydrogen phthalate at the TiO\(_2\) surface. As discussed above, the electrodes calcined at these temperatures are composed of only the anatase form and the only physical parameters changed among these electrodes are the degree of aggregation between particles and the increase in crystallinity. Therefore, it is more likely that the better crystallinity and connections between particles are responsible for the extended linear range – especially given that such improvements can decrease the degree of photoelectron/hole pairs recombination before they are captured by the strong, multi-electron transfer adsorbates. The fact that amorphous TiO\(_2\) possesses only slight photocatalytic reactivity due to the large number of surface and structural defects\(^{58,208}\) supports my argument.

For electrodes calcined at higher temperatures, it was found that not only the photohole capture rate by water is enhanced but also the maximum \( I_{\text{sph}} (I_{\text{sphM}}) \) with respect to potassium hydrogen phthalate concentration is greatly enhanced – indicating an improvement in photocatalytic activity. For electrodes calcined at 850°C, the slope of the linear part of \( I_{\text{sph}}-C \) curve observed was lower than that observed for electrodes calcined at lower temperatures. This is probably due to the low porosity of the film, which greatly
lowers the surface area of the electrode (as evidenced by the SEM images shown in Figure 2.6).

![Graph showing saturation photocurrent dependencies on the concentration of potassium hydrogen phthalate for electrodes calcined at various temperatures for half hour.](image)

**Figure 2.10** The saturation photocurrent dependences on the concentration of potassium hydrogen phthalate for electrodes calcined at various temperatures for half hour.

In order to maximise photo-efficiency in applications such as photocatalytic mineralisation of organic pollutants in water, the electrode should demonstrate lower photocatalytic activity toward water and higher photocatalytic activity toward degradation of organic compounds. Unfortunately, as the calcination temperature increases both the photocatalytic activity toward potassium hydrogen phthalate and the photocatalytic activity toward water were shown to increase. Given this, a compromise between these two conflicting factors is required.

To further look at the effect of calcination temperature on photocatalytic activity towards phthalic acid, a parameter reflecting the activity without the influence from water oxidation is required. At a given light intensity, when the saturation photocurrent reaches its maximum in high potassium hydrogen phthalate concentration range, the overall
photocatalytic oxidation process is no longer under mass transfer control, instead, the surface reactions control the overall process. This means that the $I_{\text{sphM}}$ obtained at high concentrations reflects the reactivity of the electrode toward the organic compound. However, the problem of using $I_{\text{sphM}}$ to accurately represent the reactivity of the electrode towards the organic compounds is that the $I_{\text{phsM}}$ measured is not purely resulting from the oxidation of organic compound. A component of photocurrent (blank photocurrent) due to the oxidation of water is also included and the magnitude of this component varies with electrode. In order to better present the electrode reactivity, a net maximum $I_{\text{sphM}}$ is defined as: $\Delta I_{\text{sphM}} = I_{\text{sphM}} - I_{\text{blank}}$. Since for a given electrode, $I_{\text{blank}}$ is constant, therefore, $\Delta I_{\text{sphM}}$ represent the maximum photocurrent that due purely to the photocatalytic oxidation of organic compound. The reactivity of the electrode can then be represented by plotting $\Delta I_{\text{sphM}}$ against the electrode calcination temperature (Figure 2.11).

![Figure 2.11](image)

*Figure 2.11* The difference between the maximum saturation photocurrent and its corresponding background saturation photocurrent versus calcination temperature of the electrode
It can be seen that the $\Delta I_{sphM}$ increased almost linearly with the electrode calcination temperature up to 750°C indicating the increase in the electrode reactivity. A further increase in the electrode calcination temperature resulted in a decrease in the $\Delta I_{sphM}$ indicating the dropping in the electrode reactivity.

As discussed in the previous sections, several characteristics of TiO$_2$ films may be changed when the electrode is subject to different calcination temperatures. These changes in the film parameters can have conflicting influence on the photocatalytic reactivity of the resultant electrodes. For example, the surface area drop caused by increasing calcination temperature usually decreases photocatalytic reactivity, however, better crystallinity and a degree of sintering between particles achieved at high calcination temperature are favourable for photocatalytic reactivity. By considering the results shown in the Section 2.3.2, it seems that the $\Delta I_{sphM}$ increase for the electrodes calcined with the temperatures from 500 to 600°C can be attributed largely to the improvement in connections between particles and in crystallinity of the particles. Beyond these calcination temperatures, the $\Delta I_{sphM}$ increase is partially due to the further improvement in connections between particles and crystallinity, and mainly due to the composition changes (i.e. increase in the content of the rutile phase).

By comparing the results shown in Figures 2.10 and 2.11, it can be concluded that the large $I_{sph}$ obtained from high temperature treated electrode (i.e. 850 °C) was not due to the high electrode reactivity towards the oxidation of organic compound, instead, it was due to large $I_{blank}$, which suggests the high temperature treated electrode possesses high reactivity towards the oxidation of water.

As previously demonstrated, at a given calcination temperature, some structural parameters of TiO$_2$ film electrodes may be changed with the calcination period as suggested by XRD patterns and SEM images shown in Section 2.3.2. The effect of
calcination time on electrode reactivity was subsequently investigated. Figure 2.12 shows the dependence of $I_{phs}$ on potassium hydrogen phthalate concentration for electrodes calcined at 700 and 750°C for various calcination times.

![Figure 2.12](image)

**Figure 2.12** Dependence of saturation photocurrent on potassium hydrogen phthalate concentration for electrodes calcined at 700°C and 750°C for different time duration.

For electrodes calcined at 750°C with calcination time ranging from 0.5 to 4h, the background $I_{ph}$ and the $I_{phs}$-$C$ linear range are both increased, indicating the photocatalytic reactivity toward both water oxidation and organic degradation is increased. Similarly this enhancement in photocatalytic activity can be ascribed to the increase in rutile phase composition. Electrodes calcined for longer period do not show much difference in their $I_{phs}$-$C$ relationships. Instead, the data show that $I_{phs}$-$C$ curves for electrodes calcined longer than 4hrs almost merge together, indicating the electrode status reaches equilibrium after four hours of calcination at 750°C. In addition, the $I_{phs}$-$C$ relationship of the electrode calcined at 700°C for 16h almost merges with those for electrodes calcined at 750°C for more than 4h. In agreement with the above argument the
film calcined at 700°C for 16h has similar phase composition to that calcined at 750°C for 8h as shown previously in Table 2.1.

2.3.6 Further Discussion

All results obtained in this chapter suggest that the presence of the rutile phase have a synergetic effect on the electrode photocatalytic reactivity toward phthalic acid and water. Based on semiconductor band theory, composite semiconductors with different band gaps can facilitate the transfer of electrons between semiconductors of different band energetics and the spatial separation of electron and hole pairs – consequently suppressing the recombination of photogenerated electron hole pairs \(^ {61}\). A descriptive schematic can explain the effect (see Figure 2.13).

![Figure 2.13](image)

*Figure 2.13* The schematic energy diagram of rutile form contact with anatase form TiO\(_2\) at pH 7.0 in aqueous solution.

Once electron/hole pairs are formed, electrons tend to move to rutile particles due the band gap energy difference between the anatase phase and the rutile phase. As a result, the electrons and holes are spatially separated. This spatial separation of electrons and holes will increase the lifetime of the electron/hole pairs, which is in turn suppressing the
recombination. A recent study has confirmed that at a rutile and anatase TiO$_2$ junction, the photoelectrons preferentially move to rutile side$^{214}$ which supports the above argument.

Employing a photoelectrochemical method to study the photocatalytic process offers a simple and effective means to obtain useful kinetic and thermodynamic information. The information obtained by this method can also be applied to the photocatalytic process which occurred in a slurry system. In a slurry system, for the photocatalytic degradation of aromatic compounds at higher substrate concentration, a zero order of kinetics has been frequently observed$^{85}$. The study here indicates that this is probably not solely caused by the sluggishness of electron removal by electron acceptors (oxygen), it maybe also caused by the sluggishness of photohole capture by organic compounds. Photocatalytic oxidation of water always occurs during photocatalytic degradation of organic compounds, which could not be observed if photocatalytic degradation is carried out in a slurry system. The consumption of photoholes by water does not necessarily decrease the photocatalytic efficiency of photocatalytic degradation of organic compounds. The status of TiO$_2$ photocatalyst including all the physical properties greatly influence its photocatalytic reactivity in particular for the photocatalytic degradation of aromatic compounds involving multiple electron transfer steps before it can be fully mineralised. The coexistence of rutile and anatase phases of TiO$_2$ is beneficial to the photocatalytic reactivity toward photocatalytic degradation of aromatic compounds. This probably explains why P25, a mixture of rutile and anatase form of TiO$_2$, is the best photocatalyst for use in slurry system to date.
2.4 CONCLUSION

TiO$_2$ nanoparticle colloid has been synthesized and characterised. The particle size is in the range of 6-10nm. Electron diffraction and TEM image show that the particles are well crystallised after hydrothermal treatment.

The TiO$_2$ nanoparticles have been successfully immobilised on to ITO glass. SEM image of the TiO$_2$ film has confirmed that a uniform nanoporous TiO$_2$ film can be obtained. Both X-ray diffraction and SEM images show that the particles and the extent of aggregation between particles increase as the calcination temperature increases. Below 600°C of calcination temperature, no phase transition occurs, and the film consists of almost 100% anatase form of TiO$_2$ with very small percentage of brookite form TiO$_2$. Above this temperature, the rutile form of TiO$_2$ start to form and the content of the rutile phase in the film increases as calcination temperature increases.

The saturation photocurrent reflects the photohole capture rate at the electrode surface or the photocatalytic reactivity of the electrode toward electron donors. In blank electrolyte the saturation photocurrent for electrodes calcined below 600°C stays unchanged with the calcination temperatures, above this calcination temperature the saturation photocurrent for water oxidation is increased. The trend of water oxidation photocurrent with calcination temperature is correlated to that of rutile phase change with calcination temperature. The increase in rutile phase content in the film is responsible for the increase in the photocatalytic reactivity of the electrodes toward water oxidation.

In the presence of potassium hydrogen phthalate the saturation photocurrent increases linearly with its concentration due to the diffusion limitation and reaches saturation at high concentration. The maximum $I_{phs}$ reflects the overall reactivity of the electrode towards both organic compound and water. It increases as the electrode calcination temperature
increases. $\Delta I_{phsM}$ can be used to represent the reactivity of the electrode toward organic compounds. It increases with the electrode calcination temperature up to 750°C and then decreases as the temperature is further increased.

The experimental results obtained suggest the optimal electrode calcination temperature is between 700°C and 750°C, and calcination period is ca. 16h and 2h respectively.
CHAPTER 3  PHOTOCHEMICAL OXIDATION OF WEAK ADSORBATES – GLUCOSE
3.1 INTRODUCTION

In Chapter 2, the fabrication of the particulate TiO$_2$ nanoporous electrodes was carried out and the physical and photocatalytic characteristics of the resultant electrodes were investigated. In this chapter, and the next three chapters, the investigation will focus on the photoelectrocatalytic method development and application of the developed methodologies to characterise photocatalytic processes of different compounds at the particulate TiO$_2$ nanoporous electrodes. The methodologies used for these studies are all based on photoelectrochemical principles.

The study of photocatalytic oxidative processes at photosensitive semi-conductors by photoelectrochemical methods has several distinct advantages over systems that employ colloidal suspensions of semi-conductor particles$^8, 11, 36, 40$. These include the physical separation of the oxidation half reaction (at the working electrode) from the reduction half reaction (at the auxiliary electrode), which is in contrast to the colloidal suspension system where photooxidation and reduction reactions take place on the same particle$^1, 3, 76$. This physical separation allows the reaction of interest (i.e. the photooxidation of organic substances) to be studied in isolation. For example, the rate or extent of reaction is determined only by the conditions and processes that occur (or are imposed) at the working electrode. This also allows simple quantification of the rate and extent of reaction by measurement of the photocurrent passed at the working electrode. Another advantage of the photoelectrochemical approach is that an applied potential bias is employed to minimize photoelectron-photohole recombination reactions as well as to manipulate aspects of the overall photocatalytic process. In this regard, the applied potential can be used to change the rate-determining steps in photocatalytic reactions$^8$, which can facilitate elucidation of photocatalytic oxidation mechanisms.
One of the major differences between conventional semi-conductor electrodes and particulate semi-conductor electrodes is the nature of the energy bands (conduction and valence bands) that exist within each type of electrode. One of the most well described features of conventional semi-conductor electrodes in photoelectrochemical experiments is the phenomenon of band bending within the space charge (or depletion) layer – particularly upon application of a potential bias\(^4\). In the case of particulate semi-conductor electrodes, which contain aggregates of interconnected nanoparticles, the semiconductor film electrode cannot sustain the development of a space charge layer\(^29\). Consequently, no clearly defined band bending is observed and the energy bands are essentially flat. For this reason, the applied potential bias plays quite a different role in the particulate semi-conductor electrode compared with conventional semi-conductor electrodes. The exact nature of this difference has yet to be addressed in any detail in the literature when it comes to photocatalytic oxidation of organics at both types of electrodes.

As mentioned in chapter 1, particulate TiO\(_2\) semi-conductor electrodes have been extensively employed and characterized in dye sensitized solar cell applications\(^29, 41-48\). Issues such as electron transport in the film\(^21-24, 26, 46-48\), and some fundamental semi-conductive characteristics of such films have been well investigated\(^215-217\). Although there are similarities between dye sensitized solar cell applications and the photoelectrochemical oxidation of organic substances at nanoporous TiO\(_2\) film electrodes, there are some important differences. In dye sensitized cells, the electron injection into conduction band of the film from the photo-excited dye is so overwhelmingly fast that charge separation is easily realized and the recombination of photogenerated carriers is not a big concern. In this case, electron diffusion rather than electron migration under electric field is believed to be the dominating mechanism of electron transport in the film\(^21-24, 26\). In the case of photocatalytic oxidation of organics, by direct absorption of light at TiO\(_2\), both charge carriers are still on the TiO\(_2\) surface. Effective charge separation can only be
realized by removal of one of the charge carriers and the overall efficiency depends on the
effective removal of either charge carrier\textsuperscript{29}. The mechanisms of how this happens and the
processes that control charge carrier removal at nanoporous particulate electrodes have not
been addressed in the literature.

Alcohols and carbohydrates represent important series of organic compounds occurring in
water and wastewater samples, which are weakly adsorbed to TiO\textsubscript{2} surface and some of
them are good hydroxyl radical scavengers\textsuperscript{83}. In this chapter glucose was chosen as a
model compound to study the photocatalytic degradation of weakly adsorbed compounds
at TiO\textsubscript{2} porous film electrodes. The objectives of the study in this chapter were twofold.
One was to investigate the photocatalytic oxidation behaviour of weakly adsorbed compounds
at particulate TiO\textsubscript{2} film electrodes. The other was to shed light on the overall
processes that occur during photoelectrocatalytic oxidation of organic material at TiO\textsubscript{2}
nanoporous electrodes. Questions such as which processes dominate or which processes
are rate limiting under certain experimental conditions (which have not been reported for
these electrodes) are addressed in detail. It is clear, for example, that application of a
potential bias or changes in light intensity can cause changes in the overall rate of the
photocatalytic reaction in these systems\textsuperscript{33-40}. To date, the mechanistic reasons for these
observations and the extent to which each of these parameters affects the overall
photocatalytic reaction rate have not been made clear. As has been noted, a photocatalysts
having optimal photocatalytic reactivity for the photocatalytic degradation of one organic
compound may not have good photocatalytic reactivity for another\textsuperscript{58}. The electrodes
calcined at different temperatures (having two extreme photocatalytic reactivities for
photocatalytic oxidation of potassium hydrogen phthalate as demonstrated in Chapter 2)
will be compared with glucose as well.
3.2 EXPERIMENTAL

3.2.1 Material and Chemicals

Conducting glass sheets (8-10 $\Omega \cdot \square$, Delta Technologies Limited) were adopted as substrate for TiO$_2$ film coating. Titanium butoxide (97%, Aldrich), D-glucose (AnalaR, BDH) and sodium nitrate (99%, BDH) were used without further purification. Nitric acid and sodium hydroxide employed were of analytical grade. All solutions were prepared with deionised (Milli-Q) water.

3.2.2 Preparation of the nanoporous TiO$_2$ electrodes

The TiO$_2$ colloid synthesis and immobilisation procedures are the same as described in Section 2.2.2. Most of the experiments were carried out using TiO$_2$ porous film electrode calcined at 500°C for 0.5h. Some experiments (where stated) were carried out using electrodes calcined at 700°C for 16h. The thickness of the TiO$_2$ film in both cases was ca. 1µm.

3.2.3 Apparatus and Methods

The apparatus and experimental set-up are the same as described in Section 2.2.3 for photoelectrochemical measurements. The light intensity changes were made through altering the relative position of electrolytic cell to the light source, and light intensity was measured with an UV-irradiance meter (UV-A, Beijing Normal University).

3.3 RESULTS AND DISCUSSION

3.3.1 Effect of Potential Bias and Concentration

A photocatalytic reaction at semi-conductor surfaces involves an interaction between photoholes and photohole scavengers. For a given system, the rate of the photocatalytic
reaction is determined by the concentrations of both the photoholes and the scavenger – the former being determined by the intensity of the incident radiation and the latter being determined by the bulk concentration of the scavenger (i.e. glucose in this case). When the system involves a semiconductor electrode, the magnitude of the applied potential is also important in determining the kinetic characteristics of the system. Consequently, in order to fully characterize the photoelectrocatalytic processes that occur at nanoparticulate electrodes, in this section we investigated the effect of varying applied potential, glucose concentration at a given light intensity and pH (pH 6.0). This was achieved by performing slow scan linear sweep voltammetry at varying glucose concentrations.

Figure 3.1 shows the voltammograms obtained at the TiO$_2$ particulate electrode, with or without the UV illumination, in a 0.1M NaNO$_3$ blank solution and various concentrations of glucose in 0.1M NaNO$_3$. As expected, it was found that without UV illumination, no measurable current was observed for both the blank and glucose solutions when the applied potential was more positive than –0.1V. When the applied potential was below –0.1V, a small cathodic current was observed for the blank solution (curve 16), which can be attributed to reduction processes at the underlying conducting glass (ITO) substrate. Curve 15 shows the photocurrent response of the electrode in the blank solution with UV illumination. In this case, the photocurrent increased up to approximately –0.1V before levelling off to a measurable anodic current of about 40µA – this saturated current being due to the photocatalytic oxidation of water. In all other cases, the $I_{ph}$ also increased linearly with potential before levelling off to their own saturated photocurrent values ($I_{sph}$).

The on-set potential, the starting potential from which electrons can be drawn away, reflects the energy position of electron source. It has been noted that (under illumination)
the on-set potential shifted negatively with glucose concentrations until at higher glucose concentration the on-set potential reached a constant value. This shift in on-set potential is the result of the sum of direct electrochemical reduction of water at bare ITO sites and the photocatalytic oxidation of water and glucose at TiO$_2$ surface. When the surface concentration of glucose is sufficiently high the photocatalytic oxidation rate of glucose is overwhelmingly higher than the direct electrochemical reduction rate of water at bare ITO sites the on-set potential tends to reach a constant value, which approximates the sub-band potential of the surface states in the TiO$_2$ porous film (this will be further discussed in section 3.3.4).

![Voltammograms of TiO$_2$ film electrode obtained from a 0.1M NaNO$_3$ blank and working solutions. The working solutions contain 0.1M NaNO$_3$ and various glucose concentrations. Scan rate: 5mV/s; Light intensity: 6.6mW/cm$^2$. Curves 1 to 14 were obtained from the working solutions under the UV illumination, the concentrations of glucose in turn were 0.45M, 0.20M, 0.10M, 50mM, 20mM, 10mM, 6mM, 3mM, 1.5mM, 0.8mM, 0.4mM, 0.2mM, 0.1mM, 0.02mM. Curve 15 was obtained from the Blank solution under the UV illumination. Curve 16 was obtained from the Blank and working solution without UV illumination.](image)

From the characteristics of $I_{ph}$-$E$ curves, two aspects of information can be extracted. One, from the saturation part of the curves, is the kinetic information of photohole capture
process at the TiO$_2$ interface. The other, from the linear part of the curves, is the electron transport information in the nanoporous TiO$_2$ films. The following paragraphs deal with these two respectively.

In high potential region, the overall process is controlled by photohole or surface bound photohole capture reaction$^8$. Therefore the $I_{sph}$ reflects the surface reaction rate of photoholes with electron donors. It is noted that both water and glucose oxidation contributes to $I_{sph}$. To look at the component of saturation photocurrent contributed by glucose oxidation, we define $\Delta I_{sph}=I_{sph}-I_{blank}$ ($I_{blank}$ is the saturation photocurrent of blank solution). To investigate the influence of glucose concentration on the reaction rate without the influence of electron transport in the film or the influence of electron removal rate, the $\Delta I_{sph}$ at 0.3V is plotted against concentration, as shown in Figure 3.2. Similar to the case of methanol photoelectrochemical oxidation$^8$, with respect to glucose concentration in very low concentration range the $\Delta I_{sph}$ ($I_{sph}-I_{bsph}$) linearly increases with concentration due to diffusion limitation, afterwards it gradually reaches saturation.

![Figure 3.2](image)

**Figure 3.2** The dependence of the saturation photocurrent difference in the presence of glucose and in blank electrolyte on glucose concentration.
Processing the $\Delta I_{\text{ph}} - C$ data according to the Langmuir-Hinshelwood rate law gave Figure 3.3. In the medium concentration region a fairly good linearity was obtained. In the low concentration region the experimental data deviate from the linear double reciprocal relationship due to mass transfer limitation, which was evidenced by an increase in photocurrent upon stirring the solution. In the high concentration region the experimental data also deviate from the linear double reciprocal relationship due to current doubling effect, which was evidenced by photocurrent decrease upon the stirring of solution. This type of saturation kinetic behaviour is very common, which was frequently referred to surface coverage saturation by reaction substrates$^3, 76-78, 82$. The linear double reciprocal relationship between reaction rate and concentration indicates that the photohole capture rate by glucose is a first order reaction with respect to the glucose surface concentration (not necessarily adsorbed, but within the surface reaction layer).

![Figure 3.3](image)

**Figure 3.3** The reciprocal of saturation photocurrent difference in the presence of glucose and in blank electrolyte versus the reciprocal of glucose concentration.

The most important feature of the $I_{\text{ph}} - E$ data shown in Figure 3.1 was that, at all glucose concentrations, the photocurrent response increased linearly from the on-set potential
before levelling out at higher potentials. In addition, the linear part of the curves extended to more positive potentials at higher glucose concentrations while the on-set potential was observed to shift to more negative potentials with an increase in concentration. This behaviour is markedly different to what is observed at conventional (bulk) semi-conductor electrodes in which a non-linear (exponential) $I_{ph}-E$ response is expected at potentials higher than the on-set potential $^{218,219}$.

The rate limiting process within the linear part of the curves in Figure 3.1 was electron transfer within the TiO$_2$ film and the system behaved like a pure resistance in its response to the potential change. The resistance values for each curve in Figure 3.1 can be calculated (according to Ohm’s law), by dividing the potential change by the corresponding photocurrent change within the linear part of each curve. For a given light intensity, these resistances change with glucose concentration, which in turn determines the maximum reaction rate (expressed as $I_{sph}$). Plotting the resistance ($R$) against $I_{sph}$ gives the hyperbolic curve shown in Figure 3.4.

![Figure 3.4](image)

*Figure 3.4* The resistance from the photocurrent/potential linear region versus saturation photocurrent (by changing glucose concentration).
Computer curve fitting of the data shows that the $R$-$I_{sph}$ curve fits well with the equation:

$$R = k/I_{sph} + R_0$$  \hspace{1cm} (3.1)

where $k=310 \text{ mA} \Omega$, $R_0= 245 \Omega$, and both are constant for a given electrode and light intensity.

Equation 3.1 indicates that the total resistance can be divided into two parts: one is constant and independent of glucose concentration ($R_0$), and the other varies with maximum reaction rate as determined by different glucose concentrations ($R_I = k/I_{sph}$).

The variable component of the resistance, $R_I$ can be obtained according to $R_I = R - R_0$.

Plotting $1/R_I$ against $I_{sph}$ gives a straight line as shown in Figure 3.5. Since $1/R_I$ represents the conductance, the conductance is directly proportional to $I_{sph}$. The conductance here is, in fact, the conductance of the TiO$_2$ film because the data used were obtained under conditions where overall rate of reaction was controlled by electron transport in the TiO$_2$ film. Under these conditions, an increase in the glucose concentration (an effective photohole scavenger) resulted in a faster consumption of photoholes to produce higher electron concentration in the film. This phenomenon manifested itself in the experimental observation of a decrease in the resistance (or an increase in the conductance) of the TiO$_2$ film. In other words, the linear relationship between the $I_{sph}$ and film conductance implied that the surface reaction (which is concentration dependent) determined the electron concentration in the film, and that the migration of electrons under electric field is directly proportional to the applied potential.

The constant component of the resistance, $R_0$, likely reflects the sum of TiO$_2$ crystal boundary resistances and the resistances at the ITO/TiO$_2$ interface, which is an intrinsic property of the electrode. These characteristics of TiO$_2$ particulate film electrodes have not been described by anyone else.
Figure 3.5  The dependence of the reciprocal of variable resistance on the saturation photocurrent by changing glucose concentration.

3.3.2  Effect of Potential Bias and Light Intensity

The photoelectrochemical reaction involves both photoholes and photohole scavenger. In the above section I investigated the influence of photohole scavenger concentration. In this section the influence of light intensity is investigated in attempt to further understand the overall interfacial reaction.

Figure 3.6 shows the voltammograms obtained at the TiO₂ particulate electrode in a fixed concentration of photohole scavenger (0.45M glucose in 0.1M NaNO₃) under different illumination intensities. Under each given light intensity, the photocurrent response increased linearly with applied potential before levelling off. Both the saturation photocurrent value ($I_{ph}$) and the potential range of the linear part of the $I_{ph}$-E curve increased as the light intensity were increased.
Figure 3.6 The voltammograms of the electrode in solution of 0.1M NaNO$_3$ + 0.45M glucose under illumination of different light intensity. The light intensity from top to bottom in turn: 11.72, 11.42, 10.11, 7.49, 6.10, 4.66, 3.26, 2.19, 1.56mW/cm$^2$.

It is evident that when the photocurrent levels off with respect to potential bias, the rate-determining step is the interfacial reaction, rather than the charge carrier transport in the film. Plotting the saturation photocurrent against the light intensity gives a straight line as shown in Figure 3.7, which is similar to the case of methanol photocatalytic oxidation$^8$. In fact, even in the absence of glucose the saturation photocurrent increases linearly with light intensity. In contrast, photocurrent at potentials before its saturation has a non-linear dependence on light intensity$^8$, which is attributed to the higher recombination rate at higher light intensity due to the build-up freed electrons. In TiO$_2$ slurry systems non-linear dependence of the reaction rate on light intensity is often obtained$^3$. My results here may imply that the non-linear dependence of reaction rate on light intensity is partly caused by the build-up of freed electrons due to the sluggish electron removal process in slurry systems. The results also demonstrate that potential bias can suppress the electron-hole pair recombination to certain degree by minimising the build-up of freed electrons.
rather than separating photoelectron and hole pairs. The linear dependence of $I_{sph}$ on light intensity experimentally justifies the assumption that the interfacial reaction with respect to surface bound photohole of any form is first order.

![Graph](image_url)

**Figure 3.7** Saturation photocurrent dependence on light intensity, data derived from 3.6, saturation photocurrent taken at 0.3V.

The linear part of the $I_{ph}-E$ curves obtained at low potentials again indicates that the electrode behaved markedly different to what would be expected at conventional (bulk) semi-conductor electrodes. The pure resistor type behaviour alluded to in the previous section again indicates that the rate of the reaction within the linear part of the $I_{ph}-E$ curves was controlled by the electron transport in the TiO$_2$ film. The photocurrent (rate of reaction) observed in this part of the curve reflects how fast the electrons in the semiconductor film can be removed by the applied potential. At a given light intensity, an increase in the applied potential leads to an increase in the electromotive force, which, in turn, leads to a proportional increase in the photocurrent (as expected by Ohm’s law).

Figure 3.8 shows the relationship of the resistances obtained from the linear regions of the curves in Figure 3.6 versus $I_{sph}$. Again it was found that the resistance decreased with light intensity or with the maximum reaction rate in a hyperbolic manner. Computer curve
fitting of the data revealed that the $R-I_{sph}$ curve fits equation 3.1 well with $k=364 \, mA \, \Omega$ and $R_0=245 \, \Omega$. This result again shows that a component of the total resistance is independent of light intensity or the maximum reaction rate. More importantly, the value of the constant resistance value obtained here was the same as the one obtained when the concentration of the glucose was varied. This provides strong support for the previous argument that $R_0$ is an intrinsic property of the electrode.

![Figure 3.8](image)

**Figure 3.8** The dependence of resistance in the linear photocurrent/potential region on the saturation photocurrent by changing light intensity.

The variable component of the resistance, $R_I$, can be treated in the same way as for Figure 3.5 to give Figure 3.9. The result confirms that the conductance of the film is directly proportional to the maximum reaction rate. At a particular glucose concentration, an increase in the light intensity led to an increase in the photohole concentration in the film. A higher photohole concentration makes it easier for the photohole to be consumed by its scavenger (i.e. glucose), resulting in a decrease in the resistance (or increase in conductance) of the film with increased light intensity.
3.3.3 Relationship among Photocurrent, Glucose Concentration, Potential Bias and Light Intensity

The results and subsequent data analysis presented in above two sections focus on changes in film resistances (in the linear part of the $I_{ph}-E$ curve) and how they are quantitatively related to the maximum reaction rate (as determined by glucose concentration). In this part, I complete the quantitative description of the $I_{ph}-E$ curves, shown in Figures 3.1 and 3.6, by focusing on the saturated photocurrent values where the interfacial reaction rate was at a maximum for a given glucose concentration and/or light intensity. In particular, I present an explanation why, at a certain potential, the photocurrent (maximum reaction rate) is saturated and why the potential at which saturation occurs shifts with a change in glucose concentration (Figure 3.1) and light intensity (Figure 3.6).

At potentials where the saturated photocurrents were obtained, the maximum interfacial reaction rate was first order with respect to photohole surface concentration and glucose surface concentration, as was demonstrated by the saturation photocurrent glucose
concentration relationship (Figure 3.3) and the saturation photocurrent light intensity relationship (Figure 3.7). The maximum interfacial reaction rate can therefore be expressed as:

$$Rate_m = k_1 C_s h C_{glu}$$  \hspace{1cm} (3.2)

where $k_1$ is a constant, $C_s h$ is the photohole concentration at TiO$_2$ surface and $C_{glu}$ is the glucose concentration at the TiO$_2$ surface.

Since the saturation photocurrent is directly proportional to the maximum interfacial reaction rate, then:

$$I_{sph} = k_2 C_s h C_{glu}$$  \hspace{1cm} (3.3)

where $I_{sph}$ is the saturation photocurrent and $k_2$ is a constant.

The maximum number of free electrons, $N_{max}$, in the TiO$_2$ film that are set free by the interfacial reactions at the maximum rate is proportional to $I_{sph}$:

$$N_{max} = k_3 C_s h C_{glu}$$  \hspace{1cm} (3.4)

The photocurrent ($I_{ph}$) equals the numbers of electrons collected per unit time and the magnitude of the photocurrent is determined by the saturation photocurrent and the efficiency of the electron collection, i.e.

$$I_{ph} = \alpha I_{sph}$$  \hspace{1cm} (3.5)

where, $\alpha$ is the electron collection coefficient, and is defined as:

$$\alpha = N_e / N_{max}$$  \hspace{1cm} (3.6a)

where, $N_e$ is the number of electrons collected (which is directly proportional to $I_{ph}$).

According to these definitions, the electron collection coefficient in the photocurrent/potential linear region can be easily obtained:

$$\alpha = \Delta E/(k + R_0 k_2 C_s h C_{glu})$$  \hspace{1cm} (3.6b)
where, $\Delta E$ is the potential difference between the applied potential and the on-set potential, $k$ is the slope of the linear part of the $I_{ph}-E$ curves in Figure 3.5 or 3.9 (see equation 3.1).

Equation 3.6b indicates that from the on-set potential, $\alpha$ increased from 0 to 1 linearly with applied potential for a given light intensity and glucose concentration. The maximum electron collection ($\alpha = 1$) or maximum rate of reaction can be achieved when

$$\Delta E = k + R_0 \cdot k_2 C_{sh} C_{glu}. \quad (3.7)$$

The rate of reaction will not be further increased when the applied potential is beyond this point because $k$ is no longer a constant. Equation 3.7 indicates that the magnitude of the potential difference, positive of the on-set potential ($\Delta E$), required to achieve the maximum reaction rate is linearly dependent on both $C_{sh}$ and $C_{glu}$. This can be seen in both Figures 3.1 and 3.6 where the potential at which the maximum reaction rate was achieved increased with both concentration (Figure 3.1) and light intensity (Figure 3.6).

The characteristics of the voltammograms of the TiO$_2$ film electrode in Figures 3.1 and 3.6 can be explained well by the above equations. The overall photoelectrocatalytic oxidation process at nanoporous TiO$_2$ electrodes can therefore (for the first time) be clearly described in a qualitative manner.

### 3.3.4 Further Discussion

The results and discussions presented above quantitatively characterize the $I_{ph}-E$ responses at TiO$_2$ nanoporous film electrodes and demonstrate some of the differences in the overall photoelectrocatalytic behavior of these electrodes compared with conventional semiconductor electrodes. This section develops this concept further, in a qualitative sense by further highlighting some of the fundamental differences between a particulate and a conventional semiconductor electrode. In addition, the differences between TiO$_2$
particulate film electrodes in solar cell applications and in their use in direct photoelectrocatalytic oxidation of organics is addressed.

As pointed out in the introduction it is well known that, unlike conventional semiconductor electrodes, particulate electrodes cannot sustain the development of space charge layer and consequently, the energy bands are almost flat\textsuperscript{20}. For these reasons, the applied potential plays a quite different role in the particulate and the conventional semiconductor electrodes. With a conventional semiconductor electrode, the main function of the applied potential is to regulate the band bending across the space charge region in order to, typically, minimise electron-hole recombination processes. In addition, where necessary, the applied potential bias can accelerate the interfacial electron transfer process. In the case of a particulate semiconductor electrode, the spatial separation of photogenerated hole-electron pairs can be achieved only by removal of photoholes through interfacial reactions since there is no band bending. The applied potential serves the function of collecting the free electrons made available by the interfacial reactions. In other words, the applied potential simply assists in the removal of the free electrons. It cannot control the interfacial reaction, instead the interfacial reaction rate controls the free electron concentration in the film. This fundamental difference between the two electrode types is demonstrated in Figures 3.4 and 3.7 where the conductance of the film changes linearly with the maximum reaction rate, which is determined by glucose concentration and light intensity. Under given conditions of light intensity and glucose concentration, the maximum interfacial reaction rate is fixed, so is the free electron concentration in the film. Application of the potential bias facilitates the electron transport in the film that makes the overall reaction rate swing between zero (at the on-set potential) and the maximum where $\Delta E = k + R_0 k_2 C_{\text{h}} C_{\text{glu}}$. 
As pointed out in previous sections, close inspection of Figures 3.1 and 3.6 reveals that the on-set potential changes slightly with changes in both scavenger (glucose) concentrations and light intensity at low glucose concentration and low light intensity, but approaches a constant value at higher glucose concentration. The shift of on-set potential at low glucose concentration can be attributed to the negative contribution of the cathodic current of direct electrochemical reduction at underlying ITO glass electrode. At higher glucose concentration and light intensity the constant on-set potential should reflect the energy band position of electron band. It is noticed that the constant on-set potential (-0.55V vs Ag/AgCl at pH ca. 6.0) is higher than the flat band potential expected for anatase TiO$_2$ semiconductor (ca –0.72 V vs Ag/AgCl) \(^{30}\). So this on-set potential is most likely associated with the subband position of electron traps inherent to the TiO$_2$ nanoparticles of large surface area \(^3, ^{220, 221}\). Given this, the energy level diagram for the system can be represented schematically as shown in Figure 3.10. The Fermi level of the conducting ITO substrate is controlled by applied potential. When the potential is lower than the water reduction potential the pure electrochemical reduction takes place at the underlying ITO substrate, generating a cathodic current. Under illumination of the electrode, photo-electrons are trapped by the TiO$_2$ surface groups. Once the applied potential is positive of electron trap potential a flow of electrons from the trap band to the conducting substrate occurs and an anodic current is generated. Since the carrier concentration in the film is extremely low when there is no UV illumination, no anodic current can be generated even as electrode potential is much more positive than the trap band potential. Under UV illumination, when the potential is above current onset potential (or trap band potential) and the photoholes are removed by the interfacial reactions, surface photoelectrons flow through the film to the conducting ITO substrate. Meanwhile at the bare/exposed ITO sites the direct electrochemical reduction reaction still occurs and, as a result, the total current obtained is the sum of the reduction and oxidation processes. Consequently, the
on-set potential changes slightly. But at higher glucose concentrations and higher intensities the available free electron concentration in the trap band is much higher and the reduction current is negligible compared with the anodic current from oxidation process – as a result the on-set potential approaches the trap band potential. In the next section, the change of on-set potential with pH can give a better idea about the trap band position and the difference between on-set potential and flat band potential.

**Figure 3.10**  *Schematic energy band diagram of TiO\(_2\) porous film electrode.*

Some have argued that an electric field cannot be set-up within the porous TiO\(_2\) film due to the low conductivity of TiO\(_2\) film and the screening effect by penetrating ions\(^{27}\). Apparently this argument cannot explain the linear dependence of photocurrent on applied potential in my case. The conductivity for a thin TiO\(_2\) film (i.e. about 1\(\mu\)m which is close to the UV light penetrating length) is greatly increased under illumination\(^{21}\). From the film resistance study in the above sections it has been found that, under illumination, the resistance in the film is greatly decreased as long as there are enough photohole scavengers at the TiO\(_2\) surface. Due to the great difference in mobility between ion in porosity and the free electrons in film the screening effect can be neglected and an electric filed can indeed be formed inside the film.
The main application area for TiO$_2$ particulate film electrodes to date has been in dye sensitized solar cell developments where considerable attention has been given to electron transport mechanisms within the film. Many believe the driving force for electron transport in the TiO$_2$ film is the electron concentration gradient in film $^{21, 23, 25}$. For a dye sensitized TiO$_2$ porous film this may be true because the electrons typically exist as free electrons in the film due to the extremely high electron injection rate compared with the relatively slow electron-hole recombination process $^{29, 41, 201}$. Therefore, even though there is no external applied electric field, the free electrons can still diffuse to the collecting electrodes with little chance of recombination. In my case electrons can only be set free when the photoholes are removed from the surface (by the interfacial reaction). In addition, the rate of photohole consumption is not overwhelmingly higher than the rate of electron-hole recombination and the build-up of free electrons will significantly increase the rate of photoelectrons and photoholes recombination. Consequently, the electric field in the film (induced by the applied potential) plays an important role in the overall photocatalytic oxidation reaction. This can be seen in both Figure 3.1 and Figure 3.6, where the higher the overall interfacial reaction rate the larger potential drop (applied potential) was needed to drive the electrons out of the film. This is fundamentally different to the dye sensitised solar cell applications of TiO$_2$ particulate film electrodes.

3.3.5 Effect of pH

It is known that the flat band potential and the band edge potential of oxide semiconductor have a Nernstian-type pH dependence in aqueous media$^4$. For bulk TiO$_2$ semiconductor electrode and TiO$_2$ particulate film electrode the Nernstian-type pH dependence of flat-band potential has been reported by many groups$^{20, 143, 216}$. Also the surface functional groups will change via protonation and deprotonation reactions. In these ways, the pH of solution would certainly affect behaviour of TiO$_2$ porous film electrodes and the
photocatalytic oxidation kinetics of organic compounds. Figure 3.11 shows a series of voltammograms in different pH solutions containing 0.45M glucose and 0.1M sodium nitrate.

Figure 3.11 The voltammograms of the electrode in solutions of different pH containing 0.1M NaNO\textsubscript{3} + 0.45M Glucose. From left to right the pH in turn: 11.5, 10.5, 10.0, 9.0, 8.0, 6.0, 5.0, 2.0, 1.2.

At pH 2, the photocurrent increases linearly with electrode potential from the on-set potential. The on-set potential agrees well with flat band potential reported for an anatase semiconductor electrode\textsuperscript{30}. At pH 11.5, a similar shape of $I_{ph}-E$ response was obtained as well, and the on-set potential agrees very well with the expectation from the Nernstian-type pH dependence of flat band potential. The linear increase in photocurrent starting from the on-set potential indicates that there is no energy junction (e.g. like a p-n junction) formed across the film or there is no space charge layer formed across the film. Interestingly, the $I_{ph}-E$ characteristics in the medium pH range are quite different from those at low and high pH values in that from pH 5 to pH 9.0 the on-set potential is very insensitive to pH change. However, from pH 9.0 to pH 11, two waves in the photocurrent potential response were observed. As one wave is growing the other is decreasing until at pH values above 11 one wave disappears. This could be explained by the existence of
surface states or subband traps at the semiconductor and their change with pH. But the chemistry behind this behaviour needs to be further addressed.

Quite often the on-set potential (the potential at which anodic photocurrent is observed for n-type semiconductor electrode) is used to approximate the flatband potential\textsuperscript{4, 143}. The on-set potentials at different pH were obtained from the $I_{ph}$-$E$ curves in Figure 3.11. In Figure 3.12 the dependence of the on-set potential on pH together with the surface group species distribution calculated by Kormann\textsuperscript{111} and theoretical flat band potential dependence on pH\textsuperscript{30} are shown.

![Figure 3.12](image)

**Figure 3.12** Dependence of surface hydroxyl group species\textsuperscript{111}, the photocurrent on-set potential and expected flatband potential on pH of solution, $\bullet >$TiOH$_2^+$, $\bullet >$TiO, $\blacktriangle >$TiOH, $\square$ on-set potential and dash line representing the expected $E_{flat}$-pH relationship ($E_{flat}=-0.35-0.059pH$ ($V$ vs Ag/AgCl)\textsuperscript{30}).

In low and high pH regions the on-set potentials agree very well with the flat band potentials expected from the Nerstian-type pH dependence of the flat band potential. In the medium pH region the on-set potential deviates from this expectation. Interestingly, the deviation occurs exactly in the pH region where the surface group composition stays
virtually unchanged, whereas, in pH regions where there are composition changes, the on-set potential complies well with the expected flat-band potentials. It is well documented that the flat band potential dependence of oxide semiconductors on pH is caused by the adsorption/desorption of hydroxyl ions. So the good agreement of on-set potential with flat-band potential in low pH and high pH regions indicates in these pH ranges there are not many deep traps (or if there are any, they are not substantial enough to influence the on-set potential). The good correlation of the on-set potential change in medium pH range with the percentage of >TiOH species in this pH range suggests that the major electron and hole traps are >TiOH sites. Szczepankiewicz has demonstrated (using infrared spectral technique) that on illuminated TiO\textsubscript{2} surface the >TiOH sites are the major electron traps. Based on this the on-set potential change with pH can be explained. As shown in Figure 3.10 the band energy diagram of the electrode, the energy level of the trap sites >TiOH stays unchanged with pH, but the conduction band and valence band edges changes Nernstianly with pH. At slightly acidic pH the surface groups are mainly >TiOH, so there is large amount of traps, as a result, photo-electrons are mainly trapped by these surface groups. When the electrode potential moves from negative to flat band potential because there are no electrons in the conduction band so there is no current flow. Only when electrode potential moves up above the electron trap potential the electron begin to flow (the current set on). As the trap energy level is very close to the flat band potential (-0.55V vs Ag/AgCl) in weak acidic media so the on-set potential is very close to the expected flat band potential. As pH decreases the band edge potential moves up to or above the trap potential the photoelectrons no longer fill the traps then the on-set potential is the flat band potential. As pH increases, the band edge potential or flat band potential moves toward negative direction. The flat band potential and the trap potential become further apart, as a result, the on-set potential deviates further from the flat band potential. Until up to ca. pH 9 the >TiOH amount begins to decline, except for filling up the traps
there are still some electrons left to fill the conduction band, two waves of current will appear. One is from draining out electron from conduction band of which the on-set potential is corresponding to flat band potential, the other is from draining out electrons from traps of which the potential is corresponding to the trap potential. Indeed as shown in figure 3.12 the first wave grows higher as the amount of >TiOH declines with pH. It should be pointed out that the electrode in methanol, even in blank electrolyte, has similar behaviour in terms of on-set potential variation as pH value changes. Therefore the above behaviour reflects the electrode surface properties.

As previously stated the saturation photocurrent reflects the rate or ability of organic compounds capturing photoholes or donating electrons at the electrode surface. At high glucose concentration the mass transport is not the limiting step or the glucose in the reaction layer is not limiting, under such circumstance the effect of pH value on the saturation photocurrent will reflect the effects of pH on the interfacial electron transfer process. Shown in Figure 3-13 is the dependence of $I_{sph}$ on pH value in the presence of glucose and in the absence of glucose. The $I_{sph}$ in the presence of glucose as well as the saturation photocurrent in blank electrolyte stay virtually unchanged over a large pH range mainly due to the stable percentage of surface groups of >TiOH, the main traps of photoholes. In strong acidic medium both $I_{sph}$ and $I_{blank}$ decrease slightly, probably due to the increase in the portion of >TiOH$_2^+$ surface groups that do not favour the trapping of photoholes. On the other hand, in strong basic media both $I_{sph}$ and $I_{blank}$ increase, which can be attributed to the substantial increase in the amount of >TiO$^-$ surface groups favouring the trapping of photoholes. This effect was also found in the photocatalytic oxidation of methanol at such TiO$_2$ electrodes.
3.3.6 Effect of Calcination Temperature

It has been noticed by many researchers while studying photocatalytic reactivity of TiO$_2$ photocatalyst in a slurry system that the photocatalytic reactivity of a photocatalyst depends on the type of photocatalytic reactions (or on what is oxidised) $^{40, 58}$. Photocatalytic reactions at TiO$_2$ film electrodes are no exception. The difference in the saturation photocurrent in the presence of organic compounds and in blank electrolyte reflects this as well. In the above sections the electrodes employed in the study of photocatalytic oxidation of glucose was calcined at 500°C for 0.5h. It was shown in Chapter 2 that the photocatalytic oxidation of potassium hydrogen phthalate at electrodes calcined at 500°C for 0.5h and at 700°C for 16h represents two extreme cases in photocatalytic reactivity toward oxidation of phthalic acid. In this section these two electrodes in the photocatalytic oxidation of glucose is to be compared.

Figure 3.13 The effects of pH on saturation photocurrents in the presence of 0.45M (■) glucose and in blank 0.1M NaNO$_3$ electrolyte (▲), the pH effects on on-set potential (●) and the expected flatband potential dependence on pH (dashed line).
Figure 3.14 The dependence of saturation photocurrent difference on glucose concentration for electrodes calcined at 500°C for 0.5h (♦) and at 700°C for 16h (◇).

It has been found that the behaviours of the two electrodes in term of effects of electrode potential, light intensity and pH are very similar. The saturation photocurrent reflects photohole capturing rate at the interface, the difference in saturation photocurrents at both electrodes should reflects the difference in their photocatalytic activity. Under same light intensity the saturation photocurrents of the two electrodes at various glucose concentration are compared here. Because at both electrodes water oxidation rates are different, for comparison $\Delta I_{sph}$ ($I_{sph} - I_{blank}$) is used. Figure 3.14 shows the dependence of saturation photocurrent difference ($\Delta I_{sph}$, as defined in Chapter 2) on the glucose concentration for electrodes calcined at 500°C for 0.5h and at 700°C for 16h. The trends of the $\Delta I_{sph}$ dependence on glucose concentration for both electrodes are similar. The $\Delta I_{sph}$ of electrode calcined at 700°C for 16h is slightly lower than that of electrode calcined at 500°C for 0.5h at high concentrations. This is due to the lower surface area caused by aggregation during higher temperature calcination. However, the electrode calcined at 700°C for 16h gave a $\Delta I_{sph}$ at medium concentrations, indicating a better catch-destruction
(mineralised upon reaching the TiO$_2$ surface) ability of the electrode. This again demonstrates the better photocatalytic activity of the electrode.

### 3.4 CONCLUSION

The effects of potential bias, light intensity and alcohol on photocurrent (photodegradation rate) have been investigated. At given light intensity and given alcohol concentration the photocurrent increases linearly from the onset potential, then reaches saturation (maximum photohole capturing rate at the interface). In the potential region where photocurrent increases with potential bias, the overall photocatalytic reaction is controlled by the electron transport in the film. In the potential region where the photocurrent is saturated, the overall photocatalytic reaction is controlled by the photohole capturing rate at the interface. For the first time it was shown that the conductivity of a TiO$_2$ particulate film electrode is determined by the maximum reaction rate at the interface. This is a direct evidence that in particulate semiconductor electrode electron-hole separation can only be realized via removal of one charge carrier (here photoholes). The saturation photocurrent is directly proportional to light intensity and this maximum reaction rate follows Langmuir-Hinshelwood type of kinetics. This indicates that the surface reaction is first order with respect to surface bound photohole and glucose surface concentration (in the reaction layer). The whole picture of the electron transfer process is: (1) the maximum reaction rate is determined by light intensity and surface substrate concentration, which determines the actual degree of photohole and photoelectron separation, and concentration of electron in the film; (2) without timely removal of the freed electrons, the electrons will build up at the surface, which will stop the overall reaction; (3) the actual progression of the reaction also depends on the removal of electrons, where the potential bias plays a role. Overall, the glucose concentration and light intensity decide the free electron concentration, the actual removal rate of electron depends on potential bias. The removal
rate of electron increases with potential bias until it reaches the limit which is determined by the surface reaction. It has been demonstrated by many researchers that potential bias can suppress the photoelectron and photohole recombination. But how it works has not been addressed before. In this chapter the role of potential bias has been explicitly described.

Due to the steady surface group composition across a large pH range, the saturation photocurrent (surface reaction rate) remains virtually unchanged over a large pH range from weak acidic media to weak basic media. The slight decrease in saturation photocurrent in strong acidic media is attributed to the existence of $>\text{TiOH}_2^+$ surface groups which are unfavorable in trapping photoholes. The increase in saturation photocurrent in strong basic media is attributed to the existence of $>\text{TiO}^-$ surface groups which are favorable in trapping photoholes.

The change of photocurrent on-set potential with pH correlates well with the surface group composition variation. In low pH and high pH regions the on-set potential agrees well with the flat-band potential of TiO$_2$ semiconductor electrode. In the medium pH region the on-set potential deviates away from the expected flat-band potential. The electron traps (i.e. $>\text{TiOH}$ surface groups) is believed to be responsible for this.

The photocatalytic degradation of glucose at electrodes calcined at two temperatures is very similar. The main difference is that the surface reaction rate is lowered due to the decrease in surface area of the electrode calcined at higher temperature.

Glucose gives very similar features to methanol during their photocatalytic oxidation at TiO$_2$ porous film electrodes. This is probably determined by the nature of the semiconductor electrode and similar type of interaction between these two substrates (glucose and methanol) and electrode surface.
CHAPTER 4 PHOTOCATALYTIC OXIDATION OF STRONG ADSORBATES
4.1 INTRODUCTION

In chapter 3, the photocatalytic degradation of glucose at TiO$_2$ nanoporous film electrodes was studied as an example of weak adsorbates. One common feature of weak adsorbates is that their photocatalytic degradation occurs via outer-sphere electron transfer mechanism due to the weak interaction with TiO$_2$ surface$^{37, 222}$. In contrast, other types of compounds (strong adsorbates) have strong interaction with TiO$_2$ surface, forming surface complexes. For this category of organic compounds, the photocatalytic degradation is mainly via a direct inner-sphere electron transfer mechanism$^{2, 37, 86, 223}$. Direct inner-sphere electron transfer usually is advantageous to the primary charge transfer steps$^{109, 224}$. However, for most of organic compounds, the photodegradation process involves multiple steps, in which direct inner-sphere electron transfer may be a disadvantage, as the adsorbed active intermediates can become surface recombination centres. As a consequence, the recombination rate of photoelectrons and photoholes increases resulting in a decrease in the overall photocatalytic efficiency$^{83, 86}$.

As a part of a systematic study of different adsorbates, this chapter will concentrate on the characterisation of a group of selected strong adsorbates – carboxylic acids and dicarboxylic acids. The selection of these model compounds was based on their adsorptivity, molecular size and structures$^{225, 226}$. All these strong adsorbates consist of common functional groups possessing similar adsorptivity to TiO$_2$ surface but having different number of steps and intermediates of different nature during their photocatalytic degradation. This allows the effects of these factors on the overall photocatalytic kinetics to be investigated. The investigation will be carried out using two different approaches. The first will use the methodological approach developed in the previous chapter, i.e. carrying out kinetic study of photocatalytic degradation of these compounds in bulk solution. This will be done to enable the comparison of overall photocatalytic kinetics of
different adsorbates having different number of steps and different nature of intermediates during their degradation. The second approach involves the development of new methods to characterise the kinetic and the thermodynamic (i.e. adsorption properties) properties of these compounds by transient techniques. In contrast to the first approach, in this approach the kinetic study was carried out on the adsorbed forms of substrates allowing kinetic information to be obtained without the influence of substrate diffusion and substrate resupply during experiments. This enables the effects of number of steps and nature of intermediates on the overall photocatalytic process to be further investigated in a simpler way (without the influence of substrate diffusion and resupply). The adsorption study was necessary in order to investigate the influence of adsorption (of strong adsorbates) on the overall photocatalytic degradation process.

4.2 EXPERIMENTAL

4.2.1 Material and Chemicals

Indium Tin Oxide (ITO) conducting glass sheets (8-10Ω/square, Delta Technologies Limited) were used as substrate for TiO₂ film coating. Potassium hydrogen phthalate (AR, Aldrich), formic acid (AR, Aldrich), oxalic acid (AR, Ajax Chemicals), succinic acid (99%, Sigma), malonic acid (Sigmaultra, Sigma) and glutaric acid (99%, Sigma) were used as received. All other 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).

4.2.2 Preparation of the Nanoporous TiO₂ Film Electrodes

The TiO₂ colloid synthesis and immobilisation procedures are the same as described in Section 2.2.2. Most of the experiments were carried out using TiO₂ porous film electrodes calcined at 500°C for 0.5h. Some of the experiments (where stated) were carried out using
electrodes calcined at 700°C for 16h for comparison. The thickness of the film was ca. 1µm.

4.2.3 Apparatus and Methods

The apparatus and experimental set-up are the same as described in Section 2.2.3 for photoelectrochemical measurements. The light intensity changes were made through altering the relative position of the electrolytic cell to the light source, and light intensity was measured with an UV-irradiance meter (UV-A, Instruments of Beijing Normal University). The pH values of solutions were adjusted with nitric acid and sodium hydroxide solutions. The pHs of solutions were measured and monitored with a pH meter.

Adsorption measurements were conducted in two steps. The pre-adsorption of organic compounds was performed by immersing the TiO₂ coated electrode in sample solutions containing 0.1M NaNO₃ and various concentrations of organic adsorbates for 30 minutes. After pre-adsorption, the electrode was removed from the sample solution and immediately washed with 0.1M NaNO₃ before it was transferred into a blank solution (0.1M NaNO₃), where the electrode was illuminated and the adsorbed molecules were degraded. The transient photocurrent response resulting from the degradation of pre-adsorbed phthalate molecules were recorded at a potential bias of +0.30V (vs. Ag/AgCl) applied potential bias and an illumination intensity of 6.6mW/cm². The total charge was obtained by integrating the photocurrent during the degradation period with the background charge deducted.

The transient photocurrent time profile offers some kinetic information on the photocatalytic degradation of the adsorbed organic compounds. The profiles were analysed and computer-fitted, providing a foundation for the transient kinetic study of the photocatalytic degradation of adsorbed organic compounds without the influence of
substrate diffusion and resupply from solution. This is in contrast to the kinetic study carried out in bulk solution, where re-supply of organic compounds from solution influences the overall photocatalytic degradation kinetics.

4.3 RESULTS AND DISCUSSION

4.3.1 Photocatalytic Oxidation of Substrates in Bulk Solution

4.3.1.1 Effect of Potential Bias

The effect of applied potential bias on the photoelectrochemical oxidation of potassium hydrogen phthalate (KHP) was firstly investigated. Under illumination, the $I_{ph}$-$E$ characteristics of the electrodes were obtained in the presence and absence of phthalate by linear sweep voltammetry at a potential scan rate of 10 mV/s between –0.30V and +0.50V vs. Ag/AgCl (Figure 4.1). The results show that the photocurrent increases linearly with the potential bias in the low potential region and then reaches saturation. This is similar to the photocurrent-potential relationship obtained from a porous TiO$_2$ electrode in a methanol solution or in a glucose solution (previous chapter). Such an $I_{ph}$-$E$ relationship may be explained as follows. For a given light intensity, the concentration of photogenerated electron-hole pairs (or the rate of electron–hole pair generation) is constant. The photocurrent, the actual rate of electrons reaching the back contact of the electrode, depends on two factors - the electron transport in the semiconductor film and the photohole capture process at the TiO$_2$/solution interface, both of which are vital to the suppression of electron-hole pair recombination. Before the photocurrent reaches saturation with respect to the potential bias, the electron transport across the film is the rate-determining step. As a result, a linear relationship is obtained, which is related to the film resistance and the rate of photohole capture at the surface (see discussions in Chapter 3). As increasing the applied potential increases the rate of electron transport in the semiconductor film, the rate of reduction of the photogenerated holes becomes the
dominant factor resulting in photocurrent saturation. It has been noticed that similar voltammograms were obtained under similar conditions with different strong adsorbates and weak adsorbates. This is determined by the nature of photocatalytic degradation at such electrodes under such conditions, in which the process is essentially controlled by the surface photohole capture reaction and transport of the freed electron in the semiconductor film.

![Voltammograms of the porous TiO₂ electrode in 0.1 M NaNO₃ solution of different KHP concentrations at pH 4.5, at 6.6 mW/cm² light intensity and at scan rate 10mV/s: (a) no KHP; (b) 10 μM; (c) 30 μM; (d) 50 μM; (e) 75 μM; (f) 125 μM; (g) 175μM.]

**Figure 4.1** Voltammograms of the porous TiO₂ electrode in 0.1 M NaNO₃ solution of different KHP concentrations at pH 4.5, at 6.6 mW/cm² light intensity and at scan rate 10mV/s: (a) no KHP; (b) 10 μM; (c) 30 μM; (d) 50 μM; (e) 75 μM; (f) 125 μM; (g) 175μM.

4.3.1.2 **Effect of Substrate Concentration**

As discussed in chapter 3 and in the above section, the saturation photocurrent ($I_{sph}$) with respect to potential bias reflects the photohole capture kinetics at TiO₂ surface. In order to investigate the influence of the substrate concentration of strong adsorbates on the photohole capture reaction, the $I_{sph}$ obtained at potential bias of +0.3V was plotted against substrate concentration under constant light intensity. Figure 4.2 shows the $I_{sph}$ dependence on concentration. In the absence of KHP, the $I_{sph}$ due to the water oxidation
is low. As the substrate concentration increases the saturation photocurrent linearly increases indicating that the KHP is photocatalytically oxidised at the electrode surface. The linear increase of saturation photocurrent with concentration is due to the diffusion limitation of KHP as evidenced by the increase of photocurrent upon stirring the solution.

\[ I_{ph} (\mu A) \]
\[ C (mM) \]

![Graph](image)

**Figure 4.2** The dependence of saturation photocurrent on the concentration of potassium hydrogen phthalate at +0.30V.

At high concentration range, the \( I_{sph} \) reaches maximum and then decreased indicating the sluggish photohole capture rate by the compound at surface probably due to the accumulation of potassium hydrogen phthalate molecules or their intermediates. Unlike the weak adsorbates such as glucose where the accumulation of glucose molecule or intermediates at TiO\(_2\) surface benefits the capture of photoholes, the accumulation of KHP or its intermediate is harmful to the capture of photoholes due to their inhibition effect. The reason for this may be attributed to the blockage of active sites by strong adsorption of substrate molecules or by the intermediates due to the special structure of benzene ring.

To identify the reason for this inhibition effect, the photocatalytic oxidation of dicarboxylic acids, which are also strong adsorbates, was examined under the same
It was found that all organic compounds with a benzene ring structure exhibited a similar inhibition, while dicarboxylic acids without the benzene ring structure, even at much higher substrate concentrations, showed no such inhibition effect. Therefore the inhibition effect at higher concentration could be due to the accumulation of benzene ring and partial-degraded intermediates, since the complete oxidation of the benzene ring requires 28 photoholes and involves multiple steps. After primary capture of photoholes, the adsorbed benzene ring or partial-degraded intermediates that remain at the electrode surface could facilitate the recombination of photoelectrons and photoholes. It has been reported that adsorbed phenyl groups can enhance the interfacial electron transfer of other substrates in solution. For the same reason, however, adsorbed phenyl intermediates resulting from the primary oxidation steps can act as a surface recombination centre for photoelectrons and photoholes, which leads to the decrease in the rate of overall photocatalytic oxidation.

4.3.1.3 Effect of pH

In a TiO\(_2\) nanoparticle slurry system, the insensitivity of photocatalytic degradation rate of organic compounds to pH change is frequently reported. However, the slurry approach cannot differentiate between those effects due to the insensitivity of electron accepting by oxygen and those due to the insensitivity of photohole capturing. It was found in Chapter 3 that the photocatalytic oxidation of glucose, a weak adsorbate, was also insensitive to pH change in a large pH range, which is attributed to the TiO\(_2\) surface nature and the weak interaction between the two.

Potassium hydrogen phthalate, as a strong adsorbate, interacts strongly with TiO\(_2\) surface by means of adsorption. This interaction is pH dependent due to protonation/deprotonation of both TiO\(_2\) surface and phthalate ion. The effect of pH on the photocatalytic oxidation of phthalate was therefore investigated. Figure 4.3 shows the
dependence of \( I_{sph} \) on pH both in the presence and absence of KHP at a TiO\(_2\) porous film electrodes calcined at 500°C for 0.5 hour.

\[ \text{Figure 4.3} \] The effect of pH on the saturation photocurrent both in 0.1M NaNO\(_3\) solution (●) and in the solution containing 160µM phthalate ions (○).

From Figure 4.3, it can be seen that the \( I_{sph} \) in the presence of KHP (at a concentration where diffusion is not rate-determining step) is almost unchanged within pH range of 2.0 to 10.0. As will be shown in the next section, the amount of adsorption of phthalate changes significantly in this pH range. The in-variation of \( I_{sph} \) with respect to pH change suggests that the adsorption and the primary photohole capture processes are not the controlling steps, so long as there are enough substrate molecules approaching TiO\(_2\) surface. In contrast, when pH is above 10.0, the \( I_{sph} \) drops sharply to almost the saturation current of water oxidation, implying photocatalytic oxidation of KHP barely occurs. This sharp drop in \( I_{sph} \) can be attributed to the strong electrostatic repulsion between the phthalate ion and the TiO\(_2\) surface, which prevents phthalate ion getting close enough to the surface to capture photoholes.
Overall, it can be concluded that availability of substrate molecules at the TiO₂ surface, whether strongly or weakly adsorbed, is the primary requirement for them to be photodegraded. However, once there is accumulation of substrate at TiO₂ surface, whether the adsorption is the controlling step or not depends on how complex the overall photocatalytic steps are. Whether the photocatalytic degradation of organic compounds is a homogeneous reaction involving photocatalytically generated hydroxyl radicals and organic compounds or heterogeneous surface reaction has been a subject of debate for a long time. This result directly demonstrates that the photocatalytic reactions are heterogeneous reactions.

To investigate the structure influences of the strong adsorbates on their phoathole capture ability, the effect of pH on the photocatalytic oxidation of dicarboxylic acids was carried out. Figure 4.4 shows the pH dependence of the $I_{ph}$ of these carboxylic acids at concentrations free of diffusion limitation. It can be seen that across a large pH range, from pH 2.0 to pH 10.0, the photohole capture ability of small molecules such as oxalic acid, is most influenced by pH change, which can be attributed to change in the adsorption caused by pH change. Interestingly other acids, supposedly having similar adsorption dependence on pH, show little dependence of saturation photocurrent on pH in the same pH range. The difference in the sensitivity to the pH change for different adsorbates most likely reflects the difference in the significance of the adsorption process in the overall degradation process. For formic acid or oxalic acid, only two electrons are required for complete mineralisation – meaning only one or two breakdown steps are involved. Therefore, it is unlikely that the further degradation of such intermediates will become the rate determining step due to the simplicity and high activity of these intermediates (one step further oxidation of such intermediates gives final mineralisation product). As a result, the adsorption process plays a major role. While for other more complex adsorbates, more electrons and more breakdown steps are required to achieve the complete
mineralisation. Therefore, the role of the adsorption step, which has the strongest influence on the primary photohole capture process, is less critical in the overall process, since the subsequent photohole capture steps involving intermediates may become the rate-controlling steps. Like KHP, other carboxylic acids experience sharp decreases in $I_{sph}$ at pH values above 10.0, which can be again attributed to the electrostatic repulsion between the acid molecules and the TiO$_2$ surface.

![Figure 4.4](image_url)  

**Figure 4.4** The effects of pH on the saturation photocurrent of different organic substrates at light intensity of 4.4mWcm$^{-2}$, (◇)0.1M formic acid, (●)160µM phthalic acid, (○)50mM succinic acid, (◆)50mM malonic acid, (▲)50mM glutaric acid, (△)blank solution, (□)0.1M oxalic acid.

The photocatalytic degradation of these compounds at electrodes calcined at 700°C for 16h were also investigated in terms of pH influence. Shown in Figure 4.5 is the effect of pH on $I_{sph}$. The pH effects of these compounds on their $I_{sph}$ at the electrode are very similar to that at electrode calcined at 500°C (shown in Figure 4.4). The major difference is that the magnitudes of the $I_{sph}$ are smaller for less complicated organic compounds due largely to the decreased surface area. The $I_{sph}$ values for larger complicated organic compounds were larger due to the special nature of the electrodes, as was discussed in
Chapter 2, which prolong the lifetime of photoelectron and photohole pairs. Another difference is that for the high temperature calcined electrodes, the $I_{sph}$ is less dependent on the nature of organic substrate and pH, as shown by the comparison of Figure 4.4 with Figure 4.5.

![Figure 4.5](image)

**Figure 4.5** The effect of pH on the saturation photocurrent of different organic substrates at light intensity of 4.4mWcm$^{-2}$. (●) 0.1M formic acid, (◆) 160µM phthalic acid, (◇) 50mM succinic acid, (▲) 50mM malonic acid, (□) 50mM glutaric acid, (○) blank solution, (★) 0.1M oxalic acid.

### 4.3.1.4 Effect of Light Intensity

A linear relationship between $I_{sph}$ and light intensity was observed in Chapter 3 for weak adsorbates such as glucose. Here, for comparison, the effect of light intensity on $I_{sph}$ for photocatalytic oxidation of strong adsorbates at TiO$_2$ porous electrodes was also investigated at substrate concentrations beyond the diffusion limited concentration. Figure 4.6 shows the effects of light intensity on $I_{sph}$. In all the cases, the $I_{sph}$ observed is directly proportional to the light intensity, indicating the interface reaction is first order with respect to photohole regardless of the type of the photohole scavengers involved. The
difference in slope reflects the difference in the photohole capture ability of different photohole scavengers (organic compounds). Organic compounds requiring the least number of electrons and involving the least number of intermediates, such as formic and oxalic acids, are the most effective photohole acceptors. With more complicated organic molecules, in particular aromatic compounds, their abilities to capture photoholes are decreased probably because their intermediates can act as recombination centres causing an increase in the rate of photohole and photoelectron recombination.

![Graph showing the effect of light intensity on the saturation photocurrent of different organic substrates at pH 4.0](image)

**Figure 4.6** The effects of light intensity on the saturation photocurrent of different organic substrates at pH 4.0, (◆) 0.1M formic acid, (●) 160µM phthalic acid, (◇) 50mM succinic acid, (○) 50mM malonic acid, (□) 50mM glutaric acid, (△) blank solution, (■) 0.1M oxalic acid, electrode calcined at 500°C for 0.5h.

The effect of light intensity on $I_{ph}$ for photocatalytic oxidation of strong adsorbates at electrodes calcined at 700°C was also investigated (Figure 4.7). The results observed were qualitatively similar to those observed at the electrode calcined at the lower temperature. As was discussed in Chapter 2, the electrodes calcined at 700°C for 16hrs have higher photocatalytic reactivity toward water oxidation (at any light intensity) than
electrodes calcined at 500°C. The high photocatalytic reactivity of the electrode makes the $I_{sph}$ less dependent on the structural difference of organic compounds. This is supported by the results shown in Figure 4.7 where, the $I_{sph}$ obtained from phthalate, malonate, succinate and glutarate are similar. This further supports claims in Chapter 2 that the coexistence of both the rutile and anatase phases of TiO$_2$ suppresses the recombination of photoelectrons and photoholes.

![Figure 4.7](image.png)

**Figure 4.7** The effects of light intensity on the saturation photocurrent of different organic substrates at pH 4.0, (●)0.1M formic acid, (●)160µM phthalic acid, (+)50mM succinic acid, (□)50mM malonic acid, (×)50mM glutaric acid, (○)blank solution, (◇)0.1M oxalic acid, electrode calcined at 700°C for 16h.

Overall, regardless of the electrode fabrication condition used and the type of interfacial reactions involved (with or without adsorption step), the photohole capture rate is always proportional to the light intensity. This, however, demonstrates that in slurry system the half order dependence of photocatalytic degradation rate on light intensity is not caused by the oxidation reaction of organic compounds, most likely is caused by the sluggishness of photoelectron removal reaction by oxygen.
4.3.2 Photocatalytic Oxidation of Pre-adsorbed Compounds

4.3.2.1 Methodology development for Adsorption Measurement

Adsorption plays an important role in the photocatalytic oxidation of organic compounds. In a slurry system, many attempts have been made to understand the effects of substrate adsorption on the overall photocatalysis process\textsuperscript{73-75, 85, 86, 162}. Typically, adsorption measurements at TiO\textsubscript{2} surfaces are conducted in dark by employing large surface area TiO\textsubscript{2} nanoparticle slurries\textsuperscript{73, 85, 86, 223, 225, 227}. This is done to ensure that measurable amounts of adsorbate will be removed from solution. The amount of adsorbed species is usually calculated by measuring the decrease in concentration of adsorbate in solution after separation of the slurry. Apart from the practical problems associated with this approach, there are many uncontrollable factors involved in such a measurement that result in great difficulty in maintaining desired experimental conditions. The most significant of these is the fact that adsorbate concentration in the bulk solution can change appreciably and rapidly during adsorption. The pH of the solution can also change for some adsorbates due to the deprotonation/protonation during adsorption. As a consequence, maintaining desired experimental conditions is very difficult and the adsorption value obtained is highly questionable.

In order to effectively study the effect of adsorption on the photocatalysis process, we propose an \textit{ex-situ} photoelectrochemical method to accurately quantify the adsorption of organic compounds on the TiO\textsubscript{2} surface. The method involves two steps. A TiO\textsubscript{2} porous film electrode is immersed in the sample solution containing the adsorbate for a given time to allow adsorption. The electrode is then removed from the sample solution into a separate detection solution containing only supporting electrolyte to perform the photoelectrochemical measurement. The photoelectrochemical charge generated from photoelectrochemical oxidation of the adsorbate was used to quantify the extent of surface
coverage. Immobilisation of TiO$_2$ onto a conducting substrate makes the application of photoelectrochemical techniques possible. With this new method, the adsorbate concentration depletion and pH changes in the bulk solution caused by the adsorption are negligible due to the large solution volume/electrode area ratio. The high sensitivity of electrochemical techniques ensures accurate measurement even at very low surface coverage. Phthalic acid was used as the adsorbate to test the method due to its known strong adsorption onto TiO$_2$ surfaces$^{225}$. The adsorption isotherm of phthalic acid was obtained and the binding constant was determined according to the Langmuir adsorption model. The effect of pH on phthalic acid adsorption was also investigated.

4.3.2.1.1. Principles

Figure 4.8 shows the typical photocurrent - time profiles obtained from the electrodes preadsorbed with phthalic acid and without preadsorption. It can be seen that the photocurrent decayed with time and then reached a steady value, corresponding to the oxidation of water. It is noted that the blank photocurrent obtained from the electrode preadsorbed in blank electrolyte solution was purely due to the oxidation of water. The photocurrent obtained from the electrode preadsorbed in phthalic acid, however, consists of two current components, one due to photoelectrochemical oxidation of adsorbed phthalic acid, and the other due to the oxidation of water, which is the same as the blank photocurrent. My experimental results showed that the blank photocurrent was essentially constant for the given set of experimental conditions. For a given time period, the charge passed for both cases can be obtained by integration of the photocurrent and blank photocurrent. The charge difference between the two cases is the net charge, Q, due to the photoelectrochemical oxidation of the adsorbed phthalic acid, which is indicated as the shaded area in Figure 4.8. Owing to the powerful oxidation ability of photoholes or surface bound hydroxyl radicals the adsorbed organic compounds can be
stoichiometrically mineralised. The porous nature of the electrode prevents the intermediates from leaving the reaction layer before they are mineralised – this is particularly the case for strong adsorbates. This will be further demonstrated in Chapters 5, 6 and 7 where under exhaustive photolysis condition organic compounds can be stoichiometrically mineralised. Therefore, the net charge, Q can be attributed to the photocatalytic mineralisation of the adsorbed organic compounds, which should be directly proportional to the adsorption amount of the organic compounds as is determined stoichiometrically by Faraday’s law. Further experimental evidence of this quantitative relationship is that in dilute adsorbate solutions the Q values obtained after pre-adsorption at different adsorption times is directly proportional to the adsorption time when the preadsorption is performed under diffusion controlled conditions$^9$.

![Figure 4.8](image-url)

**Figure 4.8** The ex-situ transient photocurrent/time profile of an anatase TiO$_2$ nanoporous electrode in 0.1M NaNO$_3$ after it was ex-situ preadsorbed in 5$\mu$M phthalic acid + 0.1M NaNO$_3$ solution at pH 4.0 for 8 minutes (dash line) and an electrode with no pre-absorbed phthalic acid (Solid line).
In order to measure the adsorption isotherm, the time required to reach the adsorption equilibrium at various phthalic acid concentrations were investigated. The results demonstrated that the adsorption equilibrium can be reached within 30 min of *ex-situ* pre-adsorption for all concentrations investigated. After pre-adsorption in a phthalic acid sample solution for 30 min, the TiO$_2$ porous film electrode was transferred to a 0.1M NaNO$_3$ blank solution to perform the photoelectrochemical measurement. The net charges, $Q$, were measured by integrating the net photocurrent within the degradation period as shown in Figure 4.8, which is directly proportional to the amount of adsorbed phthalic acid. Figure 4.9 shows the relationship between the net charge (amount of adsorbate) and the concentration of phthalic acid in the sample solution (i.e. an adsorption isotherm).

*Figure 4.9* The dependence of charge (after ex-situ preadsorbed for 30min in 0.1M NaNO$_3$ containing different concentrations at pH 4.0) on the concentration of phthalic acid.
As a simple adsorption model, Langmuir adsorption model has been commonly employed to study the adsorption behaviour of organic compounds at metal oxide surfaces\textsuperscript{73, 228}.

Assuming a monolayer adsorption structure, we can present the surface coverage, $\theta$, as:

$$\theta = \frac{Q}{Q_{\text{max}}}$$  \hspace{1cm} (4.1)

where, $Q$ is the net charge due to the photoelectrochemical oxidation of adsorbates and $Q_{\text{max}}$ is the maximum net charge at 100% surface coverage.

The Langmuir isotherm equation can then be written as:

$$\frac{C}{Q} = \frac{1}{Q_{\text{max}}} C + \frac{1}{Q_{\text{max}} K}$$ \hspace{1cm} (4.2)

where, $C$ is the concentration of adsorbate in the sample solution and $K$ is the adsorption equilibrium constant.

Treating the data obtained in Figure 4.9 according to the Langmuir model by plotting $C/Q$ against $C$ gives a straight line with $R^2 = 0.998$ (Figure 4.10). This implies that the adsorption data agrees well with the Langmuir adsorption model at these concentrations. The maximum charge, $Q_{\text{max}} = 4.19 \text{ mC}$, was obtained from the slope of the curve. According to Equation 4.1, the surface coverage $\theta$ can be calculated after $Q_{\text{max}}$ is determined. The adsorption equilibrium constant, $K = 4.0 \times 10^4 \text{ M}^{-1}$ was obtained from the ratio of the slope to the intercept of the curve (see Equation 4.2). The $K$ value obtained by the photoelectrochemical method was close to that of phthalic acid adsorption at TiO$_2$ (Degussa p25) obtained by traditional method\textsuperscript{225} at pH 3.6, which was $5 \times 10^4 \text{ M}^{-1}$. The agreement with the Langmuir adsorption model suggests that the adsorption is a monolayer adsorption.

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Figure 4.10 The fitting of the adsorption isotherm of phthalic acid to Langmuir adsorption model.

Adsorption of other strong adsorbates such as oxalic acid, malonic acid, succinic acid, glutaric acid and salicylic acid has also been studied by this method. Similar adsorption isotherms have been obtained. Figure 4.11 shows a typical isotherm – the adsorption isotherm of oxalic acid and the resultant data treatment according to the Langmuir adsorption model. The experimental data revealed that the Langmuir adsorption model was again well followed in the medium concentration range, while deviated from Langmuir adsorption model in very low and high concentration regions indicating different adsorption behaviour at different concentrations. These differences in the adsorption behaviour may be attributed to the formation of different types of surface complexes. Three different types of adsorption characteristics indicate that there are at least three different types of surface complexes and each has different binding strength to TiO$_2$ surface. Hug et.al $^{87}$ also reported a similar finding during their study of oxalic acid adsorption at TiO$_2$ surface using in situ FTIR spectroscopy. They obtained three different
surface complexes each having a distinct adsorption equilibrium constant. They believed this was caused by the heterogeneity of the TiO₂ surface.

Figure 4.11 Adsorption isotherm of oxalic acid ex-situ preadsorbed in different concentrations at pH 4.0 (○) and processing result according to the Langmuir adsorption model (●).

It can be seen from Figure 4.11 that the strongest bound complex is formed at very low concentrations and the corresponding charge obtained indicates this type of complex accounts for a very small fraction of the total amount adsorbed. According to Regazzoni ⁸⁶, the surface titanium ions, with fewer coordination positions occupied by O²⁻ at the crystal edges and corners, display the highest affinity for adsorbing ligands and the number of these ions is limited. The strongest bound surface complex can be attributed to adsorption at such sites. The medium strength bound complex is responsible for Langmuir behaviour in the medium concentration region and this type of complex accounts for the vast majority of the total adsorption, as demonstrated by the corresponding charge measured. The weakest bound complex formed at high concentrations accounts for a small portion of the total adsorption quantity. Titanium ions
from the most stable, perfectly cleaved (001) and (011) crystal faces of anatase, which are penta-coordinated to \(\text{O}^{2-}\) ions and complete their coordination sphere by binding \(\text{OH}^-\), are responsible for the latter two types of surface complexes. The overall adsorption characteristics of oxalic acid is similar to previously reported adsorption of salicylic acid on \(\text{TiO}_2\) surface. Interestingly, similar results were obtained for the adsorption of other dicarboxylic acids such as malonic acid, succinic acid and glutaric acid. This suggests that different dicarboxylic acids possess similar adsorption behaviour. Indeed, similar adsorption behaviour was observed for all of the strong adsorbates tested. This may be attributed to the inherent properties of \(\text{TiO}_2\). Therefore, the above explanation about the adsorption of dicarboxylic acids may be also applicable to other strong adsorbates.

In Chapter 2 I have discussed the significant difference in photocatalytic reactivity of electrodes calcined at different temperatures. This could be caused by the difference in adsorption properties of \(\text{TiO}_2\) films after calcination. To this end, the adsorption studies of the above organic compounds on \(\text{TiO}_2\) porous film electrodes calcined at 700\(^\circ\text{C}\) for 16h were also carried out. Similar adsorption isotherms were obtained and no substantial difference from electrodes calcined at 500\(^\circ\text{C}\) (in terms of adsorption behaviours) was observed. By processing the data from these isotherms according to the Langmuir adsorption model, the adsorption parameters of different organic compounds at these two kinds of electrodes were found and are summarized in Table 4.1. A most remarkable difference in the adsorption property between these two kinds of electrodes is that for the same adsorbates the electrodes calcined at 700\(^\circ\text{C}\) for 16h have a lower maximum adsorption amount than electrodes calcined at 500\(^\circ\text{C}\) for 0.5h. The decreased surface area due to particle growth at higher calcination temperature as discussed in Chapter 2 was responsible for this. The differences in adsorption constant values obtained from the two
different electrodes very likely result from experimental error rather than from the
difference in binding strength toward the same adsorbates.

Table 4.1 The adsorption parameters of different adsorbates at electrodes calcined
under two different conditions

<table>
<thead>
<tr>
<th>adsorbates</th>
<th>Electrode calcined at 700°C 16h</th>
<th>Electrode calcined at 500°C 0.5h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q_{max}(mC)</td>
<td>K(M^{-1})</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>0.45</td>
<td>3.9\times10^4</td>
</tr>
<tr>
<td>Malonic acid</td>
<td>0.42</td>
<td>3.3\times10^4</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>0.67</td>
<td>2.6\times10^4</td>
</tr>
<tr>
<td>Glutaric acid</td>
<td>0.62</td>
<td>3.0\times10^4</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td>0.49*</td>
<td>7.2\times10^4</td>
</tr>
<tr>
<td>Phthalic acid</td>
<td>0.70*</td>
<td>8.0\times10^4</td>
</tr>
</tbody>
</table>

* electrodes used different from in other series

4.3.2.1.3. Effect of pH on the Adsorption

It is widely accepted that carboxylic groups can coordinate with TiO$_2$ surfaces to form
surface complexes$^{86, 225, 229, 230}$. This process can be affected by the solution pH since the
speciation of both the TiO$_2$ surface and the phthalate molecules are pH dependent due to
protonation/deprotonation. Figure 4.12(a) shows the functional group species change of
the TiO$_2$ surface (>TiOH surface bound hydroxyl group) with pH as derived from
Kormann et. al.$^{111}$, while Figure 4.12(b) shows the species distribution of phthalic acid
(H$_2$Th) with pH, and Figure 4.12(c) shows the dependence of the adsorption amount of
phthalic acid on pH in the sample solution.
At pH 4.0 the adsorption reached maximum, which coincides with the maximum fraction of HTh\(^-\). This implies that HTh\(^-\) can be favourably adsorbed to TiO\(_2\) surface. Considering the TiO\(_2\) surface carries positive charges in acidic conditions and HTh\(^-\) carries a negative charge, the adsorption seems to benefit from the electrostatic attractive force between them. From pH 4.0 to pH 2.0 the fraction of HTh\(^-\) species in solution dropped significantly, nevertheless, only a slight decrease in the amount of adsorption was observed. Given phthalic acid at pH 2.0 mainly exists in neutral molecule form, electrostatic attraction force between molecular form of phthalic acid and electrode surface is insignificant. Therefore, the adsorption is more likely chemical bonding in nature. The sharp decrease in adsorption quantity from pH 4.0 to pH 6.0 indicates the HTh\(^-\) was more favorably adsorbed on \(>\text{TiOH}\) than Th\(^2+\) on \(>\text{TiOH}\) sites. The adsorption amount remains relatively constant from pH 6.0 to 8.0. It can be seen from Figure 4.12(a) that the TiO\(_2\) surface is essentially neutral, and therefore electrostatic attraction or

---

**Figure 4.12** Comparison of surface species distribution of TiO\(_2\) surface groups (experimental results of Kormann et. al.\(^{111}\))(a), species distribution of phthalic acid in solution (b), the adsorption dependence of phthalic acid on pH (c), adsorption was carried out on electrode calcined at 500°C for 0.5hrs in 0.1M NaNO\(_3\) containing 160µM phthalic acid for 30min.
repulsion between the adsorbate and the TiO$_2$ surface is insignificant. The significant amount of adsorption within this pH range again demonstrates that the adsorption was specific and Th$^{2+}$ can be chemically bound to the TiO$_2$ surface. As pH increased from 8.0 to 10.0, the negative charge density of the TiO$_2$ surface was increased. As a consequence, the electrostatic repulsion between Th$^{2+}$ and negatively charged TiO$_2$ surface was increased. This was obviously detrimental to the adsorption and resulted in a sharp decrease in adsorption amount.

Similar pH dependence was observed for all other strong adsorbates investigated indicating that the adsorption of these organic compounds is also highly dependent on pH due to changes in electrode surface speciation and adsorbate speciation. Comparing the pH effect on adsorption and on saturation photocurrent in bulk solution for most organic substrates, it was found no correlation between pH dependence of adsorption and pH effects on saturation photocurrent. The saturation photocurrent is less sensitive to the change of pH, as shown in the previous section, whereas adsorption amount changes greatly with pH. This lack of correlation between saturation photocurrent and the amount adsorbed further demonstrates the complexity in the role of adsorption in the overall photocatalytic process. At pH higher than 10.0 the sharp drop of saturation photocurrent for carboxylic acids coincides with insignificant amount of adsorption. But the sharp drop of saturation photocurrent is more likely due to the unavailability of organic molecules at the electrode surface caused by the strong electrostatic repulsion between electrode surface and organic substrate rather than due to the lack of chemical bonding of the adsorbates to TiO$_2$ surfaces. The behaviour of non-specific adsorbates studied in Chapter 3 supports this argument.

Among all of the adsorbates studied, only oxalic acid and formic acid showed some degree of correlation between their pH dependence of saturation photocurrent and their
adsorption dependence on pH. The major difference of these compounds from all other organic compounds investigated is that these compounds take the least steps to be mineralised and their molecules need the least photoholes to be mineralised compared with other compounds. Because of this, the adsorption step has a larger degree of influence on the overall photocatalytic process for these compounds than for other compounds. For compounds involving more steps and intermediates in the overall mineralisation process, the impact of initial adsorption process and primary charge transfer process on the overall photocatalytic degradation kinetics are less significant. As a consequence, the role of adsorption is less important in determining the overall mineralization process and therefore no obvious correlation between the steady state reaction rate \( I_{sph} \) and the amount of adsorption can be identified.

### 4.3.2.2 Photocatalytic Degradation Kinetics of Adsorbed Compounds

As discussed above, for organic compounds involving multiple steps and multiple intermediate, there seems little correlation between adsorption amount and steady state photocatalytic oxidation rate (saturation photocurrent in bulk solution). While for organic compounds involving least steps and intermediates, such as oxalic acid and formic acid, some degree of correlation between saturation photocurrent and adsorption amount (affected by pH) were observed. Furthermore, even in transient experiments where pre-adsorbed organic compounds, such as phthalic acid, are photoelectrolysed (which involves multiple intermediates) the direct correlation between initial transient photocurrent and adsorption amount still cannot be observed. Experimental evidence for this includes the fact that when preadsorbed phthalic acid is exhaustively photoelectrolysed, the half-life of the photocurrent decay curves changes with adsorption quantity rather than staying constant as would expected by a first order surface reaction. In fact, this type of non-correlation behaviour has long been observed in the photocatalytic degradation study of organic compounds in a slurry system\textsuperscript{73, 86, 89}. However, the underlying reasons still
remain unclear due to the limitations of study method employed. In order to better understand the kinetics involved in a photocatalytic degradation of organic compounds, a transient exhaustive photoelectrolysis technique was developed with the expectation of gaining the useful kinetic information of photocatalytic degradation of adsorbed organic compounds. The adsorbates selected are from simple to more complicated, with electron transfer number for complete mineralisation ranging from 2 to 20. The effects of the difference in structure, electron transfer number and intermediates on the overall photocatalytic process were investigated.

4.3.2.2.1. Photocatalytic Degradation Kinetics of Preadsorbed Oxalic Acid

Theoretically, it is widely recognised that a heterogeneous photocatalytic reaction should be a first order reaction with respect to either the surface coverage of organic adsorbates or photohole concentration at the surface\(^4\). In practice, however, the experimental data often deviate from a first order reaction with respect to the surface coverage. This has been reported to be the result of the heterogeneity of the catalytic surface\(^2\). If a uniform catalytic surface is covered by only one type of species, then a first order rate law with surface coverage should be always applicable. However, more than one type of surface complex may be formed when a heterogeneous catalytic surface is in contact with a single species in solution. Under this circumstance, the overall catalytic process is the result of contributions by the individual catalytic process of each type of surface complex, and the normal first order rate law with respect to surface coverage cannot be used to represent the overall catalytic processes. Nevertheless, the normal first order rate law should still be applicable to the individual catalytic processes of each type of surface bound complex.

As demonstrated in Figure 4.11, the overall adsorption isotherm for oxalic acid at the TiO\(_2\) electrode is potentially the result of three different types of surface complexes. If this was the case, the photocurrent decay curves may not follow a single exponential decay. This
was indeed the case for the photocurrent decay curves recorded for the photocatalytic breakdown of adsorbed oxalic acid at these electrodes. Furthermore the photocurrent decay curves revealed that the apparent half-life of these oxidation processes varied with the amount adsorbed (or surface coverage). This indicates that such a catalytic process cannot be represented by simple first order kinetics. I believe it is possible to study, in detail, the kinetics at heterogeneous catalytic surface if I could identify the individual contributions to the overall catalytic process.

If I assume that the overall photocatalytic process is the sum of the individual photocatalytic processes of each type of surface complex, then the total photocurrent, $I_{ph}$, can be described as:

$$I_{ph} = \sum_{j=1}^{n} I_{phj}$$  \hspace{1cm} (4.3)

where $I_{ph}$ refers to the total instantaneous photocurrent; $I_{phj}$ is the instantaneous photocurrent generated from photocatalytic oxidation of $j$ type of surface complex.

If we also assume that a normal first order rate law with respect to surface coverage can be applied to represent the individual catalytic processes of each type of surface complex, then the rate of reaction for a particular surface complex can be given as:

$$Rate_j = -\frac{d\theta_j}{dt} = \frac{I_{phj}}{nF} = k\theta_j C_{sh}$$  \hspace{1cm} (4.4)

where $\theta_j$ is the surface coverage of the $j$ type of surface complex and is defined by the ratio of surface concentration of this species ($C_{sj}$) to the saturated surface concentration ($C_{ssj}$) (i.e. $C_{sj}/C_{ssj}$); $n$ is the number of electrons transferred during the photocatalytic mineralization of $j$ species and $F$ is Faraday constant; $C_{sh}$ is the surface concentration of photoholes at this kind of sites.
For a given electrode and light intensity, \( C_{ssj} \) and \( C_{sh} \) are constants. Equation (4.4) can therefore be rewritten as:

\[
Rate_j = \frac{dC_{sj}}{dt} = \frac{I_{phj}}{nF} = k_j C_{sj}
\]  
(4.5)

At \( t=0 \), the initial photocurrent \( I_{phj}^0 \) is determined by the initial surface concentration of the adsorbed \( j \) species:

\[
I_{phj}^0 = nF k_j C_{sj}^0
\]  
(4.6)

Solving the differential equation (4.5) and considering Equation (4.6), gives:

\[
I_{phj} = I_{phj}^0 \exp(-k_j t) = nF k_j C_{sj}^0 \exp(-k_j t) = k_j Q_j^0 \exp(-k_j t)
\]  
(4.7)

where \( Q_j^0 \) is the charge expected for the mineralization of \( j \) adsorbed species.

Substituting Equation (4.7) into Equation (4.3), gives:

\[
I_{ph} = \sum_{j=1}^{n} I_{phj}^0 \exp(-k_j t) = \sum_{j=1}^{n} nF k_j C_{sj}^0 \exp(-k_j t) = \sum_{j=1}^{n} k_j Q_j^0 \exp(-k_j t)
\]  
(4.8)

Equation (4.8) indicates that the total photocurrent decay profile can be represented by the sum of individual exponential components corresponding to the degradation of each type of adsorbed surface complex. From this kinetic model, the information on both the adsorption amount of each adsorbed species and their photocatalytic reactivity can be obtained.

Figure 4.13 shows the photocurrent decay curves for the photocatalytic oxidation of oxalic acid adsorbed onto TiO\(_2\) from two different solution concentrations (0.05mM and 8.0mM). In both cases, it was shown that the photocurrent decay profiles of the adsorbed oxalic acid could be well curve-fitted to a double exponential expression. At other surface
coverage the decay curves were equally well fitted to the double exponential expression. That is:

\[ I_{ph} = a_0 + a_1 \exp(-a_2 t) + a_3 \exp(-a_4 t) \]  \hspace{1cm} (4.9)

where \( I_{ph} \) referred to the total photocurrent; \( a_0, a_1, a_2, a_3, a_4 \) are constants and \( t \) is the time lapse starting from illumination.

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{figure4.13.png}
  \caption{Photocurrent-time profiles and the fitting curves of oxalic acid preadsorbed in 0.1M NaNO\textsubscript{3} with 0.05mM oxalic acid (a), and with 6mM oxalic acid at pH 4.0 (b). Solid black lines are the experimental curves, circles on the black lines are fit curves.}
  \end{figure}

Of the constants in Equation 4.9, only \( a_0 \) is independent of the chemical nature and the surface coverage of a specific organic species and can be attributed to the steady state oxidation photocurrent of water, which is irrelevant to the oxidation of adsorbed organic compounds. The double exponential decay suggests that two distinct photocatalytic processes with different degradation rates occurred simultaneously at the same electrode surface. Although there may be three different types of surface complexes having been identified from the adsorption study, kinetically, only two distinct decay processes were found, which indicates that one species has quite different photocatalytic reactivity from
the other two species. The two distinct kinetic processes represent two kinetically
different adsorbed species – one is fast (denoted as $f$) and another is slow (denoted as $s$).
That is, based on the computer fitting of the experimental data, for photocatalysis of
adsorbed oxalic acid, Equation (4.8) can be rewritten as:

$$I_{ph} = I_{phf}^0 \exp(-k_f t) + I_{phs}^0 \exp(-k_s t) + k_w = k_f Q_f^0 \exp(-k_f t) + k_s Q_s^0 \exp(-k_s t) + k_w$$  (4.10)

where, $k_s$ and $k_f$ represent the rate constant for the fast and slow type of adsorbed species
respectively and are independent on surface adsorbed amount; $Q_f^0$ and $Q_s^0$ are the charge
generated from the mineralization of the fast and slow kinetic species respectively.

Comparing Equations (4.9) and (4.10), gives the following relationships:

$$I_{phf}^0 = a_1, \quad k_f = a_2, \quad I_{phs}^0 = a_3, \quad k_s = a_4 \quad \text{and} \quad k_w = a_0.$$

The charge generated from the mineralization of the fast and slow kinetic species can be
expressed as:

$$Q_f^0 = a_1/a_2, \quad Q_s^0 = a_3/a_4.$$

It is important to note that $Q_f^0$ and $Q_s^0$ represent the initial adsorbed amounts (or the
surface coverage) of the fast and slow kinetic species.

The above discussion suggests that kinetic parameters such as $I_{phf}^0$, $I_{phs}^0$, $Q_f^0$, $Q_s^0$, $k_f$, $k_s$,
$k_w$ can be obtained by comparing the empirical kinetic model (Equation 4.9) with the
theoretical kinetic model (Equation 4.10). Most importantly, this approach enables the
identification of the kinetic contribution of individual surface component of same
photocatalytic reactivity.

Using this approach, it was possible to deconvolute the total adsorption isotherm in Figure
4.11, into its fast and slow kinetic components. This is shown in Figure 4.14, where it can
be seen that the amount of the slow kinetic species exhibited a similar trend as the total adsorption isotherm shown in Figure 4.11 and accounts for most of the adsorption quantity, particularly at slightly higher solution concentrations. The slow kinetic process can be attributed to the photocatalytic degradation of the intermediate and weakly bound surface complexes. It was also found that the amount of fast kinetic species can be easily saturated at low concentration and accounted for only a small portion of the total adsorption quantity and this species can be identified as the strongest bound surface complex.

![Graph](https://via.placeholder.com/150)

**Figure 4.14**  The adsorption isotherms of the fast, slow kinetic components and the total for oxalic acid. (〇) total adsorption, (●) slow kinetic species, (△) fast kinetic adsorbed species.

Equation 4.10 predicts that $I_{phs}^0$ and $I_{phf}^0$ should be directly proportional to $Q_s^0$ and $Q_f^0$ respectively, while $k_s$ and $k_f$ are independent of $Q_s^0$ and $Q_f^0$ respectively. Both $I_{phs}^0$ and $I_{phf}^0$ can be obtained from the fitting of photocurrent decay curves (i.e. $a_3$ and $a_1$). Similarly, $k_s$ and $k_f$ can also be obtained from the curve fitting (i.e. $a_4$ and $a_2$).
A plot of \( I_{phs}^0 \) and \( k_s \) versus the amount adsorbed (\( Q_s \)) for the slow kinetic species is shown in Figure 4.15. As predicted by equation 4.10, it was found that the initial photocurrent (or initial rate) associated with the slow kinetic process (\( I_{phs}^0 \)) was proportional to the initial surface coverage of the species responsible for the slow process (i.e. the intermediate and weakest bound complexes). It was also shown that the first order rate constant associated with the slow process remained almost unchanged with the initial surface coverage. This was also predicted by equation 4.10. The average value of \( k_s \) over the entire range of surface coverage was found to be ca. 0.11 s\(^{-1}\).

![Figure 4.15](image)

**Figure 4.15** The A plot of \( I_{phs}^0 \) and \( k_s \) versus the amount adsorbed (oxalic acid) (\( Q_s \)) for the slow kinetic species (\( Q_s \)) first order constant (\( k_s \)), (●) initial reaction rate (\( I_{phs}^0 \)).

A plot of \( I_{phf}^0 \) and \( k_f \) versus the amount adsorbed (\( Q_f \)) for the fast kinetic species is shown in Figure 4.16. Again, it was found that the initial photocurrent or reaction rate was directly proportional to the amount of the adsorbed species (i.e. the strongest bound complex) and the rate constant (\( k_f \)) was independent of the adsorption amount. The average value of the rate constant for the fast kinetic species over the entire range of the
surface coverage was found to be ca. $0.65 \text{s}^{-1}$, which is approximately 6 times faster than the slow kinetic process.

![Figure 4.16](image)

**Figure 4.16** A plot of $I_{phf}^0$ and $k_f$ versus the amount adsorbed (oxalic acid) ($Q_f$) for the fast kinetic species, (●) first order rate constant ($k_f$), (□) initial reaction rate ($I_{phf}^0$).

The photocatalytic oxidation of both slow and fast degradable adsorbed oxalic acid complies well with the first order reaction kinetics. The multi-site or multi-mode adsorption model explains the photocatalytic oxidation of adsorbed oxalic acid very well. Because of the simplicity in its photocatalytic mineralization mechanism it can only be attributed to the heterogeneity of TiO$_2$ surface to which three kinds of surface complexes of different photocatalytic activity are formed. Similarly, the photocatalytic degradation of oxalic acid involves no long-lived intermediates, the surface reaction can be studied directly free of the influence of intermediates.

4.3.2.2.2. Extension of the Kinetic Model to More Complicated Adsorbates

The approach described above was subsequently employed to study the kinetics of photoelectrolysis of larger dicarboxylic acids that, compared to oxalic acid, ought to
undergo more degradative steps and involve more intermediates during their mineralization. This was done to elucidate what influence the breakdown intermediates have on the overall photocatalytic degradation kinetics. It was found that at low adsorption concentration (or surface coverage), the photocurrent decay profiles of all dicarboxylic acids investigated were similar to those of oxalic acid and the transient photocurrent responses could be fitted to the double exponential expression described above. However, at higher surface coverage, the results from the double exponential curve fitting showed that the value of the constant ($a_2$) associated with the fast process approached the value of the constant ($a_4$) associated with the slow process. In other words, the photocurrent decay curve approached a single exponential decay representing the slow process only. As the surface coverage was further increased it was found that the initial part of the photocurrent decay curves could not be fitted to any exponential decay, while the remainder of the photocurrent decay curve could still be fitted to a single exponential decay. It should be pointed out that this characteristic in photocurrent decay curve is also true for aromatic adsorbates.

Figure 4.17 shows the photocurrent decay profiles and the curve fitting data for adsorbed glutaric acid at different surface coverages. At low surface coverage, the decay curve (a) can be fitted to a double exponential expression. At medium surface coverage, the decay curve (b) approaches a single exponential decay. At high surface coverage, the initial part of the decay curve (c) is deformed to the point that it cannot be fitted to any exponential decay, while the remainder of curve (c) follows a single exponential decay. This shift from a double exponential decay (representing fast and slow processes) to a single exponential decay with increasing surface coverage was observed for all the larger dicarboxylic acids. A related study (unpublished data) showed that this was also the case for a wide range of aromatic compounds, which, like the larger dicarboxylic acids, involve a series of degradative steps and intermediate breakdown products.
Figure 4.17 The photocurrent decay profiles (solid lines) and the curve fitting data (circles) for glutaric acid preadsorbed in 0.1M NaNO₃ with different concentrations at pH 4.0, 0.04mM (a), 0.5mM (b) and 5mM (c).

Figure 4.18 shows a plot of rate constants for the fast process ($k_f$) (calculated form the curve fitting data) versus surface coverage ($Q_f$) for the different dicarboxylic acids. For all of the larger dicarboxylic acids the rate constants were found to decrease with surface coverage, whereas the $k_f$ values for oxalic acid remained constant (as shown previously in Figure 4.16). Interestingly, although the $k_f$ values change with surface coverage (indicating that the fast process does not follow first order kinetics) the trend with respect to surface coverage was very similar for all the larger dicarboxylic acids. This suggests that the overall rate characteristics of the larger dicarboxylic acids (i.e. excluding oxalic acid) are not overly influenced by their specific chemical structures. Rather, the similar rate characteristics (for the larger dicarboxylic acids) are due to the fact that the same amounts of charge (the amount adsorbed) for different dicarboxylic acids should have same equivalent adsorbate concentrations or same “photohole demand” (NB: “photohole demand” refers to the number of photoholes needed for the mineralisation of the organic compounds), but have different number of adsorbed molecules. Given that different dicarboxylic acids have similar adsorption behaviour and the main difference between the
larger dicarboxylic acids and oxalic acid lies in the number of degradative steps and intermediates formed during photocatalytic mineralization, the differences in the photocurrent responses are most likely caused by accumulation of intermediates at the electrode surface. Compounding the problem is the fact that there are more complex photohole demand characteristics for the larger dicarboxylic acids compared with the relatively simple (two per molecule) photohole demand characteristics for oxalic acid, causing less even distribution of photohole demand over the electrode surface. This may actually lead to a higher photohole/photoelectron recombination rate as adsorbed intermediates can act as photohole/photoelectron recombination centres. This latter argument is further justified by the fact that at higher light intensities (and therefore higher photohole concentrations) the fast kinetic process for the larger dicarboxylic acids is less influenced by surface coverage – thus bringing it closer to the oxalic acid case.

![Graph](image)

**Figure 4.18** A plot of rate constants for the fast kinetic process ($k_f$) (calculated from the curve fitting data) versus surface coverage ($Q_f$) for the different dicarboxylic acids preadsorbed from different concentrations of acids at pH 4.0, (○) oxalic acid, (●) malonic acid, (□) succinic acid, (■) glutaric acid.

Examination of the slow kinetic process was also carried out for the larger dicarboxylic acids. Figure 4.19 shows a plot of $I_{phs}^d$ values versus $Q_s$ values for the different
dicarboxylic acids. As in Figure 4.16 (and predicted by equation 4.10) a linear relationship was observed between $I_{phs}^0$ and $Q_s$. Importantly, the slopes of these relationships were the same for all of the dicarboxylic acids (including oxalic acid). This indicated that, for the slow process (associated with destruction of the intermediate and weakly bound surface complexes) there appears to be no discernible differences in the photocatalytic responses due to the differing chemical nature of each adsorbate. In other words the photohole concentration (at this light intensity) was sufficient to keep up with the photohole demand of the slow process for all adsorbates.

![Graph](image)

**Figure 4.19** A plot of $I_{phs}^0$ values versus $Q_s$ values for the dicarboxylic acids preadsorbed from different concentrations of acids at pH 4.0. (○) oxalic acid, (●) malonic acid, (□) succinic acid, (■) glutaric acid.

This assertion was further supported by the data in Figure 4.20, which shows the plot of $k_s$ versus $Q_s$ for all the dicarboxylic acids. The data indicate that the reaction rate constant for the slow process ($k_s$) remained essentially constant with increasing surface coverage ($Q_s$). At low surface coverage values, there is a noticeable spread of $k_s$ values for the different adsorbates. This was probably due to the error involved in measuring (and curve fitting)
the photoelectrochemical responses from the small amounts of adsorbed species (relative to the H$_2$O background). At higher surface coverage values, the $k_s$ values became more constant (i.e. $\sim 0.10\text{s}^{-1}$) and seem to be independent of the chemical nature of the dicarboxylic acid.

![Figure 4.20](image)

**Figure 4.20** The plot of $k_s$ versus $Q_s$ for all the dicarboxylic acids preadsorbed from different concentrations of acids at pH 4.0. (○) oxalic acid, (●) malonic acid, (□) succinic acid, (■) glutaric acid.

The above results indicate that in general, the overall photocatalytic response for the mineralisation of adsorbed dicarboxylic acids can be attributed to a fast kinetic component and a slow kinetic component. The effect of chemical identity/nature of the dicarboxylic acids on the slow kinetic process (associated with intermediate and weakly bound surface complexes) is less significant. Nevertheless, the effect of chemical identity/nature of the dicarboxylic acids on the fast kinetic process (associated with strongly bound surfaces complexes) is significantly different for the simple dicarboxylic acid (i.e. oxalic acid) and the larger compounds. This was due to the different photohole demand characteristics of the different compounds and the concentration of available photoholes (at the light
intensity used). For larger compounds, a high photohole demand per molecule is often the case, which means the available photoholes at the electrode surface are not sufficient for quick and complete mineralising the larger compounds (and corresponding intermediates), while for small compounds, due to the low photohole demand per molecule, the available photoholes at the electrode surface are often sufficient for quick and complete mineralising the smaller/simpler compounds such as oxalic acid.

The photocatalytic degradation kinetics of adsorbed organic compounds at electrodes calcined at 700°C for 16h have also been investigated. Similar photocurrent decay profiles were obtained. For oxalic acid the photocatalytic degradation of its adsorbed forms follows surface reaction model mentioned above in that the initial reaction rate of each adsorbed species is directly proportional to its surface concentration and the reaction constants (photocurrent decay constants) are independent of the surface coverage. For more complicated organic compounds, although the photocurrent decay of their adsorbed forms can be fitted to double exponent expression, the parameters obtained do not strictly agree with the first order surface reaction model. Similar to the above arguments long-lived adsorbed intermediates that are not able to be destroyed quickly may be responsible for this.

Distinct differences in the photocatalytic degradation kinetics of adsorbed organic compounds between electrodes calcined at 500°C for 0.5h and electrodes calcined at 700°C for 16h are: (1) For the photocatalytic oxidation of adsorbed organic compounds the fast process portion account for majority of the total charge for electrodes calcined at 700°C for 16hrs, while for electrodes calcined at 500°C for 0.5h the slow process portion accounts for the majority of the total charge. (2) For the photocatalytic degradation of adsorbed dicarboxylic acids other than oxalic acid the initial rate of the fast process always increases with total charge (adsorption amount) for electrode calcined at 700°C though it does not increase linearly, while the initial rate of the fast process disappears at
high surface coverage with electrodes calcined at 500°C for 0.5h. (3) The reaction constant of the fast process varies less dramatically with adsorption amount at electrodes calcined at 700°C for 16h than at electrodes calcined at 500°C for 0.5h. (4) For the photocatalytic degradation of the adsorbed aromatic organic compounds the decay is smoother and shows less sign of deactivation at high adsorption amount with electrodes calcined at 700°C for 16h than with electrodes calcined at 500°C for 0.5h. All these can be explained by the increase in lifetime of photoelectrons and photoholes in electrodes calcined at 700°C for 16h. The increase in lifetime of photoelectrons and photoholes due to the coexistence of anatase and rutile in electrodes calcined at 700°C for 16h determines that the intermediates are less likely to facilitate the recombination of photoholes and photoelectrons

4.4 CONCLUSION

In this chapter, the photocatalytic degradation of a group of strong adsorbates at both low and high temperatures calcined electrodes has been studied by both steady state and transient photoelectrochemical methods.

Similar to the photocatalytic degradation of weak adsorbates (methanol and glucose), the photocatalytic degradation kinetics of strong adsorbate at TiO$_2$ porous film electrodes rely on two basic processes, the electron transport in the film and photohole (or trapped photohole) capture by organic adsorbates. At low potential bias the former determines the overall response. As the potential increases the control step changes from electron transport process in the film to photohole capture process by organic compounds at the surface. At +0.3V potential bias and high substrate concentration, the pH and light intensity effect on the photohole capture rate have been investigated by steady state photoelectrochemical method. Regardless of the differences in the nature of the electrodes and the nature of the organic compounds, the photohole capture rate always increases.
linearly with light intensity. The magnitude of the rate, however, is greatly dependent on
the chemical nature of the strong adsorbates for low temperature calcined electrodes. In
contrast, at high temperature calcined electrodes, the magnitude of the rate is less sensitive
to the chemical nature of the strong adsorbates. As for the pH effect, at low temperature
calcined electrodes, the photohole capture rate for most strong adsorbates is rather
insensitive to the change in pH across a large pH range (2-10), although the adsorption
amount of these adsorbates changes with pH in this range. The magnitude of the rate is
highly dependent on the chemical nature of the adsorbates. At high temperature calcined
electrodes, the rate is also insensitive to the change in pH in the corresponding pH range.
The major difference is that the magnitude of the rate is also insensitive the chemical
nature of the adsorbates. At high pH, at both kinds of electrodes, due to negative charge
of TiO$_2$ surface, the photohole capture rate is greatly influenced according to the nature of
the electrostatic interaction between the charged surface and adsorbates.

A new method of quantifying the adsorption of organic adsorbates on TiO$_2$ has been
developed based on photoelectrochemical degradation principles. The adsorption
thermodynamics of the selected organic compounds has been investigated. For different
adsorbates investigated at the same type of electrode and different temperature calcined
electrodes their adsorption behaviours are very similar. At least three surface bound
complexes have been identified resulting from the heterogeneity of the TiO$_2$ surface. It
was also found that the adsorption of carboxylic acids changes significantly with pH due
to the speciation of both the adsorbates and the surface groups on TiO$_2$ surface, and the
adsorption of carboxylic acids is specific adsorption and electrostatic interaction plays an
important role. No correlation between their adsorption parameters and their photohole
capture rate in bulk solution has been found.
The photocatalytic degradation kinetics of adsorbed organic compounds has been investigated by analysing the photocurrent decay profiles of the adsorbed organic compounds. Mostly the photocurrent decay of the adsorbed organic compounds is composed of two processes both of which decay exponentially. These two processes are attributed to the reactivity difference of two different binding sites on TiO$_2$. For simple organic adsorbates such as oxalic acid the photocatalytic degradation kinetic follows a two-process first order surface reaction model. While for more complicated organic compounds, photocatalytic degradation of their adsorbed forms does not follow this model as is indicated by the distortion of fast process at high adsorption coverage. It was found that the chemical nature of intermediates of complicated organic compounds during their mineralisation as well as the differences in photohole demand for different adsorbates are responsible for the distortion of the fast process. In particular the intermediates from degradation of aromatic compounds may facilitate the recombination of photoelectrons and photoholes. For organic compounds involving many intermediates during their photodegradation the first step, the adsorption step, usually is not the rate-controlling step when surface coverage is high as is indicated by the non-correlation between photocatalytic reaction rates and adsorption amount.

At electrodes calcined at 700°C for 16hrs the photocatalytic degradation of adsorbed organic compounds is qualitatively similar to at electrodes calcined at 500°C for 0.5hrs. The most distinct difference is that at former electrodes the fast process is less sensitive (or less influenced by) the chemical identity of the organic adsorbates and their photohole demand characteristics.

Overall, at high temperature calcined electrodes, the insensitivity of photohole capture rate observed in both steady state and transient photoelectrochemical degradation experiments cab be attributed to the nature of the electrodes. This is the ability to resist the poisonous
effects of larger intermediates to the photohole capture process. This is in agreement with the assertion made in Chapter 2 that the coexistence of rutile phase and anatase phase in the high temperature calcined electrodes prolong the lifetime of photoelectrons and photoholes.
CHAPTER 5  COMPARISON OF PHOTOCATALYTIC DEGRADATION CHARACTERISTICS OF DIFFERENT ORGANIC COMPOUNDS AT LOW TEMPERATURE CALCINED TiO$_2$ NANOPOROUS FILM ELECTRODES
5.1 INTRODUCTION

In Chapters 3 and 4, a set of photoelectrochemical techniques has been developed for characterising the photocatalytic degradation of both weak and strong adsorbates at the particulate TiO$_2$ film electrodes. Other than the useful kinetic and thermodynamic information obtained from these studies, more importantly, the photoelectrochemical techniques employed for these studies have been proven to be unique and effective for the study of the semiconductor photocatalytic systems.

In this chapter, I adopted these techniques to characterise the photocatalytic behaviour of a range of different organic compounds of different chemical structures at low temperature calcined electrodes (500°C). Particular attention was paid to investigate the photocatalytic kinetic characteristics of different organic compounds in bulk solution by steady state photoelectrochemical method and to the comparison of these kinetic characteristics for different organic compounds. With the steady state photoelectrochemical method, the advantages of the rapidity, simplicity and effectiveness in acquiring kinetic data make possible to systematically study the photocatalytic degradation kinetics of large number organic compounds under the same conditions. Since the steady state photocurrent directly represents the photohole capture rate at electrode surfaces, therefore the kinetic data obtained from these steady state photoelectrochemical methods can be bestowed with clearly defined physical meaning. This is extremely important for interpretation of kinetic data and for gaining the meaningful information.

The study in this chapter aims to establish a strategy that kinetic characteristics of different organic compounds can be compared under the same experimental conditions, which enables the correlation of kinetic characteristics of different organic compounds to their chemical nature. It is envisaged that the strategy established here would be useful for systematic evaluation of a semiconductor photocatalysis system and more importantly
offer a guideline for the preparation of photocatalysts of high and universal activity. This is important and needs to be addressed because to date, most of published research articles in this field focused on the study of photocatalytic properties of one or one type of organic compounds\textsuperscript{57, 154, 162, 232}. The photocatalytic properties of different compounds may have been studied, but often under different conditions or by different methods\textsuperscript{166, 233}. From the studies in previous chapters and studies in slurry systems\textsuperscript{3, 58, 94, 164} it is known that different organic compounds exhibit different photocatalytic kinetic characteristics at a given electrode or photocatalyst, and a given organic compound exhibits different photocatalytic degradation kinetic characteristic at different electrodes or photocatalysts. Therefore, it is necessary to compare the degradation kinetic characteristics of different organic compounds at a given electrode or photocatalyst and compare these kinetic characteristics at different electrodes or photocatalysts under the same experimental conditions. Unfortunately, no such studies have ever been reported mainly due to the lack of suitable study methods.

Findings from Chapter 2 indicate that electrodes calcined at different temperatures had different crystalline structures and exhibited different photocatalytic activities toward degradation of different organic compounds. This chapter focuses on the systematic comparison of degradation characteristics of different organic compounds at the low temperature calcined electrodes. The systematic comparison of degradation characteristics of different organic compounds at the high temperature calcined electrodes will be carried out in Chapter 6.

The organic compounds selected for the study have different chemical structures and different adsorption properties. Chemical structure ranges from aliphatic to aromatic, from hydroxyl to carboxylic and from very simple to more complicated. The adsorption property ranges from weak adsorbates to strong adsorbates. While comparing their
degradation kinetic characteristics of different organic compounds, their differences in structure and adsorption property will also be incorporated in the discussion.

5.2 EXPERIMENTAL

5.2.1 Material and Chemicals

Indium Tin Oxide (ITO) conducting glass sheets (8-10Ω/square, Delta Technologies Limited) were used as substrate for TiO$_2$ film coating. Potassium hydrogen phthalate (AR, Aldrich), formic acid (AR, Aldrich), oxalic acid (AR, Ajax Chemicals), succinic acid (99%, Sigma), malonic acid (Sigmaultra, Sigma), methanol (99.8%, BDH), D-Glucose (99%, BDH), salicylic acid (AR, Aldrich) and glutaric acid (99%, Sigma) were used as received. Other chemicals used were of analytical grade and purchased from Sigma-Aldrich unless otherwise stated. All solutions were prepared using high purity deionised water (Millipore Corp., 18MΩcm).

5.2.2 Preparation of the Nanoporous TiO$_2$ Film Electrodes

The TiO$_2$ colloid synthesis and immobilisation procedures are the same as described in Section 2.2.2. The electrodes used in this study were calcined at 500°C for 0.5h (denoted as 5d). The thickness of the film was ca. 1µm.

5.2.3 Apparatus and Methods

The apparatus and experimental set-up are the same as described in Section 2.2.3 for photoelectrochemical measurements. The light intensity changes were made through altering the relative position of the electrolytic cell to the light source, and light intensity was measured with an UV-irradiance meter (UV-A, Instruments of Beijing Normal University). The pH values of solutions were adjusted with nitric acid and sodium hydroxide solutions. The pH values of solutions were measured and monitored with a pH electrode.
5.3 RESULTS AND DISCUSSION

5.3.1 Effect of Potential Bias

Linear sweep voltammograms at a 5d-electrode were recorded in different organic compound solutions under the illumination of same light intensity. Similar voltammograms to those shown in Figure 3.1 for glucose and Figure 4.1 for potassium hydrogen phthalate were obtained for all organic compounds investigated in this chapter. General features are summarised as follows:

(1) In all the cases, at low potential bias, the photocurrents increase linearly with potential bias. The transport of freed electrons in the film under electric field is responsible for this. The slopes of the linear photocurrent increase with respect to potential bias are determined by the saturation photocurrent (or the interfacial photohole capture rate). A typical case, for glucose, was discussed in Chapter 2.

(2) At higher potential bias, the photocurrent tends to saturate. The magnitude of the saturation photocurrent depends on the concentration of organic compounds and their chemical identities. As is discussed in previous chapters, the saturation in photocurrent is due to the limitation in photohole capture process at TiO$_2$ surface. Therefore, under the illumination of same light intensity the difference in saturation photocurrent is caused by the availability of organic compounds at electrode surface and the photohole capture ability of different organic compounds.

5.3.2 Effect of pH

The effect of pH on the steady state photocurrent ($I_{sph}$) for different organic compounds was investigated under conditions where both the electron transport inside of the semiconductor film and the available substrate at the electrode surface were not rate
limiting steps in the overall photocatalytic process. The solution pH influences the speciation of both the TiO$_2$ surface groups and organic substrates in a solution, as a result, the solution pH will influence the availability and adsorption of organic compounds at TiO$_2$ surface.

Weak adsorbates such as methanol and glucose possess the same pH dependence characteristics as discussed in Chapter 3 for glucose. The solution pH does not influence their availability and adsorption across a large pH range (2-10). The $I_{sphare}$ obtained was virtually unchanged in the pH range from pH 2 to pH 10, implying the photocatalytic oxidation rate was therefore not affected by solution pH. Above pH 10, the sharp increase in negative charge at the electrode surface benefits the trap of photoholes and increases the lifetime of photoelectrons and photoholes, which leads to an increase in the $I_{sphare}$.

For strong adsorbates such as carboxylic acids, the solution pH affects their species distributions and the interactions between these species and electrode surface. As a result, their availability and adsorption at electrode surface are affected. The photocatalytic oxidation rate should change accordingly as expected by the first order reaction law. In all the cases at pH above 10, the carboxylic acids exist in negatively charged carboxylate ions in solution, a considerably negative charged electrode surface at the same pH range greatly lowers the availability of carboxylate ions at electrode surface due to the electrostatic repulsion. As a result, the $I_{sphare}$ drops significantly or the photocatlytic oxidation rate decreases significantly. In the pH range from 2 to 10, as shown in Figure 4.12, the charged TiO$_2$ surface groups account for small portion of the surface groups, therefore, the influence of the electrostatic interaction on carboxylic acid availability at the electrode surface is not significant. However, for all the carboxylic acids the adsorption amount varies significantly with pH in this pH range. Interestingly, despite the significant changes in adsorption amounts in the pH range of 2-10 for all carboxylic acids, the
changes in the corresponding $I_{sph}$ are not as significant, and in some cases, the changes in $I_{sph}$ are insignificant. The degree of correlation of $I_{sph}$ dependence on pH with the adsorption amount dependence on pH is found depending on the chemical structure of strong adsorbates and photohole demand characteristics of the adsorbates.

For simple carboxylic acid such as formic acid and oxalic acid involving the least number of intermediates and least electrons transferred during their complete mineralization, the saturation photocurrents vary with solution pH in correspondence with their adsorption amount variation, but not in a proportional manner. For more complicated organic compounds such as dicarboxylic acids involving more steps and intermediates during their mineralisation, the $I_{sph}$ obtained changes slightly with pH, which is in contrast to the significant pH effect on the adsorption amount. When it comes to aromatic strong adsorbates such as phthalic acid and salicylic acid, the $I_{sph}$ remains virtually unchanged in the pH range (2-10) in contrast to the significant variation of adsorption amounts with pH.

The degree of correlation of $I_{sph}$ dependence on pH with adsorption amount dependence on pH reflects the degree of the role of adsorption in the overall photocatalytic degradation process. The above trend in the degree of the correlation for different adsorbates implies that chemical structure and photohole demand characteristics of adsorbates greatly influence the degree of the role of adsorption played in the overall photocatalytic process.

### 5.3.3 Effect of Light Intensity

All compounds investigated, including both weak and strong adsorbates, possess the same characteristics as described in Chapters 3 and 4.

At high substrate concentration where the availability of substrate at electrode surface is not the rate-limiting step, regardless of the chemical identities of the compounds, even in
blank electrolyte solution, the saturation photocurrent always linearly increases with the light intensity. In contrast, at potentials where photocurrent is saturated, the photocurrent increases nonlinearly with light intensity \(^8\). The extension of this finding to all organic compounds studied confirms my argument that the potential bias plays an important role in minimizing the build-up of freed photoelectrons and suppressing the recombination of photoelectrons and photoholes. This further justifies my argument that in slurry system the nonlinear increase in photocatalytic degradation rate of organic compounds is most likely caused by the sluggishness of photoelectron removal by oxygen, which causes the build-up of freed photoelectrons, as a consequence, causing the increased recombination of photoelectrons and photoholes as light intensity increases.

The acquisition of the linear relationship between saturation photocurrent and light intensity for all compounds, regardless of chemical structures and photohole demand characteristics, indicates that in all cases, the photohole capture reaction is a first order reaction with respect to photohole concentration at semiconductor surface. For a given compounds, the linear relationship indicates that the percentage of charge carrier loss due to recombination does not change with light intensity. An implication of the charge recombination behaviour may be that the removal of electrons freed through the capture of photoholes by organic compounds is efficient under higher potential bias (at potentials photocurrent is saturated), otherwise the recombination of charge carriers would not be proportional to the light intensity. The difference in \(I_{sph}\) for different organic compounds at the same light intensity is very significant. This suggests that the photohole capture rates by different organic compounds are significantly different and the photohole/photoelectron recombination rates are significantly different.
5.3.4 Effect of concentration

The effect of concentration of various organic compounds on the photocurrent was investigated. The saturation (or steady state) photocurrent \(I_{sph}\) was measured for each organic compound at different concentrations. The potential bias applied was +0.30V vs Ag/AgCl. As described before, the steady state photocurrent obtained under such conditions reflects the kinetics of photohole removal processes at the electrode/solution interface. Figures 5.1 to 5.3 show the relationships between the saturation photocurrent, \(I_{sph}\) and the molar concentration, \(C\) for different organic compounds (methanol, glucose, formic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, phthalic acid and salicylic acid) under the same experimental conditions.

Figure 5.1 shows the \(I_{sph}-C\) curves obtained for the oxidation of methanol and glucose. This category of organic compounds contains mainly hydroxyl functional groups and is known to be weakly adsorbed to TiO\(_2\) surface\(^8, 83, 234\). The results showed that the saturation photocurrent increased monotonically with substrate concentration. Detailed examination of the curves revealed that the \(I_{sph}\) increased linearly with concentration up to 0.5 mM. The linear responses obtained indicate the overall photocatalytic reaction was under diffusion-limiting conditions. When the concentration was further increased, the \(I_{sph}\) deviated from the linear response. This is due to the fact that diffusion no longer controls the overall process. After diffusion control stage, the monotonic increase of \(I_{sph}\) with substrate concentration suggests that the interaction of these compounds (or their partial degraded intermediates) with TiO\(_2\) surface do not inhibit the photohole capture process and the increase in amount of these compounds in the reaction layer facilitates the photohole capture process. The weak interaction of these compounds and their partial degraded intermediates with TiO\(_2\) surface is responsible for the behaviour. This probably
is the common characteristic of photocatalytic degradation kinetics for the weakly adsorbed and easily broken compounds.

![Graph showing photocurrent (Iph) versus concentration (C) for glucose and methanol.](image)

**Figure 5.1** The plot of $I_{ph}$ versus $C$ for glucose (○) and methanol (■), photocurrent were obtained in 0.1M NaNO$_3$ solution at pH 4.0 under 0.30V potential bias.

Figure 5.2 shows the $I_{ph}$-$C$ relationships for a group of simple aliphatic acids including formic acid, oxalic acid, malonic acid, succinic acid and glutaric acid, which have one or two carboxyl functional groups. These acids are known to be strong adsorbates at TiO$_2$ surface$^{225, 235, 236}$. It can be seen that for this group of compounds, the characteristics of the $I_{ph}$-$C$ curves differ markedly from those shown in Figure 5.1. It can be also seen that the characteristics of the $I_{ph}$-$C$ curves are also different even among the same group of compounds.
Figure 5.2 The plot of $I_{\text{sph}}$ versus $C$ for formic acid and a few dicarboxylic acids, photocurrent were obtained in 0.1M NaNO$_3$ solution at pH 4.0 under 0.30V potential bias, (a) shows the plot in the whole concentration range, (b) shows the plot in low concentration range.

Complete mineralization of the simplest aliphatic acids such as formic acid and oxalic acid involve the least number of electrons (i.e. 2e$^-$), the least number of steps and the least number of intermediates. The $I_{\text{sph}}$-$C$ curves obtained from these simple acids exhibited characteristics of a multi-wave shape, which is different to all other compounds investigated. The $I_{\text{sph}}$ increased linearly in very low concentration range and then levelled-off at slightly higher concentrations. This was followed by a further increase in $I_{\text{sph}}$ at medium concentrations before levelling off again at high concentrations. The linear
increase in $I_{sph}$ at low concentrations is due to the substrate diffusion limitation and the subsequent plateaus and increase with concentration is very likely related to the interaction of TiO$_2$ surface and the substrates (or their intermediates). This is because under diffusion control there is little chance for organic compounds or their partial degraded intermediates to accumulate at the electrode surface. Further discussion will be given in Section 5.3.6.

For larger aliphatic acids (malonic acid, succinic acid and glutaric acid) involving a larger number of electrons, more steps and more partial degraded intermediates during their complete mineralisation, $I_{sph}$ increased linearly at very low concentrations and then levelled off at slightly higher concentration (see Figure 5.2). A second wave of photocurrent increase and level off can still be observed for malonic acid but not for others. Interestingly, the magnitude of the first plateau $I_{sph}$ obtained at medium concentrations increased from oxalic acid to glutaric acid. Further explanation will be given in Section 5.3.6.

Figure 5.3 shows the photooxidation of aromatic compounds. Two model compounds selected for this study are phthalic acid and salicylic acid both having two functional groups and are known to be strongly adsorbed to TiO$_2$ surface$^{86, 225}$. The characteristics of $I_{sph}$-$C$ curves for the organic compounds of this category were found to be different to all above compounds investigated. It is apparent that the $I_{sph}$ linearly increased at very low concentration and then decreased (instead of levelling off) as the concentration increased. Furthermore, the concentration range in which this occurred was much lower than for other compounds.
Figure 5.3 The plot of $I_{sph}$ versus $C$ for phthalic acid and salicylic acid, photocurrent were obtained in 0.1M NaNO₃ solution at pH 4.0 under 0.30V potential bias.

5.3.5 $I_{sph}$-C eq Relationships

The magnitude of $I_{sph}$ is determined by a number of factors including the rate of photohole/photoelectron generation, and the rate of photohole capture by electron donors at the electron surface. For a given TiO₂ electrode at a given light intensity the former is fixed. The latter, however, is influenced by the availability of electron donors at the electrode surface and the interaction between TiO₂ surface and the electron donors. Without any doubt, under sufficient potential bias, the difference in the magnitude of $I_{sph}$ results from the competition between the rate of photoelectron/photohole recombination process and the rate of the photohole capture process. For a given TiO₂ electrode, the intrinsic characteristics of the semiconductor for photoelectron/photohole recombination are fixed. Only through the photohole capture reaction by organic compounds at the electrode surface can the rate of photoelectron/photohole recombination be further regulated. The value of $I_{sph}$ solely reflects the rate of photohole capture at TiO₂ interface that is determined by the availability of organic compounds at TiO₂ surface, their
interaction with TiO$_2$ surface, the nature of their intermediates and the molecular steric suitability of adsorbed form of organic compounds to capture photoholes.

As presented in the above section, for all the compounds in low molar concentration range the $I_{sp}$ increases linearly with molar concentration due to the mass transfer limitation. For the organic compounds investigated above, the number of electrons required for complete mineralization of these compounds varies from 2$e^-$ to 30$e^-$, and the number of steps and intermediates involved in these catalytic processes differ greatly from one to another. Clearly the linear increase of $I_{sp}$ with molar concentration indicates the availability of electron donors at electrode surface is a control factor in the overall photocatalytic oxidation process. A question raised is whether under such conditions different organic compounds reaching the electrode surface are completely mineralized. In this section this issue is firstly addressed.

When organic compounds are completely mineralized, at the electrode their oxidation can be represented by a common oxidation reaction equation as below:

$$C_yH_mO_jN_kX_q+(2y-j)H_2O \rightarrow yCO_2+qX^-+kNH_3+(4y-2j+m-3k)H^++(4y-2j+m-3k-q)e^- \quad (5.1)$$

where $N$ and $X$ represent a nitrogen and a halogen atom respectively. The numbers of carbon, hydrogen, oxygen, nitrogen and halogen atoms in the organic compound are represented by $y$, $m$, $j$, $k$ and $q$. The number of electrons can be calculated by:

$$n=4y-2j+m-3k-q \quad (5.2)$$

The number of electrons transferred for different organic compounds to be mineralized is summarized in Table 5.1.
Table 5.1  Electron transfer number for different organic compounds to be mineralised

<table>
<thead>
<tr>
<th>compounds</th>
<th>n</th>
<th>compounds</th>
<th>n</th>
<th>compounds</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>6</td>
<td>o,m,p-chlorophenol</td>
<td>26</td>
<td>Malonic acid</td>
<td>8</td>
</tr>
<tr>
<td>Glucose</td>
<td>24</td>
<td>Glycin</td>
<td>6</td>
<td>Succinic acid</td>
<td>14</td>
</tr>
<tr>
<td>Phthalic acid</td>
<td>30</td>
<td>Formic acid</td>
<td>2</td>
<td>Glutaric acid</td>
<td>20</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>8</td>
<td>Benzoic acid</td>
<td>30</td>
<td>phenylalanine</td>
<td>40</td>
</tr>
<tr>
<td>Catechol</td>
<td>26</td>
<td>hydroquinone</td>
<td>26</td>
<td>Glutamic acid</td>
<td>18</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>2</td>
<td>Salicylic acid</td>
<td>28</td>
<td>Phenol</td>
<td>28</td>
</tr>
</tbody>
</table>

According to the semiempirical treatment method of steady state mass transfer \(^{237}\), under the substrate diffusion the limiting photocurrent can be given by:

\[ I_{sph} = \frac{nFADC_sph}{\delta} \]  \hspace{1cm} (5.3)

where, \( n \) is to the number of electrons transferred for the complete mineralization of organic compounds, \( F \) is the Faraday constant, \( A \) is the surface area of the electrode, \( D \) and \( \delta \) refer to the diffusion coefficient of the substrate and the thickness of the effective diffusion layer respectively, and \( C \) is the bulk molar concentration of the organic compound. Under steady state, the thickness of the effective diffusion layer is a constant due to existence of natural convection and the similarity in viscosity of the solutions used.

If I define a new quantity, \( C_{eq} = nC \), then, Equation (5.3) predicts that under diffusion control if all substrate molecules reaching the electrode surface are stoichiometrically mineralised a linear \( I_{sph}C_{eq} \) relationship with a slope of \( FDA/\delta \) would be held for all substrates. For convenience, I define an arbitrary flux index as \( Flux^{in} = ADC_{eq} = nADC \), Equation (5.3) can therefore be written as:

\[ I_{sph} = \frac{F \times Flux^{in}}{\delta} = k Flux^{in} \]  \hspace{1cm} (5.4)
Under diffusion controlled conditions, if I assume that $\delta$ is same for all compounds under different $\text{Flux}^{in}$ and the reaction takes place stoichiometrically, then for a given electrode $k = F/\delta$ is a constant regardless of chemical identities of the substrates involved. Under these conditions, Equation (5.4) predicts a linear relationship between the $I_{phs}$ and $\text{Flux}^{in}$, and the slope, $k$, should be same for all compounds.

The diffusion coefficients of most organic compounds in 0.1M NaNO₃ are not available. But for the dicarboxylic acid series their diffusion coefficients in water at pH 4.0 are available\textsuperscript{238}, as is shown in Table 5.2.

<table>
<thead>
<tr>
<th>Organic compounds</th>
<th>Hydrogen oxalate</th>
<th>Hydrogen malonate</th>
<th>Hydrogen succinate</th>
<th>Hydrogen glutarate</th>
</tr>
</thead>
<tbody>
<tr>
<td>D ($10^{-5}$ cm$^2$/s)</td>
<td>0.987</td>
<td>0.845</td>
<td>0.783</td>
<td>0.7</td>
</tr>
</tbody>
</table>

To demonstrate that at low concentration range the photocatalytic reaction is controlled by diffusion step and under such conditions organic compounds can be stoichiometrically mineralised, the $\text{Flux}^{in}$ is obtained by multiplying the equivalent concentration with their diffusion coefficients and apparent area. Figure 5.4 shows the $I_{phs}$-$\text{Flux}^{in}$ relationships of four different compounds whose diffusion coefficients are available. At low effective equivalent flux, all compounds investigated can be fitted into a linear equation, $I_{ph} = 0.00373 \text{Flux}^{in} + 0.0193$ (mA), with $R^2$ of 0.995. This confirms that all compounds under diffusion-controlled conditions were stoichiometrically mineralised regardless of their chemical nature.
For most of the organic compounds, since their diffusion coefficients are not available, their steady state photocurrents are plotted against equivalent concentrations. Figure 5.5 shows the dependence of $I_{sp}$ on $C_{eq}$ for different compounds. It was found that within the very low $C_{eq}$ range, the $I_{sp}$ values obtained from different compounds increased linearly. More importantly, almost identical slope values can be obtained from all $I_{sp}$-$C_{eq}$ curves. The small variation in the slope values is due to the difference in the diffusion coefficients for different organic compounds. Such results can be obtained only when the real electron transfer number during the photocatalytic process is identical to the theoretical electron number required for complete mineralization. In other words, these results indicate that under such diffusion control conditions all compounds have been stoichiometrically mineralized and the chemical identities of the organic compounds are not a decisive factor in the overall photocatalytic oxidation kinetics. These results also suggest that under diffusion control conditions, all reaction intermediates are consumed before they are able to diffuse away from the electrode surface.

**Figure 5.4** The saturation photocurrent/equivalent flux relationships for different dicarboxylic acids.
Figure 5.5 The relationship between the steady photocurrent and equivalent concentration of different organic compounds in low concentration range, the experimental conditions are the same as in Figure 5.1, 5.2 and 5.3.

5.3.6 Further discussion

From the above discussion, under diffusion control conditions, regardless of the chemical nature of the compounds, all the organic molecules reaching the electrode surface are completely mineralised. The deviation of $I_{sph}$ from linear response at higher concentrations indicates that molecules reaching the electrode surface are not completely mineralised, which means that the supply of organic material at TiO$_2$ surface is not the controlling step. As is shown in the previous section for some compounds at high concentrations, high $I_{sph}$ values were obtained. This suggests that supply of photoholes is not the limiting factor either in the medium concentration range. Only explanation is that under such circumstances even though both photoholes and organic compounds are available, the photohole capture process is as efficient as under ideal conditions where there is no photohole/photoelectron recombination. This point becomes clearer in next
chapter where a high temperature calcined electrode is used in the similar study. It also
can be seen from Figures 5.4 and 5.5 that the linear ranges obtained are dependent on the
chemical nature of the compounds. Therefore, it can be concluded that the deviation of
\( I_{sph}-C \) from linearity and the differences in the linear ranges for different compounds result
from differences in the interaction between TiO\(_2\) surface and different compounds. In
addition, differences in the nature of their intermediates and differences in the molecular
steric orientation suitability of adsorbed forms to capture photoholes also contribute to the
deviation from linearity.

Glucose and methanol are not chemically adsorbed on the TiO\(_2\) electrode surface. Their
photocatalytic oxidation is not via a direct photohole transfer mechanism of the inner-
sphere surface complexes on TiO\(_2\) surface but via the heterogeneous reaction between the
surface bound hydroxyl radicals or surface bound holes and the outer sphere complexes.
The photocurrent concentration relationships deviate from linearity as concentration
increases, which is an indication of non-exhaustive mineralization of these reactants
reaching the reaction layer. However, the photocurrent increases monotonically with their
concentrations, which indicates the intermediates do not poison the electrode and the
electrode surface is fairly uniform to these molecules in the whole concentration range (an
evidence is that the reaction rate (or \( I_{sph}\)) follow Langmuir-Hinshelwood rate law). This
probably is the evidence of indirect photocatalytic oxidation via surface bound hydroxyl
radical or charge transfer via outer-sphere complexes. Once their molecules are within the
reaction layer, they get chance to react with surface bound holes or hydroxyl radicals. The
higher the substrate concentration in the bulk solution the more surface bound holes or
surface bound free radicals are captured, as a result, more photoelectrons are freed and the
less recombination occurs. It is also noted that the values of \( I_{sph}\) for glucose at medium
molar concentrations are higher than those for methanol while at high molar
cconcentrations this order is reversed. The differences in their molecular sizes, their
affinities to TiO$_2$ surface and their current doubling effects (radical intermediates inject electrons into conduction band of semiconductor as a result one photon can give out current equivalent to two electrons withdrawn) of their partial degraded intermediates are responsible for this.

Another group of organic compounds studied here are simple aliphatic carboxylic acid and aliphatic dicarboxylic acids. They are chemically adsorbed to TiO$_2$ surface forming surface complexes. Kinetically they exhibit different photocatalytic behaviour from the non-chemically adsorbed methanol and glucose, and the chemically adsorbed aromatic compounds. For the simplest acids such as oxalic acid and formic acid involving the least number of electron transfer and the least number of steps during their mineralization, the $I_{spk}$-$C$ curves (or relationship of photohole capturing rates with concentration) exhibit multiple wave characteristics. As presented in Chapter 4, the adsorption of such organic compounds at TiO$_2$ surface is not uniform due to the heterogeneity of TiO$_2$ surface. At least three types of surface complexes formed, which are the strongest, medium strength and weakest surface bound complexes were identified. The strongest bound complex is formed at very low concentrations and accounts for a very small fraction of the total adsorbed amount. The strongest surface bound complex can be attributed to adsorption at surface sites such as surface titanium ions at the crystal edges and corners. The medium strength surface bound complex is responsible for Langmuir behaviour in the medium concentration range and this type of complex accounts for the vast majority of the total adsorption. The weakest bound complex formed at high concentrations accounts for a small portion of the total adsorption quantity. Surface sites such as titanium ions from the most stable, perfectly cleaved (001) and (011) crystal faces of anatase, which are penta-coordinated to O$^{2-}$ ions and complete their coordination sphere by binding OH$^-$, are responsible for the latter two types of surface complexes. The multiple wave characteristics of $I_{spk}$-$C$ are probably related to the heterogeneous adsorption
characteristics of TiO₂ surface. For oxalic acid the first phase of increase in $I_{sph}$ with concentration is probably related to the photocatalytic oxidation of the strongest surface bound complex and the second phase of increase in $I_{sph}$ is from the contribution of both strongest and weakest surface complexes. This assignment is based on the appearance of the $I_{sph}$-$C$ waves in concentration scale (shown in Figure 5.2) and the appearance of different adsorption characteristics in concentration scale (shown in Figure 4 11). The medium strength surface bound complex, the majority form of adsorption, has little contribution to the capture of photoholes, as is evidenced by the $I_{sph}$ levelling-off in corresponding concentration range. Similar arguments were reported by Regazzoni for the photocatalytic oxidation of salicylic acid in a slurry system. In Chapter 4, I found the photocatalytic degradation rate constant for adsorbates adsorbed at these different types of sites can be different by ca. 6 times. This supports the above arguments. For formic acid the characteristics of $I_{sph}$-$C_{eq}$ relationship are similar to those for oxalic acid. For formic acid, $I_{sph}$ at medium concentrations did not tend to saturate, instead, the $I_{sph}$ kept increasing. This suggests that unlike oxalic acid the medium strength surface bound complex for formic acid seems less inactive. Probably it is due to the smaller binding strength of its medium strength surface bound complex for formic acid compared with that for oxalic acid, which bring the case of formic acid closer to the case of weak adsorbates (glucose and methanol). The fact that glucose and methanol can react at both active sites (edge and corner titanium ions) and the most abundant sites (ordinary surface titanium ions) (as is evidenced by the monotonic increase of $I_{sph}$ with concentration) support this argument.

For larger dicarboxylic acids, similarly, the first phase of increase in $I_{sph}$-$C_{eq}$ relationships can be assigned to the photocatalytic oxidation of the corresponding strongest surface bound complexes. Only the second phase of increase in $I_{sph}$-$C_{eq}$ relationships at higher concentrations gradually disappears as the organic molecule becomes larger. This
suggests that both the medium strength surface bound complexes and the weakest surface complexes contribute little to the photocurrent response for the similar reason to the case of formic acid and formic acid. However unlike for aromatic compounds, for these compounds, their accumulations and the accumulation of their partial degraded intermediates at the electrode surface do not deteriorate the overall photocatalytic process. Similarly, that the major surface complexes (at the most abundant sites), accounting for major adsorbed amount, are not very photocatalytic active may be explained by the differences in reactivity between the edge, corner titanium sites and the ordinary titanium surface sites. In Chapter 4, I have found the photocatalytic degradation rate constant for adsorbates adsorbed at these different types of sites can be different by 6 times\textsuperscript{10}. It is due to the difference in reactivity that leads to the oxidation at the more active sites to be preferentially displayed. This finding explains why there were no correlation between photocatalytic rate and the amount adsorbed for strong adsorbates reported by some researchers\textsuperscript{74, 75}. Similar explanation was also proposed for the photocatalytic oxidation of salicylic acid in a TiO\textsubscript{2} slurry system\textsuperscript{86}. It is noted that from Figure 5.2 and 5.4, the magnitude of the $I_{sph}$ plateau of the first wave increases from small dicarboxylic acid to larger dicarboxylic acid. Based on the above assignment that the first wave of increase in $I_{sph}$ with substrate concentration is due to the photocatalytic oxidation at the more active sites on TiO\textsubscript{2} surface, the difference in $I_{sph}$ for the first level-off for different dicarboxylic acids can be easily explained. For a given electrode the number of this type of more active sites is fixed, so the maximum number of molecules that can access this type of sites is also fixed. From oxalic acid to glutaric acid, the number of molecules adsorbed at these active sites is roughly the same due to the similarity in functional groups and structure. Nevertheless, the number of photoholes consumed by these adsorbed molecules increases from oxalic acid to glutaric acid, resulting an increase in the magnitude of the first level-off $I_{sph}$. As seen from Figure 5.2, the approximately similar turning-point molar
concentration (i.e. the concentration where $I_{sph}-C$ curve turns from linearity) for the group of compounds supports the claim that the similar numbers of molecules are adsorbed at the active sites for the group of compounds.

Similarly, for aromatic compounds the increase in $I_{sph}$ at very low concentration can be attributed to the photocatalytic oxidation of the strongest surface complexes adsorbed at corner and edge titanium ions. The main differences from dicarboxylic acids are that this linear increase did not go as high as for others, instead, the photocurrent dropped as the concentration increased. This is most likely caused by accumulation of the intermediates rather than by the adsorption of the compounds. The intermediates can act as photohole and photoelectron recombination centres due to the special chemical structure of the intermediates (intermediates of benzene ring will keep the conjugate structure through a few stages of oxidation $^3$). Evidence for this includes the fact that the $I_{sph}-C$ relationship of phthalic acid at pH 10.0 is the same as that at pH 4.0, but at pH 10.0 there was little phthalic acid adsorption taking place. In addition, for non-specific aromatic adsorbates such as phenol similar $I_{sph}-C$ relationships were obtained. High local photohole demand for the destruction of benzene ring on TiO$_2$ surface will cause a longer dwelling time of intermediates. The accumulation of benzene ring intermediates can act as surface recombination centres, accelerating the recombination of photoholes and photoelectrons at such sites. In contrast to the case of larger dicarboxylic acids, the aromatic compounds can deactivate the more active sites more significantly. This is in agreement with my finding that the adsorbed aromatic compounds can distort the fast photocatalytic degradation process $^{10}$ as discussed in Chapter 4.

5.4 CONCLUSION

At TiO$_2$ nano-porous TiO$_2$ film electrodes calcined at 500°C for 0.5h, the photocatalytic degradation kinetics of a number of organic compounds of different chemical structure
have been investigated by photoelectrochemical techniques and the kinetic characteristics of different organic compounds have been compared. It has been shown that the steady state photoelectrochemical method is a rapid, direct and effective method for studying the photocatalytic degradation kinetics of large number of organic compounds under the same conditions. It has also been shown that the use of photocurrent to express photocatalytic reaction rate is more direct in quantifying the photocatalytic efficiency. The newly developed strategy for evaluation/comparison of kinetic characteristics of different organic compounds has been proven to be effective.

Application of electrode potential allows for studying photocatalytic oxidation of organic compounds without the influence electron transport inside the film and focusing on the kinetics of photohole capture of organic compounds.

Results demonstrated that under conditions of diffusion control at very low concentration, all the structurally different compounds investigated are stoichoimetrically oxidized to CO$_2$ without significant amounts of intermediates leaving the surface. However, the concentration ranges of diffusion control and the maximum photohole capture rates at high concentrations are significantly different for different organic compounds. This is caused by the differences in the chemical nature of different organic compounds. Based on the structural differences and the photohole demand characteristic differences of different organic compounds, explanations have been given to the differences in linear concentration ranges of diffusion control and the significant differences in their photohole capture rates at high concentration.

This study has offered a general guideline for the preparation of highly active photocatalysts for the degradation of organic compounds. An ideal photocatalyst should be able to photocatalytically degrade all kinds of organic compounds and operate under
diffusion control at any concentrations until the photohole capture rate reaches the limit of photohole generation.
CHAPTER 6  COMPARISON OF PHOTOCATALYTIC DEGRADATION CHARACTERISTICS OF DIFFERENT ORGANIC COMPOUNDS AT HIGH TEMPERATURE CALCINED TiO$_2$ NANOPOROUS FILM ELECTRODES
6.1 INTRODUCTION

In Chapter 5, the photocatalytic degradation characteristics of different organic compounds at low temperature calcined TiO$_2$ electrodes were investigated by a steady state photoelectrochemical method in bulk solution. This photoelectrochemical method has been demonstrated to be simple, rapid and effective in studying the photocatalytic degradation kinetics of different organic compounds in bulk solution. The findings from the low temperature calcined electrodes revealed that at low substrate concentrations, regardless of the difference in chemical nature of the compounds, the overall photocatalytic process is controlled by substrate diffusion and different organic compounds are stoichiometrically mineralized; the diffusion control concentration ranges and the maximum photohole capture rates, however, are markedly different for different compounds.

It has long been known that a photocatalyst having good photocatalytic reactivity towards certain organic compounds will not necessarily have good photocatalytic reactivity towards other organic compounds$^{2, 239}$. For most applications, indiscriminate photocatalytic degradation of a wide spectrum of organic compounds is required. Whether this can be achieved or not is determined by the photocatalytic activity of the photocatalyst$^{3, 59-61, 145, 240}$. It has been widely accepted that for a TiO$_2$ photocatalyst, the crystalline form is a decisive factor that affects the photocatalytic reactivity$^{66, 194, 241}$. The change in the crystalline form of TiO$_2$ can be achieved through a thermal treatment process$^{56, 61, 94}$.

Findings from chapter 2 have demonstrated that the electrodes calcined at different temperatures for different durations possess different photocatalytic activities due to changes in the crystalline forms. In this chapter, I adopt the same strategy and conditions employed in Chapter 5 to study the photocatalytic degradation kinetics of a wide spectrum
of organic compounds at high temperature treated electrodes. The photocatalytic degradation characteristics of organic compounds of different chemical identities at the high temperature treated electrodes were systematically evaluated. In order to identify the photocatalytic characteristic differences between high and low temperature treated electrodes and to assign the causes, the findings from this chapter will be compared with the findings found in Chapter 5.

6.2 EXPERIMENTAL

6.2.1 Material and Chemicals

Indium Tin Oxide (ITO) conducting glass sheets (8-10Ω/square, Delta Technologies Limited) were used as substrate for TiO₂ film coating. Potassium hydrogen phthalate (AR, Aldrich), formic acid (AR, Aldrich), oxalic acid (AR, Ajax Chemicals), succinic acid (99%, Sigma), malonic acid (Sigmaultra, Sigma), methanol (99.8%, BDH), D-Glucose (99%, BDH), salicylic acid (AR, Aldrich), sodium acetate (AR, Ajax), phenylalanine (99%, Sigma), 3-chlorophenol (99%, Aldrich), 2-chlorophenol (99%, Aldrich), 4-chlorophenol (99%, Aldrich), catechol (99%, Sigma), hydroquinone (99%, Sigma), glycine (AR, Ajax), sodium benzoate (AR, Ajax), phenol (99%, Sigma) and glutaric acid (99%, Sigma) were used as received. All other 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).

6.2.2 Preparation of the Nanoporous TiO₂ Film Electrodes

The TiO₂ colloid synthesis and immobilisation procedures are the same as described in Section 2.2.2. The electrodes used in this study were calcined at 700°C for 16h (denoted as 7d). The thickness of the film was ca. 1µm.
6.2.3 Apparatus and Methods

The apparatus and experimental set-up are the same as described in Section 2.2.3 for photoelectrochemical measurements. The light intensity changes were made through altering the relative position of the electrolytic cell to the light source, and light intensity was measured with an UV-irradiance meter (UV-A, Instruments of Beijing Normal University). The pH values of solutions were adjusted with nitric acid and sodium hydroxide solutions. The pH values of solutions were measured and monitored with a pH meter.

6.3 RESULTS AND DISCUSSION

6.3.1 Characteristics of Potential/Photocurrent Curves

A high temperature treated TiO$_2$ film electrode (7d) was employed for this part of the study. Linear sweep voltammetry was employed to study the effect of potential bias on the photocurrent response. The experiments were conducted in 0.1 M NaNO$_3$ solutions containing different organic compounds at different concentrations. Shown in Figure 6.1 is a set of typical voltammograms obtained under illumination in the blank solution and the solutions containing different concentration of glucose. All other organic compounds used in this study exhibit similar voltammograms to those shown in Figure 6.1. It must be pointed out that all TiO$_2$ nanoporous film coated ITO conducting glass electrodes give similar voltammograms either in presence or in absence of organic compounds. In all cases, the photocurrents increase as the applied potential bias increase within the low potential range, which can be attributed to the limitation of freed electron transport in the film\(^9\). The photocurrents saturate at higher potential bias due to the limitation of photohole capture process at TiO$_2$ surface\(^9\). Such behaviour is similar to that of the low temperature calcined electrodes. The magnitude of the saturation photocurrents depends on the concentration of organic compounds and their chemical identities. In other words,
for a given light intensity (same photohole concentration), the magnitude of saturation photocurrents is determined by the availability of organic compounds at electrode surface and the photohole capture ability of the electron donors (organic compounds).

Figure 6.1 The voltammograms of the electrode in 0.1M NaNO₃ solution containing glucose of different concentrations (a) 0, (b) 0.5mM, (c) 0.1M, (d) 0.5M under illumination at pH 4.0, light intensity 6.6μW/cm².

Comparison of the voltammograms obtained at a high temperature calcined electrode with those obtained at a low temperature calcined electrode (c.f. Chapter 3) reveals that the photocurrent-potential (I₂,E) relationship in the low potential range is markedly different. The I₂,E relationship obtained at low potential bias for the low temperature calcined electrode was linear (Chapter 3), while for the high temperature treated electrode this relationship was not linear, particularly, at low concentrations. The existence of rutile phase in the higher temperature treated electrode is responsible for the difference. This is because the band gap energy (Eₕ) for anatase phase and rutile phase are slightly different. The Eₕ for the former (3.2eV) is 0.2ev higher than that of the latter (3.0eV). Alternatively the conduction band edge potential of rutile phase is 0.2V (vs SHE) more positive than that of the anatase phase, which results in the photoelectrons generated at the anatase
phase being transferred to rutile phase \(^{214}\). This means that the majority of the photoelectrons being drawn out at low concentrations are from the rutile phase, which require a more positive potential bias.

6.3.2 Effect of Solution pH

The effect of pH on the saturation photocurrent \((I_{sph})\) was investigated under the same experimental condition as used for the low temperature calcined electrode. The saturation photocurrents were measured at potential bias \(+0.30V\) with high organic substrate concentrations to ensure that the availability of organic substrates at the electrode surface and the electron transport in the semiconductor film are not rate-limiting factors.

The results revealed that the effect of pH on \(I_{sph}\) for the high temperature calcined electrode was very similar to the case of the low temperature calcined electrode.

Weak adsorbates, such as methanol, glucose and phenols, possess the same pH dependence characteristics. The \(I_{sph}\) obtained was almost independent of the solution pH within the pH range of 2 to 10. Above pH 10, the \(I_{sph}\) increased sharply due to the increase in the negative charge at the electrode surface that assists with the trapping of photoholes and increases the lifetime of photoelectrons and photoholes due to the electrostatic attraction.

Strong adsorbates, such as carboxylic acids, possess the same pH dependence characteristics. The \(I_{sph}\) obtained was again relatively independent of the solution pH within the pH range of 2.0 to 10.0. Above pH 10, the \(I_{sph}\) decreased sharply due to the decreased availability of adsorbate at electrode surface. This is because at high pH, carboxylic acids mainly exist in their ionic form leading to electrostatic repulsion from the negatively charged electrode surface. In comparison with the low temperature calcined
electrodes, the high temperature calcined electrode is even less sensitive to pH change within the pH range of 2.0 to 10.0.

### 6.3.3 Effect of Light Intensity

The effect of light intensity on the saturation photocurrent \(I_{sph}\) was investigated under the same experimental condition as used for the case of the low temperature calcined electrode. Again, the saturation photocurrents were measured at potential bias +0.30V with high organic substrate concentrations to ensure that the availability of organic substrates at the electrode surface and the electron transport in the semiconductor film are not rate-limiting factors.

The results revealed that the effect of light intensity on the saturation photocurrent \(I_{sph}\) for the high temperature calcined electrode was very similar to the case of the low temperature calcined electrode. The \(I_{sph}\) for all the compounds investigated were increased linearly with light intensity. The slopes of the \(I_{sph}/\text{light intensity}\) curves were found to be less dependent on the chemical identity of the substrate in contrast with the low temperature calcined electrodes (see Chapter 3 and 4).

### 6.3.4 \(I_{sph}\) and Molar Concentration (C) Relationships

As discussed above, the saturation photocurrent measured here reflects the kinetics of photohole capture process at the electrode surface, which is related to the photohole capture ability of electron donors and the competition between the kinetics of photohole seizure and that of the recombination of photoelectrons and photoholes. The latter is determined by the availability of organic compound at TiO\(_2\) surface and the nature of the photocatalyst (or the semiconductor electrode). Figures 6.2 and 6.3 show the \(I_{sph}-C\) relationships of different organic compounds at the high temperature treated TiO\(_2\).
electrode, under illumination of the same light intensity (6.6mW/cm$^2$) at the same applied potential bias (+0.30V) and same pH (4.0).

Figure 6.2 shows the $I_{sph}$-$C$ plot for non-aromatic organic compounds. For all the compounds investigated, $I_{sph}$ increased linearly with concentration in the low concentration range and reached saturation at high concentrations. For strong adsorbates such as glutamic acid, malonic acid, succinic acid, glutaric acid and glycine$^{225, 230, 236}$, the maximum $I_{sph}$ obtained at high concentration range was almost constant with a value around 0.40mA. Similar trends were observed for the smaller strong adsorbates such as formic acid and oxalic acid that involves the least number of electrons transferred and least number of steps during their mineralization. However, the magnitude of $I_{sph}$ at high concentrations for the smaller strong adsorbates was much higher than for the larger strong adsorbates. The difference is probably caused by the differences in the current doubling effect (radical intermediates inject electrons into the conduction band of semiconductor, as the result, one photohole consumption can generate photocurrent equivalent to two photoholes consumption). For weakly adsorbates, such as glucose and methanol, after the linear phase of increase in $I_{sph}$ with concentration, $I_{sph}$ keeps increasing at a slower pace and the maximum $I_{sph}$ was attained at much higher substrate concentration. The maximum $I_{sph}$ values lie in between the maximum $I_{sph}$ values for formic acid and oxalic acid and the maximum $I_{sph}$ values for other strong adsorbates. Again, the differences in their current doubling effect may be responsible for this. Figure 6.2 also reveals that the concentrations at which the $I_{sph}$ values start to deviate from the linearity were similar for all compounds investigated. This is different to what was observed at a low temperature treated electrode where the linear range was found to be heavily dependent on the chemical nature of the organic compounds and their adsorption properties on TiO$_2$ surface$^{242}$. This implies that the photocatalytic degradation of different organic compounds at the high temperature calcined electrode was indiscriminate. This is
in contrast to the findings from the low temperature calcined electrode, where the photocatalytic degradation rate of different organic compounds at high concentrations was heavily dependent on the chemical nature of the compounds.

Figure 6.2 The $I_{ph}$-$C$ relationships of different non-aromatic organic compounds, (a) large concentration range, (b) low concentration range.

Figure 6.3 shows the plot of $I_{ph}$-$C$ for different aromatic organic compounds. At low concentrations, linear $I_{ph}$-$C$ relationships were observed. At higher concentrations, the $I_{ph}$ decreased slightly after reaching the maximum indicating slight electrode deactivation by these aromatic compounds. This is in contrast to the results obtained from electrodes.
calcined at 500°C where a considerable inhibition effect was observed for aromatic compounds\textsuperscript{242} (as discussed in Chapter 5). In addition, the linear ranges observed using the high temperature treated electrode were more than 6 times larger than those observed using the low temperature treated electrodes\textsuperscript{242}. This indicates that the high temperature calcined electrode had a greater photocatalytic activity to completely mineralise more complicated organic compounds.

![Figure 6.3](image)

**Figure 6.3** The $I_{\text{sp}}$-$C$ relationships of different aromatic organic compounds.

Overall, within the diffusion control concentration range, depending on the number of electron transferred for the mineralization of each organic molecule, the $I_{\text{sp}}$ varied significantly for different organic compounds at the same molar concentrations. The differences in the slopes of the linear part of $I_{\text{sp}}$-$C$ curves for different organic compounds can be affected by many factors. These include the difference in their diffusion coefficients, the degree of mineralization of each organic molecule before it leaves electrode surface and the number of electrons required for complete mineralisation. In the next section these factors will be discussed further.
6.3.5 Comparison of $I_{\text{sph}}$-$C_{\text{eq}}$ Relationships

With the experimental conditions employed the magnitude of the $I_{\text{sph}}$ represents the photohole capture rate by electron donors at the electrode surface. This rate is determined by factors such as the availability of organic compounds at the TiO$_2$ surface, the rate of photohole generation, the lifetime of photoholes and the interaction of the organic compounds with TiO$_2$ surface. For a given TiO$_2$ electrode the intrinsic photohole lifetime is fixed and under illumination of a given light intensity the photohole generation rate is also fixed. Therefore the value of $I_{\text{sph}}$ is mainly determined by the availability of organic substrates at electrode surface and their interaction with TiO$_2$ surface. As presented in the above section, for all the compounds studied in low concentration range, the $I_{\text{sph}}$ increases linearly with molar concentration. This indicates that the overall photocatalytic oxidation process is controlled by the availability of substrate at electrode surface or controlled by diffusion process. For the organic compounds investigated, the number of electrons required for complete mineralization of these compounds varies from 2e$^-$ for formic acid and oxalic acid to 30e$^-$ for phthalic acid (see Table 5.1). Since elementary reactions involving more than two electrons rarely occur, the photocatalytic degradation of larger organic compounds must undergo many steps of elementary reaction. Given the differences in their chemical structure and their number of electrons required for the mineralisation of different organic compounds, the number of steps and intermediates (and chemical identities of these intermediates) involved in the complete oxidation of different compounds would differ markedly from one organic compound to another. A question is raised – under diffusion control condition, are the organic molecules reaching the electrode surface completely mineralized? This needs to be addressed first.

For the same reason described in Chapter 5 for the low temperature calcined electrodes, dicarboxylic acids were selected as model compounds to address the issue mentioned.
above. Figure 6.4 shows the $I_{sph}$-$Flux^{in}$ curves of these model compounds. It was found that $I_{sph}$ linearly responded to the change of $ Flux^{in}$ at low $ Flux^{in}$ and then saturated at high $ Flux^{in}$. The linear part of the curves was almost identical for all dicarboxylic acids investigated. This part of curves can be fitted to the linear equation of $I_{sph}=0.00365Flux^{in}+0.101$ (mA), with $R^2$ of 0.998. The intercept of 0.101 mA is the background photocurrent resulting from the photocatalytic oxidation of water. The results obtained are the same as predicted by Equation (5.4), which confirms that all assumptions made for Equation (5.4) have been met and all dicarboxylic acids under diffusion-controlled conditions were stoichiometrically mineralized regardless of their chemical identities. The results also reveal that except for oxalic acid, the maximum $I_{sph}$ observed at high $ Flux^{in}$ were very similar for all other dicarboxylic acids investigated indicating the indiscriminate mineralization of different organic compounds. This is in sharp contrast to the photocatalytic oxidation of the same compounds at the low temperature calcined electrode where the maximum $I_{sph}$ varies significantly for different compounds due to the accumulation of intermediates or incomplete mineralization of organic compounds. The exceptional high maximum $I_{sph}$ observed for oxalic acid at high $ Flux^{in}$ and the upward deviation of $I_{sph}$ at medium $ Flux^{in}$ can be attributed to the current doubling effect resulting from the injection of electrons into the conduction band of TiO$_2$ by radical intermediates. Interestingly, for other dicarboxylic acids no current doubling effect was observed. This can be explained as follows. For the current doubling effect to be observed, the accumulation of substrate molecules or partial degraded intermediates at electrode surface must occur. Because of this, under absolute diffusion controlled conditions, no current doubling effect can be observed (due to the limit of photohole acceptor at TiO$_2$ surface, with or without electron injection by radicals there is no difference in the value of photocurrent). Surface accumulation of radical intermediates does not necessarily lead to their injecting electrons into the conduction band of the
semiconductor. This is because in addition to the accumulation of substrate molecules or intermediates at semiconductor surface, the spatial orientation of these surface species has to be suitable for injection of electrons into the conduction band of the semiconductor. For larger dicarboxylic acids, the absence of current doubling effect is very unlikely due to the lack of surface accumulation. It is more likely due to the unsuitable spatial orientation of the accumulated radicals on TiO$_2$ surface.

![Graph](image)

**Figure 6.4** The plot of $I_{sph}$ versus flux for a few dicarboxylic acids at pH 4.0.

For most of the organic compounds the diffusion coefficients are not available. In order to obtain the similar kinetic information as above for a wider spectrum of organic compounds, the equivalent concentration ($C_{eq}=nC$), is employed to replace the molar concentration. By converting the molar concentration into $C_{eq}$, I effectively normalized molar concentrations of different substrates into the same concentration scale in terms of the amount of photoholes needed for their mineralization. Hence, the photohole demand for all compounds at the same $C_{eq}$ is the same.

$I_{sph}$-$C_{eq}$ relationships of non-aromatic compounds are plotted and shown in Figure 6.5. Linear $I_{sph}$-$C_{eq}$ relationships were obtained for all compounds investigated at low $C_{eq}$
values. The small differences in the slopes of linear part of these curves can be attributed to the differences in diffusion coefficients of the organic compounds. At high $C_{eq}$ values, except for formic acid and oxalic acid, the deviation of $I_{sp}$ from linear relationship for all other compounds was due to the incomplete mineralization. Under such conditions, the availability of organic compounds at the electrode surface is not limiting. For formic acid and oxalic acid, upward deviation from linearity were due to the current doubling effect, which can only be observed at higher concentrations where the accumulation of organic compounds at the TiO$_2$ surface occurs.

![Graph](image.png)

**Figure 6.5** The $I_{sp}$-$C_{eq}$ relationships for different non-aromatic organic compounds, (a) larger equivalent concentration range, (b) low equivalent concentration range.
$I_{sph}$-$C_{eq}$ curves obtained from photooxidation of aromatic compounds are shown in Figure 6.6. As in Figure 6.5, the slopes of the linear part of the $I_{sph}$-$C_{eq}$ curves were very similar for the different compounds. Moreover, the slopes of these straight lines are close to those of non-aromatic compounds. At high $C_{eq}$ values, the $I_{sph}$ values reached a maximum and then decreased slightly due to inhibition effect of benzene ring intermediates. This is in contrast to the case of photooxidation of aromatic compounds at the low temperature calcined electrodes where the $I_{sph}$ dropped sharply at slightly high concentration as shown in Figure 5.3. Although $I_{sph}$ tends to drop slightly in high $C_{eq}$ range, the degree of the inhibition is much less severe compared with the inhibition effect occurred at a lower temperature calcined electrode $^{242}$. Furthermore, the linear range observed from the high temperature treated electrode is much larger than that of electrodes calcined at low temperature $^{243}$.

![Graph](image)

**Figure 6.6**  The $I_{sph}$-$C_{eq}$ relationships for different aromatic organic compounds.

In order to further examine the linear part of the $I_{sph}$-$C_{eq}$ curves for different organic compounds, a graph at lower concentration is shown in Figure 6.7. A linear relationship
can be obtained for all the organic compounds at low concentration. Slight differences in the slopes of the linear part of the curves can be contributed mainly to the differences in the diffusion coefficient of different compounds. For oxalic acid and formic acid, the photocurrent deviated upwards from the straight line when the concentration was above 2 \( \text{meq} \) due to the current doubling effect. For compounds with alkyl groups, the photocurrent is deviated downwards from the regression line when the concentration was above 3 \( \text{meq} \) due to the intermediates leaching out of the reaction layer. For aromatic compounds the photocurrent deviated from downwards from the straight line at higher concentration, presumably due to the accumulation of benzine ring intermediates.

![Figure 6.7](image_url)

*Figure 6.7* The saturation photocurrent/equivalent concentration relationships of different organic compounds, (○) 4-chlorophenol, (●) 2-chlorophenol, (●) hydroquinone, (●) acetic acid, (●) catechol, (●) phthalic acid, (●) 3-chlorophenol, (●) glutaric acid, (●) benzoic acid, (●) phenol, (●) phenylalanine, (●) succinic acid, (●) malonic acid, (●) methanol, (●) salicylic acid, (●) glutamic acid, (●) glucose, (●) formic acid, (●) glycine, (●) oxalic acid.

At high concentrations the differences in \( I_{\text{sph}} \) for different compounds should reflect the differences in their interaction with \( \text{TiO}_2 \) surface, the nature of intermediates and the distribution of photohole demand on \( \text{TiO}_2 \) surface as was demonstrated at the low
temperature calcined electrode. It is generally accepted that the photocatalytic degradation of strong adsorbates takes place via inner-sphere charge transfer mechanism, whereas, the photocatalytic degradation of weak adsorbates occurs via outer-sphere charge transfer mechanism. The organic compounds investigated here include both strong and weak adsorbates. The affinity of these organic compounds to TiO₂ surface is expected to differ tremendously. It was demonstrated that the adsorption behaviour of strong adsorbates on the high temperature calcined electrodes was very similar to their behaviour on the low temperature calcined electrodes. However, differences in the maximum $I_{sph}$ for different compounds at the high temperature calcined electrodes are much less obvious than these differences at the low temperature calcined electrodes. This implies that the above mentioned differences (the differences in their interaction with TiO₂ surface, the nature of intermediates and the distribution characteristics of photohole demand on TiO₂ surface) for different organic compounds have a much less influence on overall photohole capture process at the high temperature calcined electrodes than at the low temperature calcined electrodes. This again demonstrates the exceptional photocatalytic activity of the electrode largely due to the long lifetime of photoholes. At a high temperature calcined electrode, the differences in $I_{sph}$ at high concentrations for different compounds probably result mainly from the difference in their current doubling effect. For the current doubling effect to occur, the relative steric position of intermediate radical to the conduction band is very important. Because of this, for the larger strong adsorbates their partially degraded radical intermediates (anchored to certain sites) may be not sterically favourable for injection of electrons to the conduction band sites. In contrast, small strong adsorbates (formic acid and oxalic acid) undergo only one radical intermediate in their mineralization therefore the radical intermediate tends to be less likely bound and free to find the right sites to inject electrons. The exceptional high $I_{sph}$ at high concentrations for small strong adsorbates may suggest that the corresponding radical intermediates are in a favourable
stERIC position to inject electrons into conduction band of TiO$_2$. That the maximum \(I_{ph}\) values for non-specific adsorbates such as methanol and glucose at high concentrations lie between those for small strong adsorbates and those for larger strong adsorbates supports the above arguments.

Overall, the above results demonstrate that all organic compounds, irrespective of their chemical identities, undergo stoichiometric degradation under diffusion control as indicated by linear photocurrent responses. More importantly, the linear concentration ranges on an equivalent concentration scale for different organic compounds are very similar, which is in great contrast to the case of lower temperature treated electrodes where the linear range is significantly dependent on the chemical identities of organic compounds $^{242}$. This is a remarkable finding, given the enormous differences in their chemical identities, the number of electrons transferred, and number of elementary steps and intermediates involved during their mineralisation.

There are three major differences between this high temperature treated electrode and those calcined at lower temperatures. One is the linear ranges of different organic compounds obtained from the high temperature treated electrode, in particular for aromatic compounds, are significantly extended. Another is that the photocatalytic oxidation occurring at the high temperature treated electrode tends to be indiscriminate in regard to the type of organic compounds. The third is the inhibition effect by aromatic compounds observed at the high temperature treated electrode is much less severe. These major differences can all be attributed to the coexistence of anatase and rutile phases in the high temperature treated electrode. The coupling of these two phases allows the vectorial displacement of electrons from the anatase phase to the rutile phase that retards the photoelectrons/hole recombination. In effect, the spatial separation of photoelectrons from photoholes is realized, which, in turn, prolongs the lifetime of photoelectrons and
photoholes. Owing to the longer lifetime of photoholes, this high temperature treated electrode can oxidize a wide spectrum of organic compounds in a more effective manner.

6.4 CONCLUSION

For electrodes calcined at 700°C for 16h, the potential bias effect on this electrode is similar to that on the low temperature calcined electrodes. When it comes to the pH effects on the photocatalytic degradation of different organic compounds, the same trend of pH effect on their photocatalytic degradation at the electrode as that at a low temperature calcined electrode was observed. The major difference between the two electrodes is that the high temperature calcined electrode is even more insensitive to the pH changes for the same organic compound. Similarly, the photocurrents from the photocatalytic degradation of different organic compounds increases linearly with light intensity, but the slopes of photocurrent/light intensity lines are less dependent on the chemical identities of organic compounds. When it comes to the concentration effect on photocatalytic degradation of different organic compounds at the electrode, it is remarkable to find that the photocatalytic reactions of different organic compounds can proceed under diffusion limitation in a very large concentration range. The chemical nature of the compounds has much less effects on their photocatalytic degradation kinetics at the electrode than at the low temperature calcined electrodes. The electrode has an excellent resistance to the poisonous effect of intermediates, in particular, of the intermediates from aromatic compounds.
CHAPTER 7 QUANTIFICATION AND KINETIC STUDY OF PHOTOCATALYTIC DEGRADATION OF ORGANIC COMPOUNDS IN A THIN LAYER PHOTOELECTROCHEMICAL CELL
7.1 INTRODUCTION

All studies carried out in the previous chapters (with the exception of the kinetic studies of pre-adsorbed organic compounds and adsorption thermodynamic studies in Chapter 4) were based on a non-exhaustive degradation of organic compounds in bulk solution. Under these conditions, the ratio between the solution volume and the electrode area is often very large. Consequently, the change in the substrate concentration in the bulk solution is negligible during the experiment\(^8\).\(^{11}\). For this reason, a steady state mass transfer condition can be achieved and a limiting (steady state) photocurrent can be obtained. Mathematically, the semi-infinite boundary conditions can normally be adopted in solving the differential equations of Fick’s laws to obtain the relationship between the photocurrent and the substrate concentration\(^{237}\). In addition, the photocurrent is probably the only measurable parameter that can be used to express the photocatalytic kinetics in a non-exhaustive degradation mode in bulk solution.

The circumstances are very different when the photocatalytic degradation is carried out in a thin layer photoelectrochemical cell. Firstly, the ratio between the solution volume and the electrode area is very small, which makes the substrate concentration in the bulk solution decrease rapidly during the experiment\(^{237}\). As a result, steady state mass transfer condition could not be sustained and a limiting photocurrent cannot be obtained. Secondly, the semi-infinite boundary conditions are invalid for a thin layer cell process because the thickness of the concentration depletion layer is limited by the thickness of the cell (<200µm)\(^{237},^{244}\). Hence, the mathematical treatment of a thin layer system is quite different to that in a non-exhaustive degradation mode in bulk solutions\(^{237},^{244}\). The most important feature of a thin layer system is that exhaustive photodegradation can be easily achieved. One of the advantages of the exhaustive degradation mode is that the Faraday’s Law can be employed to accurately quantify the extent of the degradation. High accuracy
can be achieved due to the use of charge (integration of photocurrent) instead of photocurrent to express the degradation process. The use of charge to express the degradation process can greatly minimise (if not completely eliminate) the effect of many interfering factors of the solution processes such as the rate of mass transfer in the solution and interfacial processes such as adsorption. It should be mentioned that one of the attractive features of photoelectrochemical method is that the charge due purely to the photocatalytic degradation of organic compounds can be easily measured.

This chapter aims to investigate the characteristics of exhaustive photocatalytic degradation of organics in a thin layer cell system. Specifically, the investigation will focus on quantifying the extent of the photodegradation and characterising the kinetics of the exhaustive degradation.

Although the photocatalytic degradation of a wide spectrum of organic compounds has been investigated previously, quantitatively characterising the extent of photocatalytic degradation has not been realised. This is mainly because the characterisation methods used in the past are incapable of obtaining the required information. Most of these methods employed particulate slurry systems and the measurement of reaction rate is based on the disappearance of the original compound in the bulk solution. As previously mentioned, the accuracy of measurement in such slurry systems is highly questionable due to the complicated experimental procedures involved. In addition, the use of the original compound disappearance to quantify the extent of the degradation is scientifically inaccurate. This is because the photocatalytic degradation of organic compounds, even the most simple ones such as formic and oxalic acids, will take a few steps and involve intermediates. Therefore, the original compound disappearance cannot be used to represent the extent of degradation due to the unknown degradation stages of organic compounds during experiments.
Again, most of reported the kinetics studies of photocatalytic degradation of organic compounds were carried out in slurry system using the disappearance of original substrate to describe the reaction rate. This type of kinetic data does not reflect the photoefficiency of the photocatalytic degradation of organic compounds because intermediates are also photocatalytically degraded at the same time. Particularly, when it comes to different organic compounds, these data for different organic compounds are un-comparable due to the differences in the number of intermediates and the differences in the reactivity of intermediates. Therefore, these data cannot offer meaningful information about the photocatalytic activity and photoefficiency of a system. In order to overcome these problems and to achieve my aim, a new methodology will be developed in this chapter. Photocurrent, the expression of the reaction rate used, directly reflects the ability of photohole capture of organic compounds or the reactivity of organic compounds with surface bound hydroxyl radicals or with trapped photoholes. This rate is an instantaneous rate and can be measured in-situ regardless of whether the original substrate or intermediates are reacting at the electrode surface. Under exhaustive photoelectrolysis, if intermediates formed during the photocatalytic mineralisation of organic compounds are less reactive, the reaction rate (photocurrent) decay would be not smooth. If they could not be mineralised the charge would be different from that expected for total mineralisation. A large number of organic compounds of different structures and properties were selected for the investigation.

It is important to note that this is the first time that the study of photocatalytic degradation of organic compounds at TiO$_2$ in a thin layer cell has been carried out. I expect the findings from this investigation will enable us to better understand the semiconductor photocatalytic processes in thin layer cell under exhaustive degradation mode as well as serve a more specific purpose – the findings will be used as the theoretical foundation to
develop a new analytical method for environmental monitoring, which will be detailed in the next chapter.

7.2 EXPERIMENTAL

7.2.1 Material and Chemicals

Indium Tin Oxide (ITO) conducting glass slides (8Ω/square) were commercially supplied by Delta Technologies Limited. Titanium butoxide (97%, Aldrich), potassium hydrogen phthalate (AR, Aldrich), D-glucose (AR, BDH), oxalic acid (AR, Ajax Chemicals), succinic acid (99%, Sigma), malonic acid (Sigmaultra, Sigma), glutaric acid (99%, Sigma), p-chlorophenol (99%, Aldrich), acetone (AR, BDH), acetic acid (AR, BDH), glycine (AR, Ajax) and methanol (99%, BDH) were used as received. Other chemicals were of analytical grade and purchased from Aldrich or Sigma unless otherwise stated. All solutions were prepared using high purity deionised water (Millipore Corp., 18MΩ cm).

7.2.2 Preparation of the Nanoporous TiO₂ Film Electrodes

The TiO₂ colloid synthesis and immobilisation procedures are the same as described in Section 2.2.2. The electrodes used in the study were calcined at 700°C for 16h.

7.2.3 Thin Layer Photoelectrochemical Cell

A schematic representation of the thin layer photoelectrochemical cell is shown in Figure 7.1. The material used for the cell body was glassy Teflon. The cavity of the thin layer was defined by an aperture in the spacer, which was 0.20 mm in thickness and 9.30 mm in diameter. To minimize edge effects, the diffusion of material into and out of the cell cavity during an experiment was made as small as possible in comparison with the electrode area.
**Figure 7.1** Schematic diagram of the thin layer photoelectrochemical cell.

### 7.2.4 Apparatus and Methods

The experimental set-up is the same as described in Figure 2.2 except that the thin layer photoelectrochemical cell is used instead of the bulk solution cell. A built-in saturated Ag/AgCl electrode and built-in platinum mesh were used as the reference and auxiliary electrodes respectively. To minimize the solution resistance influence on the photocurrent response, 2M NaNO₃ electrolyte was used as the supporting electrolyte. Sample solution was injected into the thin layer cell with a syringe through the inlet channel. Care was taken to eliminate the air bubbles in the thin layer cell cavity. After the injection of a sample solution, a time period of 30s was allowed to elapse (to release the pressure inside the thin layer cavity) before illumination and data acquisition.

### 7.3 RESULTS AND DISCUSSION

#### 7.3.1 Photocurrent/Potential Response of the Cell

The purpose of this experiment was to select a suitable potential bias for thin layer cell applications. A photoelectrochemical cell with thin layer configuration normally possesses large $iR$-drop due to the high resistance of the thin solution channel between the
working and the reference electrodes. This may affect the actual potential at the working electrode and the characteristics of the current-potential responses. In order to minimise these influences a high electrolyte concentration (2.0 M NaNO₃) was employed. Figure 7.2 shows a typical current-potential response of a TiO₂ porous film electrode in the thin layer photoelectrochemical cell obtained from a 2.0 M NaNO₃ solution under illumination with a potential scan rate of 5 mV/s. The characteristics of the $I_{ph}$-$E$ curve are similar to those obtained from the bulk solution cell. Most importantly, the photocurrent is saturated at the similar potentials to those in a bulk cell, which indicates the supporting electrolyte concentration of 2.0 M (NaNO₃) was sufficient in maintaining the low $iR$-drop.

In order to obtain a photocurrent response free of the influence of electron transport in the film and focus on reactions at the interface, a potential bias of +0.30V was adopted for all subsequent experiments.

![Figure 7.2](image)

**Figure 7.2** Linear potential sweep voltammogram of a TiO₂ porous film electrode in 2M NaNO₃ solution in this cell under illumination at 5 mV/s.

### 7.3.2 Transient Photocurrent Response and Charge Measurement

The photocurrent-time profile of the electrode in the thin layer cell under a constant applied potential bias was obtained. Figure 7.3 shows a set of typical transient...
photocurrent decay curves of the electrode in the thin layer cell obtained from a 2.0 M NaNO₃ solution with and without potassium hydrogen phthalate. In blank electrolyte solution, a smaller photocurrent response spike was observed, which can be attributed to transient response of water photocatalytic oxidation. The photocurrent decayed rapidly to a steady state current, which can be attributed to steady state water oxidation. In the case of potassium hydrogen phthalate oxidation, a large photocurrent spike was observed. The photocurrent obtained here consists of two components. One is due to the photocatalytic oxidation of organic compound and another is due to the photocatalytic oxidation of water. The continuous decay of the photocurrent was due to the continuous depletion of the organic compound in solution caused by the photocatalytic degradation. When all organic compounds in the solution were consumed, the photocurrent decayed to a steady photocurrent that is the same as the limiting water oxidation current.

To quantify the photocatalytic degradation of organic compounds, the measurement of the net charge, \( Q \), due purely to the photocatalytic degradation of organic compound is required in this study. For a given time interval (the time required for organic compound photocurrent decays to the water oxidation current), the charge passed for each case equals the area below the photocurrent curve, which can be obtained by integration of the corresponding photocurrent with time. The net charge can then be obtained by subtracting the charge due to the photocatalytic oxidation of water from the total charge due to the photocatalytic oxidation of both organic compound and water, which is indicated as the shaded area in Figure 7.3. This shaded area therefore represents the photoelectrochemical charge passed for the exhaustive degradation of the potassium hydrogen phthalate.
Figure 7.3 Transient photocurrent response of the electrode in the thin layer cell, (dash line) 2.0M NaNO₃, (solid line) 2.0M NaNO₃ plus 100µM potassium hydrogen phthalate.

7.3.3 Stoichiometry of Photocatalytic Degradation

7.3.3.1 Photocatalytic Degradation of Phthalate

In order to examine the extent of degradation, the quantitative relationship between the net charge and organic compound concentration was first investigated using phthalic acid as an example. At the electrode, complete oxidation of phthalic acid can be given according to the stoichiometry of the reaction:

\[ C_8H_6O_4 + 12H_2O = 8CO_2 + 30H^+ + 30e^- \]  \hspace{1cm} (7.1)

30 electrons are therefore required for complete mineralisation of one molecule of phthalic acid. According to Faraday’s law, the relationship between the net charge and the concentration of KHP can be given as:

\[ Q = nFVC=30FVC=kC \]  \hspace{1cm} (7.2)
where, $Q$ is the net charge, $V$ is the volume of the thin layer cell, $F$ is Faraday constant, $C$ is the initial concentration of potassium hydrogen phthalate and $k = nFV$, which is a constant for a given compound and cell.

Equation 7.2 indicates that if the reaction takes place according to the stoichiometry as shown in Equation 7.1, then a linear relationship between the net charge and the initial concentration of KHP should be obtained. Given a cell volume of 13.6µL (as determined by the dimensions of the thin layer cell) the theoretical slope of the straight line should be ca. $k = 0.0393 \text{ mC/µM}$. Figure 7.4 shows the plot of net charge against the initial concentration of KHP. A linear relationship with a slope of 0.0414 $\text{mC/µM}$ and $R^2$ of 0.991 was obtained, which is in an excellent agreement with theoretical prediction of Equation 7.2. This implies that exhaustive degradation of KHP has been achieved and the reaction occurred according to the stoichiometry of the reaction shown in Equation 7.1. In other words, this result shows that the degradation of KHP was exhaustive.

![Figure 7.4](image)

**Figure 7.4** Charge obtained versus initial concentration of potassium hydrogen phthalate.

The excellent linear relationship obtained in Figure 7.4 suggests that the background charge generated from water oxidation is fixed regardless of substrate concentration
change. This is an advantageous feature of the technique that allows the accurate measurement of photocatalytic degradation of organic compounds.

7.3.3.2 Photocatalytic Degradation of Different Organic Compounds

In this section, the above photoelectrochemical method was employed to study the photocatalytic degradation of other organic compounds.

If I assume that all the organic compounds are fully mineralised, the oxidation of the photocatalytic oxidation of different organic compounds at the electrode follows the following general equation:\textsuperscript{182}:

\[ C_y H_m O_j N_k X_q^+ (2y-j) H_2 O \rightarrow y CO_2 + q X^- + k NH_3 + (4y-2j+m-3k) H^+ + (4y-2j+m-3k-q) e^- \] (7.3)

Where, \( N \) and \( X \) represent nitrogen and halogen atom respectively. The numbers of carbon, hydrogen, oxygen, nitrogen and halogen atoms in the organic compound are represented by \( y, m, j, k \) and \( q \).

The number of electrons transferred for complete mineralization is therefore given by the following equation:

\[ n=4y-2j+m-3k-q \] (7.4)

Shown in Table 7.1 are the numbers of electrons transferred for the mineralization of different compounds studied.

<table>
<thead>
<tr>
<th>Table 7.1</th>
<th>Electron transfer number for complete oxidation of different compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>n</td>
</tr>
<tr>
<td>Methanol</td>
<td>6</td>
</tr>
<tr>
<td>Glucose</td>
<td>24</td>
</tr>
<tr>
<td>Nitrite</td>
<td>2</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td>28</td>
</tr>
<tr>
<td>Phthalic acid</td>
<td>30</td>
</tr>
</tbody>
</table>
The quantitative relationship between the net charge and the substrate concentration can be given according to Faraday’s law:

\[ Q = nFVC = (4y-2j+m-3k-q)FVC = kC \]  \hspace{1cm} (7.5)

Where \( k = nFV = (4y-2j+m-3k-q)FV \), is a constant for a given compound and cell.

Figure 7.5 shows the plot of the net charge (\( Q \)) versus the molar concentration (\( C \)) for the different organic compounds. Two mixed samples, Mixture 1 and Mixture 2, were also used. The compositions of these mixed samples are given in Table 7.2. The non-characteristic electron transfer number for mixture 1 is 17, and for mixture 2 is 19.2.

<table>
<thead>
<tr>
<th>Table 7.2</th>
<th>Molar composition of two mixtures of different organic compounds used.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mixture 1</strong></td>
<td><strong>Molar percentage</strong></td>
</tr>
<tr>
<td>Compounds</td>
<td></td>
</tr>
<tr>
<td>Phthalic acid</td>
<td>10%</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td>10%</td>
</tr>
<tr>
<td>Glucose</td>
<td>10%</td>
</tr>
<tr>
<td>Phenol</td>
<td>10%</td>
</tr>
<tr>
<td>Methanol</td>
<td>20%</td>
</tr>
<tr>
<td>Acetone</td>
<td>20%</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>20%</td>
</tr>
</tbody>
</table>

Similar to the case of phthalic acid, a linear relationship between the net charge and concentration were obtained for all compounds investigated. As expected the photoelectrochemical charges obtained from different compounds at the same concentration were vastly different and the slope of the \( Q-C \) curves for different compounds increased as the number of electrons required for complete mineralisation of the substrate was increased. The experimental slopes obtained for all substrates investigated agreed well with the theoretical slope values calculated according to Equation 7.5 when the cell volume of 13.6 \( \mu \)L and \( n=4y-2j+m-3k-q \) were adopted. These data suggest that all samples investigated, including the mixed samples, were stoichiometrically mineralised according to Equation 7.4. The results also suggest that
Equation 7.5 is generally applicable to exhaustive photocatalytic degradation of all organic compounds tested.

Figure 7.5 The plot of $Q$ versus $C$ for different compounds.

In order to further confirm that the net charges obtained from the photocatalytic mineralisation of different organic compounds truly reflect the degree of degradation, a concept of equivalent concentration, $C_{eq}=nC=(4y-2j+m-3k-q)C$, is again employed. The molar concentration of each compound is normalised to the equivalent concentration. According to Equation 7.5, the quantitative relationship between the net charge and the equivalent concentration can be given as:

$$Q = FVC_{eq}=kC_{eq} \quad (7.6)$$

where $k = FV$, is a constant for a given cell.

Equation 7.6 indicates that the net charge, $Q$, is directly proportional to the equivalent concentration, $C_{eq}$. However, an important difference between Equations 7.5 and 7.6 is that the slope, $k$, in Equation 7.6 depends only on the cell volume and is independent of
compounds. This is an advantage for theoretical studies since all compounds should give the same slope if complete oxidation is achieved. The difference between the experimental slope and the theoretical slope can then be used to quantify the extent of the oxidation. The theoretical slope for the thin layer cell used in this study is \( k = 1.31 \times 10^{-3} \text{ mC/\mu eq} \).

![Graph showing Q-C curves for different compounds.](image)

**Figure 7.6** Charge obtained vs. the equivalent concentration for different compounds.

Figure 7.6 shows the \( Q-C_{eq} \) curves for different compounds. The solid line in the figure is the theoretical line calculated according to Equation 7.6. The results revealed that the \( Q-C_{eq} \) relationship obtained for all compounds investigated, including the two mixtures, are almost identical and all agreed well with the theoretical prediction. The slight deviations from the theoretical line are probably the result of the experimental errors caused by edge effects in the thin layer cell\(^{237} \). This result indicates that the measured net charge originated purely from photocatalytic oxidation of the compounds. This result also indicates that complete mineralisation, assumed by Equation 7.6, was fulfilled and all compounds were stoichiometrically oxidised to their highest oxidation state according to
Equation 7.3. In addition, the excellent linear relationship between experimental charge and $C_{eq}$, and the excellent agreement of the experimental Q-$C_{eq}$ relationship with theoretical Q-$C_{eq}$ relationship also imply an almost constant rate of photocatalytic oxidation of water in the presence of different compounds at different concentrations. This is an advantage of my approach that ensures the simplicity and accuracy of the measurement.

As mentioned at the beginning of this chapter, the findings of this section will be used as the theoretical foundation to develop a new analytical method for environmental monitoring. In this regard, the stoichiometrically mineralisation of the mixed samples provide us with a new way of quantifying the extent of degradation of a mixed sample. Considering the measurement of chemical oxygen demand (COD), an important aggregate organic parameter for water quality, the analytical principle also lies in the quantifying the extent of oxidation. The only difference is that for COD, the extent of oxidation is presented with respect to the equivalent O$_2$ concentration while in here the extent of oxidation is presented with respect to an equivalent concentration. This leads us to believe that photoelectrochemical technique developed here could be used as a theoretical foundation for development of a new analytical method for COD determination. This will be discussed in the next chapter.

### 7.3.4 Kinetics of Photocatalytic Degradation in the Thin Layer Cell

#### 7.3.4.1 Fitting of the Photocurrent Decay Profiles

When the thin layer photoelectrochemical cell is employed, except for very high substrate concentration, a smooth photocurrent decay profile can be obtained during the exhaustive photocatalytic degradation of all compounds. All of the photocurrent-time profiles at relatively low substrate concentration range can be fitted to a double exponential expression:
\[ I_{ph} = I_0 + k_1 \exp(-k_2 t) + k_3 \exp(-k_4 t) \]  \hspace{1cm} (7.7)

where \( I_0 \) is a constant for a given cell and given experimental conditions, which is assigned to the photocatalytic oxidation of water. The double exponential decay indicates that there are two photocatalytic kinetic processes taking place. \( k_1 \) and \( k_3 \) are the pre-exponential factors, while \( k_2 \) and \( k_4 \) are the exponential decay constants of the slow and the fast kinetic processes respectively.

Shown in Figure 7.7 is a set of typical photocurrent decay curves and corresponding curve-fitting results. It shows that the experimental curves are fitted well to the double exponential expression given by Equation 7.7.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7_7.png}
\caption{The experimental photocurrent decay profiles (solid line) and their fitting data (symbols on the solid lines), (a) 20\(\mu\)M, (b) 80\(\mu\)M, (c) 200\(\mu\)M of sodium hydrogen succinate.}
\end{figure}

In order to obtain the values of \( k_1, k_2, k_3, \) and \( k_4, \) the photocurrent decay profiles from different compounds at different concentrations were fitted with the double exponential photocurrent decay expression given by Equation 7.7. For each compound, a set of \( k \)
values were obtained corresponding to its equivalent concentration, $C_{eq}$. The use of equivalent concentration to replace the molar concentration enables easy comparison between different compounds. This is because the photohole demand for different compounds at the same equivalent concentration is the same. Consequently, the kinetic information obtained better reflects the effect of chemical nature of each type of compound on the kinetic process.

$k_1$ is the pre-exponential factor of slow kinetic component, which determines the magnitude of the initial photocurrent of this component or the initial rate of the process. For different compounds, the values of $k_1$ are markedly different at the same molar concentration. Interestingly, when the concentration are normalised to a non-specific concentration (equivalent concentration), the values of $k_1$ are much closer. Figure 7.8 shows the plot of $k_1$ against $C_{eq}$ for different substrates.

![Figure 7.8](image_url)  
*Figure 7.8 The plot of $k_1$ vs $C_{eq}$ for different compounds.*

In all cases, a linear relationship between $k_1$ and $C_{eq}$ was observed at very low concentrations. For some compounds, $k_1-C_{eq}$ deviated from the linear relationship at higher concentrations, which will be discussed in the next section. In all cases, at very
low concentrations, the slopes of the $k_1$-$C_{eq}$ curves were very similar. This indicates that the quantity of organic compounds rather than the chemical nature of the compound mainly determines the pre-exponential factor of the slow kinetic component. A common intercept of all plots at the $k_1$ axis was also observed. This intercept is caused by the transient response from photocatalytic oxidation of water.

$k_2$ is the exponential decay constant of the slow kinetic component. The exponential decay constant $k_2$ decreases with concentration for a given compound and approaches a constant value at higher concentrations. For different compounds the values of $k_2$ are markedly different at the same concentration. Interestingly, when the concentration are normalised to a non-specific concentration (equivalent concentration), the values of $k_2$ are very close and show similar variations with changes in $C_{eq}$. Figure 7.9 shows the plot of $k_2$ against $C_{eq}$ for different substrates. For all compounds investigated, the exponential decay constant, $k_2$, decreased with $C_{eq}$ at low concentrations and approaches an almost constant value at higher concentrations ($C_{eq}>2000 \mu$eq). This trend implies a transition of rate determining step for the slow photocatalytic process. This will be further discussed in the next section. The similar variations in $k_2$ with the non-characteristic concentration $C_{eq}$ for different compounds indicates that the photohole demand is a decisive factor in the kinetics of the slow photocatalytic degradation process of different compounds and their chemical identities have little influence on their photocatalytic degradation kinetics (for this slow kinetic process). This finding supports my claim that the electrodes calcined at 700°C for 16hrs have an exceptional good ability to suppress the recombination of photoelectrons and photoholes in that regardless of the chemical identity of the organic compounds the kinetic behaviours of different organic compounds are similar.
By considering the results observed for both $k_1$ and $k_2$, it is obvious that the slow kinetic component is mainly determined by the nature of the semiconductor electrode and the chemical nature of the compound has a limited effect on this component.

![Figure 7.9](image)

**Figure 7.9** The plot of $k_2$ vs $C_{eq}$ for different compounds.

$k_3$ is the pre-exponential factor of the fast kinetic component that determines the magnitude of the initial photocurrent or initial rate of the fast kinetic process. For non-specific adsorbates such as methanol, glucose, nitrite and p-chlorophenol, the value of the constant is very small and remains virtually unchanged with concentration. In contrast, for strong adsorbed compounds such as phthalic acid, oxalic acid, malonic acid, succinic acid, glutaric acid and the mixture (containing strong adsorbates), the value of $k_3$ is much larger and changes significantly with concentration. The value of $k_3$ increases with concentration at low concentration, and reaches maximum, and then drops at high concentrations. The maxima occur at significantly different molar concentrations for different compounds. Interestingly, however, plotting the value of the constant against the
$C_{eq}$ gives similar maximum concentration (concentration where maximum in $k_3$ occurs) as shown in Figure 7.10.

![Figure 7.10](image)

**Figure 7.10** The plot of $k_3$ vs $C_{eq}$ for different compounds.

The data in Figure 7.10 show that $k_3$ for different substrates can be distinguished into two groups. For the first group (including methanol, glucose, nitrite and p-chlorophenol), the $k_3$ values of this group are virtually unchanged with substrate concentration and are much smaller in comparison to the other group. For the second group (including oxalic acid, malonic acid, succinic acid, glutaric acid, phthalic acid and mixture), $k_3$ values are generally much larger. As $C_{eq}$ was increased, the $k_3$ values for a given substrate increased initially in the low concentration range and then decreased in high concentration range. Comparison of the two groups in terms of their adsorption property showed that the first group corresponded to weak adsorbates while the second group corresponded to strong adsorbates. Clearly the value of $k_3$ is related to the amount of the adsorbates at electrode surface in adsorbed form. The increase in the value of $k_3$ at low concentration is due to the increase in the amount of the adsorbed forms. The level-off and drop-off of $k_3$ values at high concentration are not due to the decrease in the amount of the adsorbed forms of
the substrates, but due to the accumulation of the adsorbed compounds and/or their intermediates, accelerating the recombination of the photoelectrons and photoholes. Similar trends in variation of $k_3$ with $C_{eq}$ for different strong adsorbates suggest that the total photohole demand is the critical factor rather than the differences in their interaction with TiO$_2$ surface.

$k_4$ is the exponential decay constant for the fast kinetic process. Figure 7.11 shows the plot of $k_4$ against $C_{eq}$ for different compounds. In all cases, an increase in the $C_{eq}$ results in a decrease in $k_4$. As with $k_2$, the $k_4$ values are also markedly different for different compounds at the same molar concentration. When the $C_{eq}$ is used instead of the molar concentration, the values of $k_4$ for different compounds are, again, very similar at the same $C_{eq}$ and the change of $k_4$ with the $C_{eq}$ follow the same trend for all compounds. Also, like $k_2$, $k_4$ is affected mainly by the relative proportion of photohole supply and photohole demand, and the chemical identities of the compounds have little influence on it.

![Figure 7.11](image-url)  
*Figure 7.11  The plot of $k_4$ vs equivalent concentration for different compounds.*
Overall, the photocurrent profile obtained from thin layer cell photocatalytic oxidation processes can be represented by a double exponential expression as shown in Equation 7.7. The photocurrent obtained here represents the instantaneous rate of photocatalytic reaction. Based on this, I can easily conclude that the overall rate of photocatalytic reaction is determined by two distinct kinetic processes. $k_1$ and $k_3$ obtained were in the same order of magnitude for a given compound at the same $C_{eq}$ (see Figures 7.8 and 7.10). Nevertheless, the contribution of the slow kinetic component to the overall rate of reaction exists throughout the overall process while the contribution of the fast kinetic component to the overall rate of reaction is mainly at the initial stage of the overall process. This is because for a given compound at a given $C_{eq}$, the fast decay constant ($k_4$) obtained is at least one magnitude of order higher than that of the slow decay constants ($k_2$) (see Figures 7.9 and 7.11) at low concentrations. The large $k_4$ values make the fast kinetic photocurrent component quickly decrease to its minimal soon after the process is commenced. Even though the values of both $k_2$ and $k_4$ decrease as $C_{eq}$ is increased, the extent of the decrease for $k_4$ is much greater than the decrease in $k_2$ values. In addition, for a given compound $k_4$ obtained at high concentrations approached the same value as $k_2$. This is probably because for the fast kinetic process the amount of the preadsorbed compounds is no longer dominating the fast kinetic photocatalytic process due to the overwhelmingly high substrate concentration. Under such conditions, the double exponential photocurrent decay becomes a single exponential decay and Equation 7.7 can be rewritten as:

$$I_{ph} = I_0 + (k_3 + k_4) \exp(-kt)$$

(7.8)

where $k$ is the exponential decay constant of the overall photocatalytic process.
7.3.4.2 Further discussion

In the above section, a double exponential photocurrent decay model based on the computer fitting of experimental photocurrent decay profiles was presented. This section is devoted to clarifying the physical meaning of these empirical parameters. This was done by comparing the fitted values of the constants with the estimated values of the constants based on the existing kinetic models for thin layer electrochemistry. It has to be pointed out that this is not a precise treatment but an estimation. From the variations of the fitted $k_1$, $k_2$, $k_3$ and $k_4$ values with adsorption properties and concentrations of compounds, it was evident that the fast kinetic process was related to the photocatalytic oxidation of pre-adsorbed compounds (before illumination started) at the electrode surface, while the slow kinetic process was related to the photocatalytic oxidation of substrates from solution (not pre-adsorbed).

For a given compound, under diffusion controlled conditions, a thin layer kinetic model may be adopted to represent the photocurrent under the same mass transport conditions, i.e.:

$$ I_{ph}(t) = nFAD\frac{\partial C(x,t)}{\partial x} \bigg|_{x=0} = \frac{2nFAD\bar{C}^0}{l} \sum_{m=0}^{\infty} \exp\left(-\frac{(2m+1)^2 \pi^2 Dt}{4l^2}\right) $$  \hspace{1cm} (7.9)

where $I_{ph}(t)$ is the instantaneous photocurrent at $t$, $n$ is the number of electrons transferred, $A$ is the apparent area of the electrode surface, $l$ is the thickness of the thin layer cell, $F$ is the Faraday constant, $D$ is the diffusion coefficient of the compound, $\bar{C}^0$ is the initial substrate concentration, $m$ is a whole number (0, 1, 2..) and $t$ is the time elapsed starting from the switch-on of the illumination.
In practice, the fast decay terms in Equation 7.9 can be omitted because the time scales of the very fast terms are not in the time scale of my interest and the time scale of my measurements. I have:

\[
I(t) = \frac{2nFADC^0}{l} \exp\left(-\frac{\pi^2Dt}{4l^2}\right) = \frac{2FADC_{eq}}{l} \exp\left(-\frac{\pi^2Dt}{4l^2}\right)
\]  

(7.10)

where \(C_{eq}\) is the initial equivalent concentration of the substrate.

Theoretically, Equation 7.10 should be equivalent to the slow kinetic component shown in Equation 7.7 under diffusion controlled conditions and I have:

\[
k_1 = \frac{2FADC_{eq}}{l} \quad \text{and} \quad k_2 = \left(-\frac{\pi^2Dt}{4l^2}\right)
\]  

(7.11)

For a given cell and compound, \(F, A, D\) and \(l\) are fixed. Equation 7.11 indicates that \(k_1\) should be directly proportional to the equivalent concentration, \(C_{eq}\), which was demonstrated in Figure 7.8. The calculated \(k_1\) value according to Equation 7.11 is 6.3 \(\mu\)A at 100 \(\mu\)eq substrate concentration (adopting \(1\times10^{-5}\) \(\text{cm}^2\text{s}^{-1}\) for \(D\)), which is close to the experimental \(k_1\) values of 5.2-7.5 \(\mu\)A (with the constant intercept for transient water oxidation deducted). This indicates at very low substrate concentrations the slow kinetic process is mainly controlled by diffusion.

Equation 7.11 also indicates that for a given cell, \(k_2\) depends on only the diffusion coefficient of the compound and should be independent of concentration. My experimental results shown that \(k_2\) is also dependent on the \(C_{eq}\). When \(D=1\times10^{-5}\) \(\text{cm}^2\text{s}^{-1}\) is adopted, the \(k_2\) value estimated by Equation 7 is 0.062 \(\text{s}^{-1}\), which is fairly close to the experimental values of ca 0.038 \(\text{s}^{-1}\) at 10 \(\mu\)eq. This further suggests that at very low concentration the slow process is mainly controlled by diffusion. The variation of \(k_2\) with
concentration clearly indicates that the slow kinetic process is not purely controlled by diffusion and the control step shifts from diffusion control to other steps.

In the case where the dynamic reaction is controlling step for the slow kinetic process, a surface reaction controlled kinetic model can be applied by assuming that concentration is relatively uniform at any cross-section throughout the cavity of the cell:

\[
\frac{dC(t)}{dt} = \frac{Ak(\phi)C_t}{V}
\]  
(7.12)

Solving Equation 7.12 gives:

\[
C(t) = C^0 \exp\left(-\frac{Ak(\phi)t}{V}\right)
\]  
(7.13a)

or

\[
I_{ph}(t) = nFAk(\phi)C^0 \exp\left(-\frac{Ak(\phi)t}{V}\right) = FAk(\phi)C_{eq} \exp\left(-\frac{Ak(\phi)t}{V}\right)
\]  
(7.13b)

where \(n\) is the electron transfer number, \(F\) is Faraday constant, \(V\) is the volume, \(A\) is the electrode area, \(k(\phi)\) is the apparent photocatalytic oxidation rate constant relevant to the light intensity, \(C_t\) is the instantaneous molar concentration, \(C^0\) is the initial substrate concentration and \(C_{eq}\) is the initial equivalent concentration of the compound.

If Equation 7.13b is applicable to the slow kinetic component shown in Equation 7.7 under surface reaction controlled conditions, I then have:

\[
k_1 = FAK(\phi)C_{eq} \quad \text{and} \quad k_2 = \left(-\frac{A(\phi)t}{V}\right)
\]  
(7.14)

For a given cell and light intensity, \(F, A,\) and \(k(\phi)\) are fixed. Equation 7.14 indicates that \(k_1\) should be directly proportional to the equivalent concentration, \(C_{eq}\), which has been
demonstrated in Figure 7.8. Taking the average value of 0.01s $^{-1}$ for $k_2$ at high concentration (2000 µeq) to calculate $k(\varphi)$, the calculated $k_1$ value according to Equation 7.14 is 25.5 µA at substrate concentration of 2000 µeq, which is close to the experimental $k_1$ values of 20-30µA.

From the above rough assessment the slow photocatalytic degradation process can be assigned to the photocatalytic oxidation of non-preadsorbed compounds. It is controlled by the dynamic reaction process at higher substrate concentrations and by diffusion at very low concentration. In the medium substrate concentration range, the slow photocatalytic process is controlled by a combination of both the substrate diffusion step and dynamic reaction step. This is in agreement with the finding that $k_2$ values are independent of the light intensity at very low concentration while dependent on the light intensity at high substrate concentration.

Based on the assignment, the differences in the value of $k_1$ with equivalent concentration for different compounds can be explained. For oxalic acid and nitric acid, at very low concentrations the slow photocatalytic oxidation process is controlled by diffusion, under such condition the current doubling effect can not be fulfilled (for the current doubling effect to be observed, the compound at surface must not be depleted), therefore similar slope of linear $k_1-C_{eq}$ for oxalic acid to those for other compounds was observed. At high concentrations due to the photocatalytic oxidation process is controlled by kinetic process and the compound at surface is not depleted. Under such condition the current doubling effect can be displayed as a result the value of $k_1$ for oxalic acid is much higher than for other compounds. This is similar to observations discussed in Chapter 5 where in bulk cell at low oxalic acid concentrations where diffusion controls, the slope of linear $I_{sphe-C_{eq}}$ equalled those for other organic compounds but at higher concentrations much higher $I_{sphe}$ for oxalic acid than for others was observed.
Based on the features of the fast kinetic process, it can be assigned to the photocatalytic oxidation of the pre-adsorbed substrates (before illumination started). Depending on the affinity of organic compounds to the TiO$_2$ surface, the equivalent amount of pre-adsorption would be different for different organic compounds at the same molar concentration therefore the contribution of photodegradation of the different adsorbed organic compounds to the overall photocurrent would be different. The increase in $k_3$ for strong adsorbates at low concentrations indicates that the amount of pre-adsorbed compounds is increased. The differences in magnitudes of $k_3$ for different organic compounds clearly show this inference. Another evidence for this assignment is that at the pH above 10 where electrode surface is negatively charged and adsorption of phthalic acid is not expected, $k_3$ value is very small similar to other weak adsorbates. Whereas, glucose for which at pH above 10 the adsorption is expected, $k_3$ value of significant magnitude is obtained. The level-off and decrease of $k_3$ at high substrate concentration logically is not due to the decrease in the adsorption amount but due to the recombination of the photoholes and photoelectrons via the partial degraded intermediates. This fast kinetic process certainly is not a simple process but a combination of a few processes as discussed in Chapter 4 about the photocatalytic degradation kinetics of adsorbed organic compounds. With the technique used in this Chapter, further separating them is impossible.

Based on the experimental results it can be concluded that the photocatalytic degradation kinetics of different organic compounds are very similar. This is largely due to the exceptionally high oxidation power of photoholes at TiO$_2$ and the relatively long lifetime of the photoholes at the electrode causing indiscriminate oxidation of all the substrates investigated.
7.4 CONCLUSION

For the first time, the photocatalytic degradation of organic compounds has been studied in the thin layer photoelectrochemical cell by electrochemical methods. By simple subtraction of electrochemical charge in the absence of organic compounds from the charges in the presence of organic compounds, the charges for the photocatalytic degradation of different organic compounds agree well with the theoretical charges corresponding to their complete mineralisation. This, on one hand, has demonstrated that organic compounds with different chemical identities can be stoichiometrically mineralised and on the other hand their mineralisation can be quantified by electrochemical methods with little interference from water oxidation. This provides an excellent base for this approach to be applied for analysis of COD, which will be dealt with in next chapter.

The transient photocurrent can be used to represent the photocatalytic degradation rate. Different organic compounds, when photocatalytic degraded at the electrode in thin layer cell, undergo two kinetic processes, a fast kinetic process and a slow kinetic process. The fast one is attributed to photocatalytic degradation of the pre-adsorbed of organic compounds (surface complexes in the case of strongly adsorbed organic substrates) and the slow one to solution phase organics. The pre-exponential parameters of both processes are related to their initial amounts of corresponding forms (pre-adsorbed and solution phase organics) as is expected by first order reaction law. The variation of the rate constant for the fast kinetic process is most likely related to the heterogeneity of the electrode surface, very common for heterogeneous reactions. The variation of rate constant for the slow kinetic process at low concentration is the result of a transition of rate-controlling step from diffusion to dynamic step, due largely to the change in ratio of photohole supply over photohole demand. The values of each constant for different
organic compounds are markedly different at the same molar concentration. However, at the same equivalent concentration, the values of each constant for different organic compounds are very similar. This indicates that chemical identity is not the critical factor in their photocatalytic degradation kinetics rather the photohole demand is the critical factor. This again demonstrated the electrodes have a universal reactivity towards different organic compounds and have an excellent resistance against the deactivation effect by, in particular, the large photohole demanding organic compounds.
CHAPTER 8 DEVELOPMENT OF A DIRECT PHOTOELECTROCHEMICAL METHOD FOR RAPID DETERMINATION OF CHEMICAL OXYGEN DEMAND
8.1 INTRODUCTION

The fundamentals of photocatalytic degradation of organic compounds at particulate TiO$_2$ film electrodes have been systematically investigated in the previous chapters. The findings indicate that this type of electrode is capable of complete mineralization of wide spectrum of organic compounds in aqueous solutions. The findings also indicate the extent of the photocatalytic oxidation of different organic compounds can be accurately quantified by the resultant photocurrent or charge. Especially, the findings in Chapter 7 with exhaustive degradation mode in a thin layer cell where the charge obtained from mineralization of different organic compounds including those mixtures is directly proportional to the equivalent concentration, which provide us with a firm theoretical foundation for new analytical method development.

The aim of the work presented in this chapter was to develop a novel analytical technique for environmental analysis applications.

As mentioned in Chapter 1, the oxygen demand of water and wastewater represents one of the most important measurable parameters for water quality. There are many inherent problems associated with the measurement of oxygen demand with the two standard methods currently in widespread use$^{181-183, 185-190, 192, 249-251}$. In recent years, a great deal of effort has been devoted to the development of rapid and environmentally friendly new methods for the determination of chemical oxygen demand (COD)$^{182, 183, 188, 190, 192, 249, 250, 252, 253}$. All these new developments have been based on either electrocatalytic$^{188, 190, 192, 250}$ or photocatalytic$^{182, 183, 249, 252, 253}$ oxidation principles. Though the electrocatalytic oxidation method has demonstrated many advantages over the traditional COD methods (such as the rapidity of the analysis, the directness in the
acquisition of analytical signal and the ease of incorporation into on-line analysis monitoring system), the reliability of these new methods are still far from being satisfactory for practical use\textsuperscript{254}. This is mainly due to the fact that the electrocatalytic oxidation method is incapable of oxidizing a wide spectrum of organic compounds indiscriminately.

Photocatalytic oxidation methods, on the other hand, utilize TiO$_2$ particles as the photocatalyst to replace the traditional oxidizing agent (e.g. Cr(IV)). In this process, the oxygen concentration change during photocatalytic degradation of organic matter is measured as the analytical signal using a pair of oxygen electrodes. This depletion of O$_2$ is then correlated with standard COD methods\textsuperscript{254}. The photocatalytic degradation approach is more promising in comparison with electrocatalytic degradation methods due to the strong oxidation power of illuminated TiO$_2$ particles. Despite this, the approach suffers several problems. These include the low fraction of degradation, which is a trade-off for a faster analysis time, low sensitivity caused by the small change in oxygen concentration during degradation, limited dynamic working range due mainly to the low solubility of oxygen in water and the need to control experimental temperature since the accuracy of oxygen concentration measurement by oxygen electrode is highly temperature dependent. Furthermore, the low degradation efficiency makes the method matrix dependent, thus requiring calibration. Because COD is an aggregate parameter, it is difficult to define an appropriate calibration standard, which would be universally applicable to all matrixes. This affects the accuracy and reproducibility of the method. In summary, a significant improvement is required before this method can be practically used – a judgment backed up by researchers themselves with their statement that: “the responses were neither sensitive enough nor reproducible”\textsuperscript{183, 252}. 


The work in this chapter focused on the development of a direct photoelectrochemical method for rapid determination of chemical oxygen demand, namely, PECOD method. The exhaustive photocatalytic degradation in a thin layer photoelectrochemical cell was adopted for analytical method development. TiO$_2$ nanoporous film electrodes calcined at 700°C for 16h were employed due to their indiscriminate photocatalytic oxidation properties.

8.2 EXPERIMENTAL

8.2.1 Materials and Sample Preparation

Indium Tin Oxide (ITO) conducting glass slides (8Ω/square) were commercially supplied by Delta Technologies Limited. Titanium butoxide (97%, Aldrich), potassium hydrogen phthalate (AR, Aldrich), D-glucose (AR, BDH), beef extract (Sigma), peptone (DIFCO laboratories), urea (AR, Ajax), glutamic acid (99%, Sigma). Other chemicals were of analytical grade and purchased from Aldrich or Sigma unless otherwise stated. Artificial water samples and dilution of real waste-water samples were prepared using high purity deionised water (Millipore Corp., 18MΩcm).

The OECD synthetic wastewater sample was prepared according to the Organization for Economic Corporation and Development Guidelines (OECD) with a little modification, which contains 150mg/L peptone, 110mg/L beef extract and 30mg/L urea. This synthetic sample is often used for the calibration of BOD and COD analysis systems. The GGA (glucose and glutamic acid) synthetic sample is often used for BOD$_5$ standard, which contains 150mg/L of glucose and 150 mg/L of glutamic acid and was prepared according to the APHA standard methods.

The real samples used for this study were collected from various industrial sites in South
East Queensland (Australia) including wastewater treatment plants, sugar plants, breweries, canneries and dairy plants. All samples were preserved according to the guidelines. When necessary, both synthetic and real samples were diluted to a suitable concentration prior to analysis. After dilution, the same sample was subject to the analysis by both standard COD and photoelectrochemical oxygen demand (PECOD) methods. For PECOD method solid NaNO₃, equivalent to 2M, was added as a supporting electrolyte.

8.2.2 Preparation of the Nanoporous TiO₂ Film Electrodes

The TiO₂ colloid synthesis and immobilisation procedures are the same as described in section 2.2.2. The electrodes used in this chapter were calcined at 700°C for 16h.

8.2.3 Apparatus and Methods

The experimental set-up is the same as described in Figure 2.2 except that the thin layer photoelectrochemical cell is used instead of the bulk cell. The schematic diagram of the thin layer photoelectrochemical cell was shown in Figure 7.1. The cavity of the thin layer was defined by an aperture in the spacer, which was 0.20 mm in thickness and 9.30 mm in diameter. The area of the thin layer was 0.68cm², while the volume of the anodic compartment was 13.6µL. A built-in saturated Ag/AgCl electrode and a built-in platinum mesh were used as the reference and auxiliary electrodes respectively. To minimize the solution resistance influence on the photocurrent response, 2.0M NaNO₃ electrolyte was used as the supporting electrolyte. A voltammograph (CV-27, BAS) was used for application of potential bias in the transient photocatalysis experiments and linear potential sweep experiments. Potential and current signals were recorded employing a Macintosh computer (7220/200) coupled to a Maclab 400 interface (AD Instruments). Illumination was carried out using a 150W xenon arc lamp light source with focusing
lenses (HF-200W-95, Beijing Optical Instruments). To avoid the sample solution being heated-up, the light beam passed an UV-band pass filter (UG5, Avotronics Pty, Limited) prior to illumination of the electrode surface. Sample solution was injected into the thin layer cell with a syringe through the inlet channel. Care was taken to eliminate the air bubbles in the thin layer cell cavity. A delay of 30 s was allowed after sample injection sample solution before illumination of the electrode surface commenced.

Standard COD values (dichromate method) of all samples were measured with a COD analyser (NOVA 30, Merck).

The electrochemical charges for the photocatalytic degradation of organic matters were obtained in the same way as described in section 7.3.2.

Correlation analysis was employed to evaluate the agreement between the COD values measured by PECOD and by the standard method. The Pearson Correlation coefficient was used as a measure of the intensity of association between the values obtained from the PECOD method and the standard COD method. This was employed for the data in Figures 8.5 and 8.6. To characterize the trend of the two-way scattergram in Figures 8.5 and 8.6, the slope of the principle axes of the correlation ellipse was calculated. This was done in preference to simple linear regression analysis since regression analysis assumes the x-values are measured with no (or negligible) error and that the y-values are the dependent, normally distributed variables. This is not the case for correlation between PECOD values and the standard COD values.

8.3 RESULTS AND DISCUSSION

8.3.1 Principles

TiO_2 photocatalysis leads to stoichiometric mineralisation of organic compounds. The
oxidation of organic compounds at the electrodes can be represented by the following electrode reaction equation:\textsuperscript{182, 252}

\[ C_yH_mO_jN_kX_q^+ + (2y-j)H_2O \rightarrow \]

\[ yCO_2 + qX^- + kNH_3 + (4y-2j+m-3k)H^+ + (4y-2j+m-3k-q)e^- \] (8.1)

where N and X represents a nitrogen and a halogen atom respectively. The numbers of carbon, hydrogen, oxygen, nitrogen and halogen atoms in the organic compound are represented by \( y, m, j, k \) and \( q \).

According to Equation 8.1, the number of electrons transferred for a given organic compounds can be calculated:

\[ n = 4y - 2j + m - 3k - q \] (8.2)

The charge for the mineralization of organic matter can be measured experimentally. In order to minimize the degradation time and maximize the degradation efficiency, the photoelectrochemical catalytic degradation of organic matter was carried out in a thin layer photoelectrochemical cell. This process is analogous to bulk electrolysis in which 100% of the analytes is electrolyzed and Faraday’s Law can be used to quantify the concentration by measuring the charge passed if the charge/current produced is the result of photoelectrochemical degradation of organic matter. That is:

\[ Q = \int I_{ph} dt \] (8.3)

where \( I_{ph} \) is the photocurrent from the oxidation of organic compounds and \( t \) is time elapsed upon illumination.

With exhaustive degradation mode, the measured net charge, \( Q \), is a direct measure of the
total amount of electrons that results from the complete mineralisation of all compounds in the sample. Since one oxygen molecule is equivalent to 4 electrons transferred ($O_2 +4H^+ +4e^- \rightarrow 2H_2O$), the measured $Q$ value can be easily converted into an equivalent $O_2$ concentration (or oxygen demand). The equivalent COD value can therefore be represented as:

$$COD (mg / L of O_2) = \frac{Q}{4FV} \times 32000 \quad (8.4)$$

Equation 8.4 can be used to quantify the COD value of a sample since the net charge, $Q$, can be obtained experimentally and for a given photoelectrochemical cell, while the volume, $V$, and the Faraday constant, $F$, are known constants.

For a given solution composition of given organic compounds the theoretical charge ($Q_{\text{theoretical}}$) for mineralization can also be calculated:

$$Q_{\text{theoretical}} = nFVC \quad (8.5)$$

where $C$ is the molar concentration of the compounds.

The theoretical COD value can then be calculated according to $Q_{\text{theoretical}}$ as:

$$COD_{\text{theoretical}} (mg / L of O_2) = \frac{Q_{\text{theoretical}}}{4FV} \times 32000 = 8000nC \quad (8.6)$$

The closeness of the measured COD and the theoretical COD values for known concentrations of known compounds is a direct test of the proposed concept.

**8.3.2 Optimization of Analytical Signal**

In previous chapters, the effect of various experimental parameters on
photoelectrochemical oxidation of organic compounds at the TiO$_2$ film electrode has been investigated $^{11}$. In order to obtain the suitable experimental conditions for this particular analytical application, the system was further optimized.

The effect of applied potential bias and light intensity were investigated. As the applied potential bias was increased up to a critical value, a linear increase in the rate of oxidation was observed. Beyond the critical value, the rate of oxidation leveled off. The critical values of the potential bias were between +0.08 V and +0.18V vs Ag/AgCl reference electrode depending on the light intensity and the concentration of organics in the solution. In order to ensure a sufficient potential bias under various conditions and at the same time minimizing the direct electrochemical reaction, a potential bias of +0.30V was selected for all experiments (see also Section 7.3.1). The rate of oxidation at sufficient potential bias was directly proportional to the applied light intensity. For this study, a light intensity of 6.6mW cm$^{-2}$ was selected.

The pH impact on the reaction rate and signal sensitivity was also investigated. The result showed that in the pH range from pH 2-10, the photocurrents in solutions with and without organic compounds remains almost unchanged with pH, which is similar to the situation in TiO$_2$ slurry system where the photocatalytic degradation rate of organic compounds is little influenced by pH change $^{123}$. Beyond this pH range the electrodes are not physically stable.

In thin layer cell due to the very thin solution channel between working electrode and reference electrode the large solution resistance often impairs the current signal. As discussed in Chapter 7 for my thin layer cell when 2M NaNO$_3$ supporting electrolyte is used well defined photocurrent signal can be obtained.
8.3.3 Measurement of Analytical Signal

Figure 8.1 shows a set of typical photocurrent-time profiles obtained from the exhaustive degradation of a potassium hydrogen phthalate (KHP) solution and from oxidation of a blank solution in the thin-layer photoelectrochemical cell. The net charge for the exhaustive degradation of KHP can be obtained in the same way as described in 7.3.2. For all the other samples, the same approach was applied to obtain the net charge. This net charge can then be used to quantify the COD value of a sample according to Equation 8.4.

![Figure 8.1](image.png)

**Figure 8.1** Photocurrent response of (a) 2M NaNO₃ and (b) a 2M NaNO₃ solution containing potassium hydrogen phthalate.

8.3.4 Validation of Analytical Principle

In order to make meaningful comparisons between the standard COD method and the PECOD method, potassium hydrogen phthalate, the organic standard employed in the
standard COD method, was chosen for method validation experiments. Figure 8.2 shows the relationships between the net photoelectrochemical charge and the theoretical COD value. The theoretical COD value was calculated based on Equation 8.6 using the molar concentration of KHP.

![Figure 8.2](image)

**Figure 8.2** The relationship of photoelectrochemical charge with theoretical COD value for potassium hydrogen phthalate solution.

As predicted by Equation 8.4, an excellent linear relationship ($R^2=0.9962$) between the net charge obtained from the exhaustive photocatalytic degradation and the theoretical COD value was obtained. More importantly, the experimental slope (0.15931 mC/COD (mg/L of O$_2$)) obtained from the above data is almost identical to the theoretical slope ((0.163 mC/COD (mg/L of O$_2$)) calculated from Equation 8.4. This demonstrates that the photoelectrolysis process is exhaustive and the degree of potassium hydrogen phthalate oxidation is complete. This also demonstrates that a 100% charge collection efficiency has been achieved. In other word, the charge generated from the photocatalytic degradation of organic compounds can be quantitatively collected.

A number of different organic compounds and their mixture with known concentrations
were also investigated. Figure 8.3 shows the plot of the net charge against the theoretical COD values calculated from Equation 8.6 (see the data sets 1 to 8). The data set 9 was obtained from a sample mixture containing equal molar concentration of all organics used for individual experiments. By converting the molar concentrations of individual organic compounds into the equivalent theoretical COD concentrations, I effectively normalized the molar concentration scale into the same measurement scale, i.e. the theoretical COD scale. Therefore, the charge measured for all compounds should fit onto one linear line if the analytical principle proposed in Equation 8.4 is correct.

\[ y = 0.16x - 0.0531 \]
\[ R^2 = 0.992 \]

The result revealed that all compounds investigated including the mixture sample, were fitted into a linear line with \( R^2 = 0.992 \), which demonstrates the viability of the proposed analytical principle. The slope of the curve can be used to evaluate the degree of photoelectrochemical catalytic degradation (oxidation). The theoretical slope of the curve

**Figure 8.3** The quantitative relationship between the net charge and theoretical COD: 1: p-chlorophenol; 2: potassium hydrogen phthalate (KHP); 3: methanol; 4: d-glucose; 5: malonic acid; 6: succinic acid; 7: glutaric acid; 8: glycine; 9: mixture of 1 to 8 with equal COD concentration of each.
equal to 0.163 mC [mgL\(^{-1}\) of O\(_2\)]\(^{-1}\) can be calculated according to Equation 8.4 by substituting 13.6\(\mu\)L (the designed cell volume) for the volume of the thin layer cell. The experimental slope obtained was 0.160 mC [mgL\(^{-1}\) of O\(_2\)]\(^{-1}\), which is 98% of the theoretical slope value (the 2% error is likely to be an error in estimating the actual volume of the cell). These results suggest that all organic compounds investigated were stoichiometrically oxidized. This can be further evidenced by plotting the PECOD values against the theoretical COD values as shown in Figure 8.4, where the line of best fit with the slope=0.9957 and \(R^2=0.990\) were obtained. This demonstrates that the method measures essentially the theoretical COD values.

Figure 8.4 The correlation between the PECOD and traditional COD methods. 1: p-chlorophenol; 2: potassium hydrogen phthalate (KHP); 3: methanol; 4: d-glucose; 5: malonic acid; 6: succinic acid; 7: glutaric acid; 8: glycine; 9: mixture of 1 to 8 with equal COD concentration of each.

The detection limit, linear range and reproducibility were also examined. It was found that a real detection limit of 0.20 mgL\(^{-1}\) COD with linear range up to 200 mgL\(^{-1}\) COD can be achieved under the experimental conditions employed. It is noted that the detection
limit can be further improved by increasing the sample volume and the linear range can be increased by decreasing the sample volume. The reproducibility was evaluated by performing 17-replicate analyses of a KHP sample at a concentration equivalent to 15.0 mgL\(^{-1}\) COD. The relative standard deviation obtained was 0.87%.

8.3.5 Analysis of Synthetic and Real Samples

The applicability of the proposed principle was further tested using three other different types of synthetic samples and measuring their COD values by both the PECOD method and the standard COD method as shown in Figure 8.5.

![Figure 8.5](image_url)

**Figure 8.5** The correlation between the PE and standard dichromate COD methods for the synthetic COD test samples. 1: KHP; 2: GGA; 3: OECD; 4: Mixture of the compounds 1 to 8 in Figure 3 with equal COD concentration of each.

The COD values obtained from the two methods agreed well as demonstrated by the high significant correlation between the two sets of COD values \((r=0.995, P<0.001, n=27)\) and the slope of the principle axis of the correlation ellipse of 0.9887. At 99% confidence
interval, this slope was between 0.9400 and 1.0400 – with the ideal slope being unity.

Analysis of several types of real samples was also carried out. These real samples were collected from various industrial sites and were again analyzed by both standard dichromate COD and newly developed PECOD methods. The correlation between the two methods is given in Figure 8.6.

\[
y = 1.0040x - 0.0384 \\
r = 0.987 \\
P < 0.001 \\
n = 15
\]

Figure 8.6  The correlation between the PECOD and standard dichromate COD methods for the real sample measurements. 1 to 3 are the samples collected from wastewater treatment plants; 4 to 6 are the samples collected from sugar plants; 7 to 11 are the samples collected from brewery manufacturers and cannery manufacturers; 12 to 15 are the samples collected from dairy and food production plants.

A highly significant correlation \( r = 0.987, P < 0.001, n = 15 \) between the two methods was obtained indicating the two methods agreed very well. More importantly, the slope of the principle axis of the correlation ellipse of 1.004 was obtained. This almost unity slope value suggests both methods were accurately measuring the same COD value. Given a 95% confidence interval, this slope was between 0.9237 and 1.0916. This implies that I can be 95% confident that the true slope lies between these two values. Considering that
there are analytical errors associated with both the PECOD and the standard method measurements and that these errors contribute to scatter on both axes, the strong correlation and slope obtained provides compelling support for the suitability of the PECOD method for measuring chemical oxygen demand.

At this stage, a major problem associated with the photoelectrochemical method is the interference by chloride ion in the samples. Preliminary experiments indicate that when the concentration of chloride ion exceeds 0.5mM the photocurrent decay curve was deformed. Under such condition it is not possible to accurately determine the photoelectrochemical charge associated with the degradation of organic compounds due to the photocatalytic oxidation of chloride ion at the electrode. Work to eliminate (or mask) the chloride interference is currently being carried out but is not part of the present study.

8.4 CONCLUSION

A novel COD analytical method has been proposed and experimentally validated. The developed method has also been successfully applied to determine the COD of a range of synthetic and real samples. The method is sensitive, with detection limits as low as 0.2 mgL$^{-1}$ COD. The method is also environmentally friendly, robust, rapid and easy to be automated. It requires only 1 to 5 minute to complete an assay and consumes very limited reagent (electrolyte only). More importantly, this method is a direct and absolute method. It does not require calibration standards. The method, in principle, measures the theoretical COD value due to the extraordinary high oxidation efficiency and accuracy of charge measurement. This method is free of the matrix effect due to the highly effective photoelectrochemical system employed that is capable of fully oxidizing a wide spectrum of organics in the sample exhaustively.
At current stage, the method cannot be used for samples with chloride concentration exceeding 0.5mM. Further studies are currently in progress to overcome the problems associated with chloride interference. I am confident that this method can be further developed into an on-line real-time COD monitoring system.
CHAPTER 9  GENERAL CONCLUSIONS
A series of simple, rapid and effective photoelectrochemical methodologies have been developed and successfully applied to the study of kinetic and thermodynamic characteristics of photocatalytic oxidation processes at TiO$_2$ nanoparticulate films. This work represents the first systematic study of TiO$_2$ photocatalysis by photoelectrochemical techniques. The methodologies developed have been demonstrated to be effective and useful. A number of significant findings have been made for the first time, which shed light on many aspects of photocatalytic processes at TiO$_2$ surfaces. More importantly, the methodologies developed and the new findings in this work are highly valuable for future studies in this field. These have a far-reaching significance beyond what have been described in this thesis.

As an application of the systematic studies of photocatalytic processes by photoelectrochemical techniques, a rapid, direct, absolute, environmental-friendly and accurate COD analysis method was successfully developed, which achieved degradation of organic matter and acquisition of an analytical signal at the same time.

Throughout this work, a number of electrochemical techniques were adapted to fit for the study of photocatalytic processes. The following outlines the techniques adapted or developed:

1. Linear sweep voltammetry was adapted for the investigation of effects of potential bias on the overall photocatalytic process at particulate semiconductor electrodes. It was found that at TiO$_2$ nanoporous film electrodes potential bias can change the overall control step of photocatalytic processes – from electron transport limitations at low potential bias to the photohole capture process at high potential bias.

2. A transient technique (illumination step method analogous to potential step method in conventional electrochemistry), at potentials where electron transport in the film
was not the controlling step, was developed for the measurements of strong adsorbate adsorption on TiO$_2$ surfaces. The photocatalytic degradation kinetics of the pre-adsorbed adsorbates can be studied by processing photocurrent-time responses, which offers photocatalytic degradation kinetic information without the influence of electron transport in the films, the mass transfer process of reactants and the kinetics of electron removal process.

3. A steady state photocurrent method, carried out in bulk solution at potentials where electron removal process was not rate determining step, was developed for the investigation of photohole capture kinetics. This method allows the rapid and direct acquisition of the photocatalytic degradation kinetic data of large number of organic compounds under the identical conditions.

4. A thin-layer photoelectrochemical technique, analogous to the thin-layer exhaustive electrolytic technique, was developed. This allows the quantification of photocatalytic degradation of organic compounds and study of photocatalytic degradation kinetics of organic compounds in an exhaustive degradation mode.

In this work, these techniques were employed for the study of photocatalytic processes on TiO$_2$. The following summarises the important general conclusions from the study:

1. By employing steady state photocurrent methods and choosing phthalic acid as the model compound, the photocatalytic activity of the TiO$_2$ nanoporous films calcined at various temperatures and for different lengths of time was evaluated. The photocatalytic activity of films was compared with their physical structures. It was found that films with mixed anatase and rutile phases calcined at high temperature exhibited high photocatalytic activity. A model was proposed based on semiconductor band theory, which explained this finding. That is, due to the band edge position differences in anatase and rutile semiconductors,
photoelectrons transfer from anatase phase to rutile phase, resulting in spatial separation of photoelectrons from photoholes. As a result, the lifetime of photoelectrons and photoholes is increased, leading to a decrease in the rate of photoelectron/photohole recombination. The finding confirmed other researchers’ speculation that the coexistence of the rutile phase with the anatase phase had a synergistic effect on the photocatalytic activity of TiO$_2$ photocatalysts.

2. By employing linear sweep voltammetry and choosing glucose (an effective photohole scavenger) as a model compound, the characteristics of the photocatalytic processes at nanoparticulate semiconductor electrodes were investigated. Characteristics of the nanoporous semiconductor electrodes markedly different from bulk semiconductor electrodes have been observed in that within a large range of electrode potentials above the flat band potential the electrodes behaved as a pure resistance instead of exhibiting the variable resistance expected for bulk semiconductor electrode. The magnitude of the resistance was dependent on the properties of the electrodes and the maximum photocatalytic oxidation rate at the TiO$_2$ surface determined by the light intensity and organic compound concentration. Through the analysis of the resistance, it was found that the mechanism of electron transport in the film was the electron migration under electric field. A long existing hypothesis that in nanoparticulate semiconductor systems the photoelectron/photohole separation can only be achieved by the removal of at least one charge carrier, via reaction at the semiconductor surface, was proven to be true. It was found that the role of potential bias at nanoparticulate semiconductor electrodes was to remove electrons freed by the photohole capture reaction at the TiO$_2$ surface, which is totally different from its role in bulk semiconductor electrodes. This cleared up the misunderstandings in literature regarding the role of potential bias. A model was proposed, which
explained well the special characteristics of particulate semiconductor electrodes (nanoporous semiconductor electrodes). This is the first clear description of the overall photocatalytic process at nanoparticulate semiconductor electrodes. The investigation set a theoretical foundation for employing photoelectrochemical techniques to study the kinetics and thermodynamics of photocatalytic processes.

3. By using the transient technique (illumination step method), the adsorption of a number strong adsorbates at both low temperature and high temperature calcined TiO$_2$ nanoporous films was investigated. Similar adsorption characteristics for different adsorbates on different films were observed. In all the cases, three different surface bound complexes were identified, which was attributed to the heterogeneity of the TiO$_2$ surface. The photocatalytic degradation kinetics of pre-adsorbed organic compounds of different chemical nature was studied. Two different photocatalytic processes, exhibiting different rate characteristics, were observed. This was, again, attributed to the heterogeneity of the TiO$_2$ surface corresponding to heterogeneous adsorption characteristics. By modelling the photocatalytic degradation processes of different adsorbed organic compounds, the catalytic first order rate constants of both the fast and slow processes were obtained for different organic compounds. It was found that for different adsorbates of different chemical nature the magnitudes of rate constant for the slow kinetic process were very similar, while the magnitudes of rate constant for the fast process were significantly affected by the photohole demand characteristics of different adsorbates. Photohole demand distribution at the TiO$_2$ surface, depending on the size and structure of the adsorbed molecules, was believed to be responsible for the difference. At the mixed phase TiO$_2$ nanoporous electrodes both the fast and slow kinetic processes were found to be much less dependent on the photohole demand characteristics of the adsorbed molecules.
This is because the photoelectron transfer between anatase phase and rutile phase spatially separates the photoelectrons and photoholes, which prolong the lifetime of photoelectrons and photoholes.

4. By employing the steady state photocurrent method, the photocatalytic degradation kinetic characteristics of both strong adsorbates and weak adsorbates of different chemical structures were compared at pure anatase TiO₂ nanoporous films as well as at anatase/rutile mixed phase TiO₂ nanoporous film electrodes. At the former electrodes, for all the different organic compounds studied, the photocatalytic reaction rate increased linearly with concentration at low concentrations. Under such conditions it was demonstrated that the overall photocatalytic process was controlled by diffusion and was independent of the chemical nature of organic compounds. In other words, all the molecules reaching electrode surface were stoichiometrically mineralized. However, the linear concentration range and the maximum photocatalytic reaction rate at high concentrations were significantly dependent on the chemical nature of the organic compounds. This was explained by the difference in the interaction of different organic compounds with TiO₂ surface, the difference in their photohole demand distribution at the TiO₂ surface and the difference in their nature of intermediates formed during their photocatalytic mineralization. In contrast, at the latter electrodes, the linear ranges (diffusion control concentration range) and the maximum reaction rates at high concentration were larger than at the former electrodes and much less dependent on the chemical nature of the organic compounds. The spatial separation of photoelectrons and photoholes (due to the presence of rutile phase and anatase phase) and the increase in the lifetime of photoelectrons and photoholes are responsible for the excellent photocatalytic activity of the electrodes. Overall the photocatalytic degradation kinetic characteristics of different organic compounds
depend on the photohole supply (i.e. light intensity), the supply of organic compounds, the interaction between the organic compounds and the TiO$_2$ surface, and the intrinsic photoelectron/photohole recombination nature of the photocatalyst. If the photohole supply rate were infinite, all organic compounds regardless of chemical identities at any concentrations at any TiO$_2$ nanoporous film electrodes would be degraded under diffusion control. On the other hand, if there were no photoelectron/photohole recombination (or the lifetime of photoelectron/photohole is so long that the recombination would not become a determining factor), the photocatalytic oxidation of any organic compounds, regardless of chemical identities, would take place under diffusion control up to concentrations until the photohole capture rate reaches the limit of photohole supply (at the point photoefficiency of 100% would be achieved). Unfortunately these extreme conditions are either not practical or not economical. The finding, however, point out a general direction in the pursuit for photocatalysts of high and universal activity towards photocatalytic degradation of a wide spectrum of organic pollutants.

5. The photocatalytic oxidation of different organic compounds at the mixed phase TiO$_2$ nanoporous electrodes were investigated in a thin layer photoelectrochemical cell. Exhaustive photocatalytic oxidation was performed. It was found that the charge derived from exhaustive oxidation agreed well with theoretical charge expected for the mineralisation of a specific organic compound. This finding was true for all the compounds investigated and was also true for mixtures of different organic compounds. The photocatalytic degradation kinetics of different organic compounds of different chemical identities in the thin layer cell was also investigated by the photoelectrochemical method. Two kinetic processes of different decay time constants were identified and were attributed to the
degradation of preadsorbed compounds and the degradation of compounds in solution. For the degradation of compounds in solution, a change in the overall control step from diffusion to heterogeneous surface reaction was observed. By examination of the degradation rate constant of the process (slow kinetic process), it was found that for different organic compounds the variation of the rate constant is determined by the photohole demand rather than by the chemical identities of the compounds. The kinetics of the fast kinetic process, on the other hand, is greatly affected by the adsorption properties of the specific compounds. For the strong adsorbates the rate is much larger than for weak adsorbates. However the rate constant of the process is independent of the chemical identities of the compounds and the variation of the constant is also determined by the photohole demand. The similarities in photocatalytic degradation kinetics for different organic compounds can be partly attributed to the nature of TiO$_2$ photocatalysis and partly (particularly at high substrate concentrations) attributed to the long lifetime of photoelectrons and photoholes due to the coexistence of anatase and rutile phases in the film.

6. Based on the principles of exhaustive photoelectrocatalytic degradation of organic matter in a thin layer cell, a novel, rapid, direct, environmentally-friendly and absolute COD analysis method was developed. The method was tested on synthetic samples as well as real wastewater samples from a variety of industries. For synthetic samples with given compositions the COD values measured by the method agree very well with theoretical COD value. For real samples and synthetic samples the COD values measured by the method correlated very well with those measured by standard dichromate COD analysis method.
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