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Mixed-valence titanium oxide materials as photocatalyst and electrocatalyst

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Thesis submitted for the degree of PhD
The University of Edinburgh
January 2024
Declaration

I declare that this thesis has been composed solely by myself and that it has not been submitted, in whole or in part, in any previous application for a degree. Except where states otherwise by reference or acknowledgment, the work presented is entirely my own.

Yishu Zhang

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January 2024
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Lay Summary

Water use in the world is expected to grow continuously, and water scarcity has been a severe problem all around the world, especially in low-income countries. Approximately 26% of the world’s population lack safely managed drinking water services. Wastewater treatment is an effective way of reducing freshwater contamination and increasing the recycling of water. The aim of wastewater treatment is to remove toxic pollutants and kill microbes, and make the water safe to drink or use in daily life. Due to the high energy demand and high cost, large scale water treatment facilities are difficult to apply in low-income areas. Low-cost materials for smaller scale water treatment facilities were studied in this work.

Two kinds of water treatment systems were used in this work. The first one used electricity to produce chlorine from saline water on the surface of a solid material, such that the chlorine can destroy the pollutants. The second one used light, which when shone on a solid material, can lead to destruction of the pollutants on the surface of the material. Both of these can be efficient methods for water treatment, the first one only need a small amount of the electricity, and the second one only requires sunlight.

The solid materials used in the water treatment systems above were all titanium oxides, which is a series of low-cost, non-toxic and stable materials, and have appropriate properties for efficiently removing pollutants in water. Powder material applied to water treatment can lead to a problem that removing and collecting the powders after use, which can be difficult. In this work, these materials were first prepared as powders, then immobilized on glass slides, so they can be easily removed from water after use, and used multiple times.
Abstract

Mixed-valence titanium oxide materials have been reported as potential catalysts in water purification. Ti(III) doped titanium dioxide (TiO\(_2\)), also called “black TiO\(_2\)”, has been thought as a better photocatalyst than TiO\(_2\) without Ti(III), because doping Ti(III) leads to a larger light absorption range and a better charge separation without disrupting the crystal structure and band structure of pristine TiO\(_2\). Ti\(_2\)O\(_3\) and Magnéli phase titanium oxide (chemical formula Ti\(_n\)O\(_{2n-1}\), n=3~9) have been studied as electrode materials for electrocatalytic water purification, since they have higher conductivities than most semiconductor materials, and also have high stability in the electrochemical system. In this work, mixed-valence titanium oxide materials were synthesized and immobilized on substrates in order to enable convenient reuse. Photocatalytic and electrocatalytic tests of the materials against different model pollutants in water were carried out and discussed.

Ti\(_2\)O\(_3\) powder was immobilized on FTO glass slides to form electrodes for electrocatalysis by doctor blading and annealing under air. XRD patterns showed that nearly all of Ti(III) in Ti\(_2\)O\(_3\) remained after annealing at 400 °C for 30 min. Electrochemical characterization measured in chloride-rich electrolyte showed that the chlorine evolution reaction (CER) was more favorable than the oxygen evolution reaction (OER) for the Ti\(_2\)O\(_3\) film electrode. The Ti\(_2\)O\(_3\) film electrode showed high efficiency of free chlorine production, which leads to a good performance in degrading methyl orange (97.9% in 1.5h) and tetracycline (78.0% in 1.5h) via chlorine evolution. Pollutant degradation reaction by chlorine is observed to be the major reaction (75%) in this electrochemical water treatment system, while direct electron transfer (DET) reaction also contributed to pollutant degradation. Ti\(_2\)O\(_3\) film electrodes can work efficiently for several cycles with the help of an easy regeneration step between cycles.

Magnéli phase titanium oxide materials were synthesized via two carbothermal reduction methods and were immobilized on FTO glass slides to form electrodes by the same method as Ti\(_2\)O\(_3\) powder. PXRD patterns and SEM
images of Magnéli phase titanium oxide powder samples showed that among samples prepared via the same method, increased annealing temperature led to more highly reduced phase with bigger particle size. Although Magnéli phase titanium oxide film electrodes showed ability to oxidize chloride and degrade organic pollutants, electrochemical characterization suggested poor conductivities and unfavourable kinetics, which led to a low yield of chlorine evolution and low efficiency of pollutant degradation.

Ti(III) doped TiO$_2$ materials were produced via sodium borohydride (NaBH$_4$) reduction, carbothermal reduction, and solvothermal reaction. Powder materials were then immobilized on plain glass slides to form thin films. All samples were found to have different quantities of Ti(III) doping, while the crystal structure are anatase and/or rutile, the two main polymorphs of TiO$_2$. Samples made by solvothermal reaction were able to absorb more visible light, and catalyze a 50% degradation of Rhodamine B in 3h under 410 nm LED light.
Contents

Declaration ................................................................................................................................. 1
Acknowledgements ..................................................................................................................... 2
Lay Summary .................................................................................................................................. 4
Abstract .......................................................................................................................................... 5
Chapter 1  Introduction ................................................................................................................ 10
  1.1  Challenges of water treatment ............................................................................................. 10
  1.2  Mechanisms of photocatalytic and electrocatalytic water treatment on semiconductors ............................................................................................................................. 11
    1.2.1  Photocatalytic mechanism of semiconductors .............................................................. 11
    1.2.2  Electrocatalytic mechanism of semiconductors ............................................................ 13
  1.3  Pristine TiO$_2$ and black TiO$_2$ as photocatalysts .............................................................. 16
    1.3.1  TiO$_2$ as a photocatalyst .............................................................................................. 16
    1.3.2  Black TiO$_2$ and its properties .................................................................................... 17
    1.3.3  Synthesis methods of black TiO$_2$ ................................................................................ 21
    1.3.4  Further modifications of black TiO$_2$ .......................................................................... 24
    1.3.5  Performance of black TiO$_2$ as a photocatalyst .......................................................... 25
  1.4  Ti$_2$O$_3$ and its application as an electrocatalyst ................................................................. 28
    1.4.1  Ti$_2$O$_3$, synthesis and properties .............................................................................. 28
    1.4.2  Applications of Ti$_2$O$_3$, especially as an electrocatalyst .......................................... 30
  1.5  Magnéli phase titanium oxides and their applications ....................................................... 31
    1.5.1  Properties of Magnéli phase titanium oxides ............................................................... 31
    1.5.2  Synthesis methods of Magnéli phase titanium oxides ................................................. 35
    1.5.3  Magnéli phase titanium oxides as electrocatalysts .................................................... 37
  1.6  Summary .................................................................................................................................. 42
References ..................................................................................................................................... 45
Chapter 2  Experimental ................................................................................................................ 51
  2.1  Chemicals and materials ..................................................................................................... 51
  2.2  Sample preparation by doctor blading ................................................................................ 51
  2.3  Diffuse Reflectance, Kubelka Munk equation and Tauc plots .......................................... 52
  2.4  X-ray Powder Diffraction and crystallite size from the Scherrer
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3.2</td>
<td>Electrochemistry</td>
<td>91</td>
</tr>
<tr>
<td>4.3.3</td>
<td>Mott-Schottky plot</td>
<td>93</td>
</tr>
<tr>
<td>4.3.4</td>
<td>Free chlorine capture and MO degradation</td>
<td>95</td>
</tr>
<tr>
<td>4.3.5</td>
<td>Electrocatalytic test</td>
<td>97</td>
</tr>
<tr>
<td>4.4</td>
<td>Conclusions</td>
<td>100</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>102</td>
</tr>
<tr>
<td>Chapter 5</td>
<td>Low-cost black titanium dioxide preparation and application in</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>photocatalytic water treatment</td>
<td></td>
</tr>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>103</td>
</tr>
<tr>
<td>5.2</td>
<td>Experimental</td>
<td>104</td>
</tr>
<tr>
<td>5.2.1</td>
<td>P25 TiO₂ reduction using NaBH₄</td>
<td>104</td>
</tr>
<tr>
<td>5.2.2</td>
<td>Solvothermal method</td>
<td>105</td>
</tr>
<tr>
<td>5.2.3</td>
<td>Carbothermal reduction</td>
<td>106</td>
</tr>
<tr>
<td>5.2.4</td>
<td>Film formation</td>
<td>106</td>
</tr>
<tr>
<td>5.2.5</td>
<td>Photocatalytic testing</td>
<td>107</td>
</tr>
<tr>
<td>5.3</td>
<td>Result and discussion</td>
<td>109</td>
</tr>
<tr>
<td>5.3.1</td>
<td>Black TiO₂ produced by NaBH₄ reduction</td>
<td>109</td>
</tr>
<tr>
<td>5.3.2</td>
<td>Black TiO₂ produced by solvothermal method</td>
<td>113</td>
</tr>
<tr>
<td>5.3.3</td>
<td>Reduced TiO₂ prepared via carbothermal reduction</td>
<td>118</td>
</tr>
<tr>
<td>5.4</td>
<td>Conclusions</td>
<td>123</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>126</td>
</tr>
<tr>
<td>Thesis conclusion and outlook</td>
<td></td>
<td>127</td>
</tr>
<tr>
<td>Published work</td>
<td></td>
<td>130</td>
</tr>
</tbody>
</table>
Chapter 1  Introduction

1.1 Challenges of water treatment

Water scarcity has been a severe problem across the world as a result of physical water stress and freshwater pollution.\(^1\) Two billion people worldwide still lacked a safely-managed drinking water service in 2020.\(^2\) Wastewater containing contaminants produced by industrial, agricultural, medical and domestic activities has been a worldwide environmental problem.\(^3\) Wastewater collection and treatment help prevent contaminants from entering the environment, thereby protecting freshwater systems and human health.\(^2\) The sixth Sustainable Development Goal (SDG 6) set by United Nation aims to ensure availability and sustainable management of water and sanitation for all. Target 6.3 of SDG 6 gives a global goal of “by 2030, improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally”.\(^4\)

Although progress has been made on wastewater treatment in recent decades, approximately 44% of domestic wastewater and 70% of industrial wastewater worldwide was not safely treated prior to release into the environment.\(^1\)\(^2\) Furthermore, clear disparities of proportions of wastewater being safely treated were found between high-income countries and low- and middle-income countries, indicating that progress remains uneven across the globe.\(^5\) On average, high-income countries treat about 70% of the wastewater they generate, while in low-income countries, only 8% of industrial and municipal wastewater undergoes treatment of any kind.\(^4\) Poor water quality in low-income countries is often related to low levels of wastewater treatment.\(^1\) Wastewater treatment plants applied to urban and industrial wastewater need a wastewater collection network and facilities for physical, chemical and biological processes, along with high energy and material costs. Large centralized water treatment systems require a large up-front capital expenditure and relatively high operation and maintenance costs, which
makes the application of water treatment systems difficult in low-income countries. Small-scaled and low-cost water treatment systems are expected to be a solution to water pollution problems in low-income areas.

In recent years, photocatalytic and electrocatalytic water treatment have attracted a lot of attention from researchers. Both of them can be applied in limited spaces or even small containers, and the processes are quite easy and safe. Electrocatalytic water treatment systems need much less energy than traditional water treatment systems, while photocatalytic water treatment systems may only need sunlight as the energy source. A series of non-toxic and stable semiconductors have been shown to be effective in photocatalytic and electrocatalytic reactions for removing contaminants in wastewater.\textsuperscript{[6][7]}

1.2 Mechanisms of photocatalytic and electrocatalytic water treatment on semiconductors

1.2.1 Photocatalytic mechanism of semiconductors

Toxic organic molecules, toxic metal ions and bacteria are three main targets for removal from contaminated water.\textsuperscript{[8]} Research in recent years showed that semiconductor photocatalysts are highly effective in photo-oxidation of organic pollutants,\textsuperscript{[9]} photo-oxidation or reduction of toxic metal ions\textsuperscript{[10]} and producing radicals for destroying or deactivating bacteria\textsuperscript{[11]} in waste water. Current methods for water purification typically use stoichiometric reagents and/or ultraviolet (UV) light, which is high cost in terms of reagents and energy.\textsuperscript{[8]} As a low-cost and environment-friendly method, semiconductor photocatalysis has potential real world applications.

The band structure of semiconductor materials helps in harvesting energy from photons. The crystal orbitals of a semiconductor form a band structure which has a filled valence band (VB) and an empty conduction band (CB). The energy difference of these two bands is called the band gap ($E_g$) of the semiconductor. When the semiconductor absorbs a photon with greater
energy than that of its band gap, a high energy electron is promoted from valence band to conduction band, leaving a high energy hole in the valence band. These high energy species can then undergo surface reactions with electron donors (D) or acceptors (A), returning the semiconductor to its original state. During the photoreaction in water, holes can react with hydroxide ions (OH\(^-\)) to produce hydroxyl radicals (•OH) and electrons are trapped by oxygen molecules in water to generate superoxide radical anions (O\(_2\)•\(^-\)). The general process is described schematically in Figure 1.1.

![Figure 1.1 Mechanism of semiconductor photocatalytic process, showing energies of conduction band (CB) minimum, valence band (VB) maximum, high energy electron (e\(^-\)), high energy hole (h\(^+\)), electron acceptor (A) and electron donor (D)\(^{[12]}\)](image)

Charge recombination (Figure 1.1, process (2)) often happens quite easily in this process and has become a major barrier to overcome in semiconductor photocatalysis. In this case, charges do not react with electron donor or acceptor species on the surface, and conduction band electrons return to holes in the valence band very quickly. Energy from the absorbed photon is wasted after charge recombination. Many efforts have been made to reduce the
charge recombination, generally focusing on transporting charges faster to the material surface and increasing the lifetime of charges.\[^{13}\]

In order for a semiconductor to be photocatalytically active in water, the redox potential of the photogenerated valence band hole must be sufficiently positive to generate absorbed •OH radicals, which can subsequently oxidize the organic pollutants, and the redox potential of the photogenerated conduction band electrons must be sufficiently negative to be able to reduce absorbed O\(_2\) to O\(_2^-\).\[^{9,14,15}\] Figure 1.2 shows some frequently used semiconductor materials and their band positions. By comparing the band positions of semiconductors and the redox potentials of reactive oxygen species (ROS), TiO\(_2\), ZnO, SnO\(_2\), Fe\(_2\)O\(_3\), WO\(_3\) and ZrO\(_2\) are potentially good as photocatalysts in water.\[^{14}\]

![Figure 1.2 Band positions of frequently used semiconductor materials, and redox potentials of ROS\[^{14}\]](image)

**1.2.2 Electrocatalytic mechanism of semiconductors**

Electrochemical advanced oxidation processes (EAOPs) have been considered as an effective technology for degrading a wide range of organic pollutants in waste water,\[^{16}\] because of their high efficiency and broad
Compared with traditional advanced oxidation processes such as UV radiation, ozone based processes and Fenton's reaction, EAOPs need less energy and a smaller scale, which makes them easy to be applied in decentralized wastewater treatment or combined with other technologies. A wide range of semiconductors has been produced and applied to EAOPs, in which metal oxides (SnO$_2$, PbO$_2$ etc.), dimensionally stable anodes (DSAs) (RuO$_2$-TiO$_2$@Ti, IrO$_2$-RuO$_2$@Ti etc.), boron-doped diamond (BDD) and Magnéli phase Ti$_4$O$_7$ are the most frequently studied and even commercialized. These electrocatalysts have been reported to show high efficiency in degrading contaminants including dyes, pesticides, pharmaceuticals, perfluorinated organic compounds, phenolic compounds, aliphatic acids, etc.

In commonly used EAOPs, water is electrolyzed on the anode surface and hydroxyl radical (·OH) is produced for unselective degradation of pollutants (Equation 1). Pollutant molecules can also be oxidized on the surface of the electrode via direct electron transfer (DET) reactions. Some kinds of organic pollutant have proven difficult to oxidize by ·OH, such as perfluorinated organic compounds, and DET reactions were found to be the rate-limiting step for the oxidation of compounds that are unreactive towards ·OH. Chloride, a commonly present anion in waste water, can be converted to free chlorine species (Cl$_2$, HClO, ClO$^-$) by electrooxidation, and take part in the degradation of organic pollutants. Free chlorine species were also reported effective in degrading organic molecules that are not reactive with ·OH.

In the electrochemical water treatment system containing chloride, oxygen evolution reaction (OER) (Equation 2), chlorine evolution reaction (CER) (Equation 3) and hydroxyl radical production are in competition with each other. Both ·OH and chlorine are able to oxidize organic pollutant molecules, however O$_2$ does not react with pollutants in water. Electrocatalysts for water purification are therefore expected to have a high overpotential for OER to reduce the energy loss caused by oxygen evolution. Hydrogen evolution reaction (HER) process usually happens on the cathode of electrochemical
water treatment system.\textsuperscript{[16]} The process of pollutant degradation in chloride-rich electrolyte is described schematically in Figure 1.3. Many real wastewater samples will contain enough chloride to enable this process, and no additional reagent will be needed in the system. Factors such as pH, temperature, chloride concentration, the adsorption energy of reactive species (Cl\textsuperscript{-}, H\textsubscript{2}O, etc.) and active sites (usually metal atoms) on the surface of the electrocatalyst also affect the selectivity of OER, CER and \cdot OH production.\textsuperscript{[24][25][26]}

\begin{align*}
\text{H}_2\text{O} & \rightarrow \cdot \text{OH} + \text{H}^+ + e^- \quad (E^\circ = 2.74 \text{V vs. SHE}) \\
2\text{H}_2\text{O} & \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \quad (E^\circ = 1.23 \text{V vs. SHE}) \\
2\text{Cl}^- & \rightarrow \text{Cl}_2 + 2e^- \quad (E^\circ = 1.36 \text{V vs. SHE})
\end{align*}

(Equation 1)\textsuperscript{[25]} (Equation 2) (Equation 3)\textsuperscript{[27]}

*Figure 1.3 Mechanism of semiconductor electrocatalytic process in chloride-rich electrolyte*
1.3 Pristine TiO$_2$ and black TiO$_2$ as photocatalysts

1.3.1 TiO$_2$ as a photocatalyst

TiO$_2$ is one of the most efficient and most studied semiconductor photocatalysts. It has been widely used in solar applications including hybrid solar cells and photocatalysts, because of its low-cost, low-toxicity and high-stability. Solid TiO$_2$ has three different phases, rutile, anatase and brookite. Brookite has been seldom discussed when comparing semiconductor materials because it is a less stable polymorph of TiO$_2$ and relatively difficult to prepare. The band gap of anatase and rutile TiO$_2$ were widely reported as approximately 3.2 eV and 3.0 eV respectively, while the band gap of brookite was reported as 3.26 eV. The three polymorphs have some slight differences in band gap and photocatalytic activity, and anatase has been observed as the superior photocatalyst. Some studies report that free hydroxyl radicals are generated at the anatase/water interface but not at the rutile/water interface, which may be an explanation to the superiority of anatase. The commonly used P25 TiO$_2$ nanopowder catalyst contains approximately 80% anatase and 20% rutile. Previous research suggests that the charge separation across the anatase/rutile phase interface increases its photocatalytic efficiency. Electrons can rapidly transfer from small rutile crystallites to trapping sites in bulk anatase that have a lower energy than rutile, which leads to a more long-lived charge separation.

However, two limitations affect the photocatalytic efficiency of TiO$_2$. Although the wide band gap of more than 3.0 eV is suitable for producing reactive oxygen species, the use of solar energy in TiO$_2$ photocatalytic systems is restricted to UV light, less than 5% of the total solar radiation. Also, the fast recombination of photogenerated electrons and holes in TiO$_2$ means the rate of surface reactions taking place on it would be low. P25 TiO$_2$ is one good example of decreasing charge recombination in TiO$_2$ through electron transfer from small rutile crystallites to bulk anatase, but the efficiency still has space for improvement.
Many developments have been made in TiO$_2$ photocatalysts according to recent research. The modifications can be sorted into four types, including nanostructure modifications\textsuperscript{[34]}, band gap narrowing through doping\textsuperscript{[35]}, deposition of plasmonic metal nanoparticles\textsuperscript{[36]} and the formation of composite materials with other inorganic semiconductors\textsuperscript{[37]}. Among these modifications, Ti$_{3}^{3+}$ self-doped TiO$_2$, which is also called “black TiO$_2$”, has become a popular research topic.

1.3.2 Black TiO$_2$ and its properties

Black TiO$_2$ was first produced and reported in 2011 by Chen \textit{et al.}\textsuperscript{[38]}. The name comes from its black appearance different from the usual white color of TiO$_2$. Reduced TiO$_2$ samples with colors of gray, blue and yellow were also prepared and reported.\textsuperscript{[39][40]} Black TiO$_2$ materials have potential applications in pollutant degradation,\textsuperscript{[41]} photocatalytic hydrogen production,\textsuperscript{[42]} CO$_2$ reduction,\textsuperscript{[43]} Dye Sensitized Solar Cells (DSSCs),\textsuperscript{[44]} electrochemical applications involving Li/Na/Mg ion batteries\textsuperscript{[45][46]} and supercapacitors.\textsuperscript{[47]} It can even be used for photothermal therapy in medical science.\textsuperscript{[6]}

Most studies have suggested that black TiO$_2$ can be considered as Ti$_{3}^{3+}$ self-doped TiO$_2$, and can be written as TiO$_2$-$x$, indicating the existence of oxygen vacancies\textsuperscript{[48]}. The majority of studies on black TiO$_2$ report the existence of Ti$_{3}^{3+}$ and oxygen vacancies as the main defect species.\textsuperscript{[6]}

Black TiO$_2$ is known to exist as different polymorphs, in the same way as pristine TiO$_2$. Anatase, rutile and anatase-rutile mixtures are all reported as being prepared. It is widely reported that black TiO$_2$ materials, prepared by reducing white TiO$_2$, retain the structure of the white TiO$_2$ from which they are prepared.\textsuperscript{[6]}

The band structure of Black TiO$_2$ is different from pristine TiO$_2$ due to the defects in its structure and its solar absorption is expanded into the visible light range, which leads to a higher solar energy utilization and a higher photocatalytic efficiency for water splitting and water treatment.\textsuperscript{[38]} Lots of band gap data of black TiO$_2$ have been reported, with values varying from 1.54 eV\textsuperscript{[38]}
to 2.8 eV$^{[49]}$, while some studies reported a band gap similar with pristine TiO$_2$ (more than 3.0 eV)$^{[50]}$. Studies on the band structure of black TiO$_2$ suggested that defect species in black TiO$_2$ introduce localized states between the conduction band and valence band, which contribute to the light absorption expanding into the visible light range.$^{[43]}$ It is suggested that Ti$^{3+}$ and oxygen vacancies in black TiO$_2$ trap the photoexcited holes and electrons and decrease the charge recombination.$^{[51]}$ Black TiO$_2$ materials are expected to make improvement in solar energy harvesting of pristine TiO$_2$ by expanding solar absorption into the visible light range, and reducing charge recombination of pristine TiO$_2$ by improving charge separation, therefore they have attracted lots of interest by researchers.

Many studies into the structure and morphology of black TiO$_2$, especially from reduction of pristine TiO$_2$ have been carried out. Most of the comparisons between X-ray powder diffraction (XRPD) patterns of pristine TiO$_2$ and reduced TiO$_2$ showed that the phase was retained after reduction. However, high-resolution transmission electron microscopy (HRTEM) images of reduced TiO$_2$ showed that a disordered layer appears on the surface of TiO$_2$ particles, and may form a “core-shell” structure.$^{[49]}$ Plenty of Ti$^{3+}$ and oxygen vacancies exist in the disordered layer and the structure of the surface layer becomes different, while the bulk retains its phase and crystallinity. Some studies reported that defect species also formed in the bulk.$^{[6]}$

XPS was frequently used in characterizing black TiO$_2$ samples. By comparing Ti 2p and O 1s spectra of pristine TiO$_2$ and black TiO$_2$, the existence of Ti$^{3+}$ and different chemical bond environments of oxygen were suggested. He et al.$^{[39]}$ reported that in XPS spectra of black TiO$_2$ the Ti 2p peak shifted to a lower binding energy. They also suggested that a shift to lower energies of a peak indicates a higher concentration of Ti$^{3+}$. Sinhamahapatra et al.$^{[52]}$ reported a well-formed tail towards lower binding energy in the XPS spectrum of a black TiO$_2$ sample, as evidence for the presence of Ti$^{3+}$. Wang et al.$^{[40]}$ reported that small peaks appeared at the lower binding energy side of Ti$^{4+}$ peaks, which indicates the existence of Ti$^{3+}$. However, Chen et al.$^{[53]}$ reported
that there was no shift in peak position or new peaks, to show the existence of Ti\(^{3+}\) in XPS results of their black TiO\(_2\) products. Analyses of O 1s XPS spectra were also reported in many studies/investigations. Some suggested that the peaks came from lattice oxygen, oxygen deficiency and surface adsorbed oxygen species\(^{[54]}\), while others explained that the higher binding energy peaks came from the presence of surface hydroxyl groups (Ti-OH)\(^{[52]}\). There is still no clear link between the synthesis method of black TiO\(_2\) and the type of defect species existing in the product.

The discovery of a disordered layer has raised attention to the limitation of XPS characterization. XPS can only detect the surface (around 1 nm depth) of the samples\(^{[6]}\), so the XPS spectra may only show the defect concentration in the disordered layer. Electron spin resonance (ESR) was used in some studies to further characterize the defect species in both the disordered layer and bulk of black TiO\(_2\) samples.\(^{[6]}\) Hou et al.\(^{[51]}\) suggested that surface oxygen vacancies (SOVs) usually possess two electrons, while bulk single-electron-trapped oxygen vacancies (SETOVs) possess single electron. ESR can detect species that have single electron, therefore Ti\(^{3+}\) and bulk SETOVs can be detected by ESR.

According to diffuse reflectance spectra (DRS) results in the literature, black TiO\(_2\) can absorb a wide range of sunlight from the ultraviolet and even into the infrared range.\(^{[49]}\) Black TiO\(_2\) can absorb more energy from sunlight than white TiO\(_2\), which increases the efficiency of photoreactions under solar radiation. The band gap of black TiO\(_2\) materials can also be analyzed from Tauc plot calculated from DRS results.

DRS and XPS characterization results indicating how the band structure changes in black TiO\(_2\) have been reported.\(^{[6]}\) Figure 1.4 shows four possible (a-d) band structure changes which were suggested in the literature. For the conduction band, a mid-band state produced by Ti\(^{3+}\) may appear under its edge, or there may be a tail under the band. For the valence band, there may be a tail above it, or the valence band is expanded by oxygen vacancies.
Results in previous studies often give a combination of these situations. Wang et al.\cite{45} reported a shift of valence band from 1.58 eV to 1.05 eV measured by Valence band XPS. Godoy Junior et al.\cite{55} reported a tail above the valence band and some additional energy levels under conduction band, based on Tauc plot and XPS result. Ullattil et al.\cite{56} reported that according to Tauc plot and Valence band XPS, band tails appear at both the conduction band and the valence band.

Valence band XPS is one of the most frequently used characterization methods for studying the band structure of black TiO$_2$. However, it is often ignored that XPS can only detect the surface of samples, around 1 nm depth. The band structure of the whole material may not be shown completely.

Hou et al.\cite{51} discussed the different effects of SOVs and SETOVs. SETOVs can induce the formation of an intermediate energy band under the conduction band of TiO$_2$, thereby expanding the light absorption into the visible region.

*Figure 1.4 Possible band structure changes in black TiO$_2$ summarized from literature*\cite{6,45,55,56}
However, SETOVs can act as recombination centers for electrons and holes, which will decrease the photocatalytic efficiency of TiO$_2$. SOVs can increase the light absorption and trap electrons to promote the separation efficiency of photogenerated charges, but excessive SOVs may also be recombination centers. In order to get the best performance in photocatalytic reactions, the concentration ratio of bulk SETOVs and SOVs should be adjusted carefully by modifying synthesis methods of black TiO$_2$ materials. Positron annihilation lifetime spectroscopy (PALS), a technology that can detect the γ ray emitted from electrons annihilating positrons in oxygen vacancies, has been used to verify the type and relative concentration of oxygen vacancies of the samples, and study the relationship between the concentration ratio of bulk SETOVs/SOVs. The sample which has the best photocatalytic efficiency in their study was reported to have a concentration ratio of bulk SETOVs/SOVs = 0.95.

Li et al.$^{[57]}$ prepared black TiO$_2$ nanotubes and suggested that a shell of Magnéli phase Ti$_4$O$_7$ was formed on the surface of their black TiO$_2$ nanotubes. The Magnéli phase Ti$_4$O$_7$ has a narrow band gap of approximately 1.5 eV, which may contribute to the visible light absorption of black TiO$_2$ nanotubes. XPS results suggested that an equal amount of Ti$^{3+}$ and Ti$^{4+}$ stabilized the black TiO$_2$ nanotube surface. Magnéli phases are discussed more thoroughly in section 1.5.

### 1.3.3 Synthesis methods of black TiO$_2$

Although hydrogenation was the first and most studied route for producing black TiO$_2$, various synthesis methods have been reported in recent years. Most routes begin with Ti(IV) compounds, including pristine TiO$_2$, TiCl$_4$ and titanium tetraalkoxide, while some routes use Ti metal or low oxidation state titanium compounds.$^{[46]}$

The first research group who produced black TiO$_2$ used a Hy-Energy PCTPro high-pressure hydrogen system for hydrogenating TiO$_2$ in a 20.0 bar H$_2$ atmosphere at about 200°C for 5 days.$^{[38]}$ No color change was observed for
their black TiO$_2$ nanocrystals over 1 year after they were synthesized. Pure H$_2$, H$_2$/Ar, and H$_2$/N$_2$ atmospheres were all reported effective at reducing white TiO$_2$, but this kind of synthesis route usually requires high temperature or high pressure, and sometimes the reaction may last for several days.[46]

Chemical reduction of pristine TiO$_2$ is another kind of frequently used black TiO$_2$ synthesis route. Active metals (Mg, Al, Zn etc.) and reducing reagents (NaBH$_4$ etc.) were reported as effective at preparing black TiO$_2$.[6][54][58] Sinhamahapatra et al.[52] mixed pristine TiO$_2$ and Mg powder together and heated the powder in a tube furnace at 650 °C for 5 h in the flow of 5% H$_2$/Ar. They found the molar ratio of TiO$_2$ and Mg influences the reduction level, which further affects photocatalytic performance. He et al.[59] heated a mixture of pristine TiO$_2$ and NaBH$_4$ at 300 °C under N$_2$ atmosphere for a certain time which ranged from 5 min to 60 min. They reported a gradual colour change from white to dark blue with an increase of heating time. Liu et al.[59] treated TiO$_2$/g-C$_3$N$_4$ with 0.1 mol·L$^{-1}$ NaBH$_4$ solution at room temperature to produce TiO$_2$-x/g-C$_3$N$_4$.

Electrochemical anodization of Ti metal was reported as a method of producing black TiO$_2$ nanotube arrays. Zhou et al.[47] reported a two-step method for preparing black TiO$_2$ nanotube arrays for supercapacitors. The first anodization process was performed in a two-electrode system consisting of Ti foil and platinum mesh electrode materials as anode and cathode, using ethylene glycol containing 0.5 wt % NH$_4$F and 10 wt % H$_2$O as electrolyte at a constant potential of 20 V for 2 h. Then the reduction process was carried out in a three-electrode system using TiO$_2$ nanotube arrays, saturated calomel electrode (SCE), and Pt mesh as working, reference, and counter electrodes, at different potentials and different reaction times. They found that excess reduction driven by high potential caused a decrease of capacitance. The sample polarized cathodically at −1.4 V for the period of 10 min exhibited the highest capacitance in their research.
Hydrogen reduction, chemical reduction and electrochemical reduction-anodization usually requires a high cost of reagent and/or energy, and sometimes the conditions of reaction are difficult. In recent years, researchers have aimed to find easy, fast and eco-friendly black TiO$_2$ synthesis routes in order to expand its application in the real world. Black TiO$_2$ prepared by a solvothermal method, a ‘one pot’ gel combustion method and a UV light-induced electron doping method were reported.

Hao et al.$^{[60]}$ reported a solvothermal method for producing black TiO$_2$. Titanium tetrabutoxide was added dropwise into ethylene glycol under vigorous stirring and the pH value of the mixture was adjusted to 10.17 using dilute aqueous ammonia. Then the mixture was transferred in a stainless-steel autoclave and heated to 200 °C for 24 h. The precipitate was collected by centrifugation, then washed and dried at 60 °C. The product was shown to be anatase nanoparticles with a size of 10-20 nm, and results from XPS and electron paramagnetic resonance (EPR) spectrum suggested the existence of Ti$^{3+}$.

Ullattil et al.$^{[56]}$ reported a ‘one pot’ gel combustion strategy for preparing black TiO$_2$. Titanium tetrabutoxide was mixed with diethylene glycol and stirred for 30 min. Then a certain volume of water was added, and the solution was stirred for a further 15 min. The mixture was finally heated in a furnace at 300 °C for 2 h. The product was found to be the TiO$_2$ polymorph anatase, and defective surface layer was seen in HRTEM images. XPS result suggested the existence of Ti$^{3+}$.

Li et al.$^{[48]}$ developed a UV light-induced electron doping method for producing black TiO$_2$. Pristine TiO$_2$ nanoparticles were prepared by mixing TiCl$_4$ and ethylene glycol, and adding water during refluxing in an atmosphere of N$_2$. Excess ethylene glycol was removed by heating at 300 °C for 6 h. The prepared TiO$_2$ nanoparticles were suspended in methanol and subject to irradiation with UV light using a 125 W high-pressure Hg lamp with the main output at 313 nm. Finally, the nanoparticles were heated at 340 °C in an Ar
atmosphere for 2 h. A disordered layer of 1 nm thickness was found on the surface of their products by HRTEM. The existence of Ti$^{3+}$ and oxygen vacancies were suggested by XPS and EPR spectra.

The synthesis route plays a major role in defining the properties of black TiO$_2$.$^6$ Research has shown that for hydrogen reduction and chemical reduction methods, conditions like temperature, pressure, reagent dosage and reaction time may all affect the properties of the product.\textsuperscript{[51][61]} However, it is difficult to compare the properties of black TiO$_2$ materials synthesized by different routes. The concentration of defect species in black TiO$_2$ prepared by different routes can be quite different. There is also no clear link between the concentration of defect species and the photoreaction efficiency.

1.3.4 Further modifications of black TiO$_2$

Combining black TiO$_2$ materials and other semiconductor materials was also studied in recent years. The combination of TiO$_2$ and another narrow band gap semiconductor material can form heterojunction structures, which increases the separation of electron-hole pairs and promotes the efficiency of photocatalysis.$^6$\textsuperscript{[62]}

Liu \textit{et al.}$^6$\textsuperscript{[63]} produced a 3D mesoporous black TiO$_2$ (MBT)/MoS$_2$/MBT sandwich-like nanosheet photocatalyst through a facile mechanochemistry method combined with a solid state reduction process. The introduction of MoS$_2$ and the Ti$^{3+}$ species narrowed the band gap of TiO$_2$. Under visible-light irradiation, the MBT/MoS$_2$/MBT sandwich-like nanosheet photocatalyst achieved excellent methyl orange degradation and H$_2$ evolution compared with pure TiO$_2$, black TiO$_2$, mesoporous TiO$_2$/MoS$_2$/mesoporous TiO$_2$, and MoS$_2$. The excellent photocatalytic performance of MBT/MoS$_2$/MBT was attributed to the synergistic effect of the MoS$_2$/TiO$_2$ composite, Ti$^{3+}$ species, and the 3D sandwich-like heterojunction structure, which favored the absorption of visible light and the separation and transfer of photogenerated charges.

Sun \textit{et al.}$^6$\textsuperscript{[64]} reported a synthesis route of magnetic Fe$_2$O$_3$/mesoporous black TiO$_2$ hollow sphere heterojunctions through wet-impregnation and surface
hydrogenation. The photoresponse of the material was extended into the near infrared region. In the photocatalytic tests against methyl orange and metribuzin, magnetic Fe$_2$O$_3$/mesoporous black TiO$_2$ materials had a much better performance than single black TiO$_2$. Moreover, the photocatalysts could be separated easily by a magnet, which favored the recycling of catalysts in practical applications.

Hu et al.[65] synthesized a MBT/SiO$_2$/g-C$_3$N$_4$ nanosheets via a sol-gel reaction, followed by calcination and surface hydrogenation strategy. The composite material showed huge improvements in the photocatalytic degradation performance of phenol and reduction of Cr(VI) under visible-light irradiation. The photocatalytic H$_2$ production rate of the composite material under visible light was improved dramatically compared with that of mesoporous TiO$_2$/SiO$_2$ and g-C$_3$N$_4$.

Modifying black TiO$_2$ with other semiconductors further improves the light absorption, charge separation and charge transfer of the materials. Advantages of the other semiconductors can also be introduced, which contributes to the application of hybrid materials.

**1.3.5 Performance of black TiO$_2$ as a photocatalyst**

For degrading pollutants in water, black TiO$_2$ materials were reported to be effective in degrading dye molecules, degrading organic molecules and reducing toxic metal ions. Table 1.1 gives some examples of black TiO$_2$ applied in pollutant degradation. Extended light absorption, improved charge separation and surface defects contribute to the good performance of black TiO$_2$ materials in photocatalytic reactions. It is worth noting that studies into black TiO$_2$ photocatalysts for water treatment usually focus on only one or two kinds of model pollutants in their photocatalytic tests. This may cause an incomplete view of the performance of black TiO$_2$ photocatalysts. A wider range of model pollutants in photocatalytic tests helps to fully investigate the potential of black TiO$_2$ photocatalysts in real water treatment applications.
Table 1.1 Examples of black TiO$_2$ applied in photocatalytic pollutant degradation

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Model Pollutant</th>
<th>Light Source</th>
<th>Photocatalytic Degradation Measure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesoporous black TiO$_2$/MoS$_2$/TiO$_2$</td>
<td>Methyl Orange</td>
<td>300 W Xe Lamp ($\geq$420 nm)</td>
<td>89.86% degradation after 120 min</td>
</tr>
<tr>
<td>TiO$_2$-x/Ag/g-C$_3$N$_4$</td>
<td>Methylene Blue</td>
<td>300 W Xe Lamp ($\geq$420 nm)</td>
<td>99% degradation after 180 min</td>
</tr>
<tr>
<td>Black TiO$_2$</td>
<td>Methylene Orange</td>
<td>500 W Xe Lamp ($\geq$420 nm)</td>
<td>43.1% degradation after 180 min</td>
</tr>
<tr>
<td>Black TiO$_2$</td>
<td>Methylene Blue</td>
<td>solar illumination</td>
<td>100% degradation after 12 min</td>
</tr>
<tr>
<td>Black TiO$_2$ thin film</td>
<td>Methylene Blue</td>
<td>6 UV-visible germicide lamps 15 W</td>
<td>60% degradation after 90 min</td>
</tr>
<tr>
<td>Magnetic Fe$_2$O$_3$/mesoporous black TiO$_2$</td>
<td>Methyl Orange (MO) metribuzin</td>
<td>300 W Xe lamp (AM 1.5 filter)</td>
<td>99.8% degradation after 40 min (MO) 99% degradation after 60 min (metribuzin)</td>
</tr>
<tr>
<td>Black TiO$_2$ nanotube arrays</td>
<td>Cr(VI)</td>
<td>300 W Xe lamp</td>
<td>48.15% reduction after 100 min</td>
</tr>
<tr>
<td>Material</td>
<td>Compound</td>
<td>Lamp Type</td>
<td>Degradation/Reduction</td>
</tr>
<tr>
<td>---------------------------</td>
<td>----------------</td>
<td>----------------------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>Black TiO$_2^{[60]}$</td>
<td>Cr(VI)</td>
<td>300 W Xe Lamp</td>
<td>95% reduction after 1 min</td>
</tr>
<tr>
<td>Ag/La-TiO$_2-x^{[67]}$</td>
<td>tetracycline</td>
<td>300 W Xe Lamp (≥420 nm)</td>
<td>98% degradation after 90 min</td>
</tr>
<tr>
<td>Black TiO$_2^{[68]}$</td>
<td>tetracycline</td>
<td>1000 W Xe Lamp (≥400 nm)</td>
<td>66.2% degradation after 240 min</td>
</tr>
<tr>
<td>gC$_3$N$_4$/Black-TiO$_2^{[41]}$</td>
<td>Rhodamine B</td>
<td>50 W LED lamp (450-650 nm)</td>
<td>58.2% degradation after 30 min</td>
</tr>
</tbody>
</table>
1.4 Ti$_2$O$_3$ and its application as an electrocatalyst

1.4.1 Ti$_2$O$_3$, synthesis and properties

Ti$_2$O$_3$ is a titanium oxide with all the titanium cations in oxidation state +3. The thermodynamically stable phase of Ti$_2$O$_3$ is called α-Ti$_2$O$_3$, which has a trigonal-corundum structure, the same as that of Al$_2$O$_3$. In recent years, new polymorphs of Ti$_2$O$_3$ such as orthorhombic Ti$_2$O$_3$ (ο-Ti$_2$O$_3$) and cubic Ti$_2$O$_3$ (γ-Ti$_2$O$_3$) were also synthesized, which were stabilized as thin films on substrates. Although Ti (III) is not the most stable oxidation state, Ti$_2$O$_3$ is stable under ambient air. Li et al. observed a surface layer of approximately 4.5 nm that appears disordered with inhomogeneous contrast to the crystalline Ti$_2$O$_3$ core. The layer was then found to have Ti$^{4+}$. This Ti$^{4+}$-containing shell was regarded as a protecting layer to prevent further oxidation of Ti$_2$O$_3$ particles. Ti$_2$O$_3$ particles remain its main crystal structure after exposure to outdoor ambient conditions for one month.

The most impressive difference between TiO$_2$ and Ti$_2$O$_3$ is their band structures. TiO$_2$ has a wide bandgap with a value of $E_g \approx 3.0$ eV, while Ti$_2$O$_3$ has an ultra-narrow bandgap with a value of $E_g \approx 0.1$ eV. It is well-known that the bandgap of TiO$_2$ is between the filled O 2p orbitals as valence band and the empty Ti 3d orbitals as conduction band. In Ti$_2$O$_3$, one electron is left in the Ti 3d orbital, and 3d$^1$ electrons form a strongly correlated electron system. The strong Coulomb interaction among 3d$^1$ electrons creates a gap between Ti 3d orbitals. According to Mott-Hubbard theory, the Ti 3d band is split into a lower Hubbard band (LHB) and an upper Hubbard band (UHB), wherein the UHB is empty and the LHB is filled by the Ti 3d$^1$ electrons. The band gap of Ti$_2$O$_3$ is then located between UHB and LHB. The on-site Coulomb repulsion ($U$) between UHB and LHB is smaller than the charge-transfer energy ($\Delta$), therefore Ti$_2$O$_3$ is described as a Mott insulator. Schematics describing the band structures of TiO$_2$ and Ti$_2$O$_3$ are shown in Figure 1.5.
Due to the special electronic structure, Ti$_2$O$_3$ has a high conductivity of $\sigma \approx 160$ S cm$^{-1}$, while TiO$_2$ is highly insulating ($\sigma < \approx 10^{-7}$ S cm$^{-1}$). The difference of band gap also leads to a difference of light absorption. Ti$_2$O$_3$ has strong absorption over the full solar spectrum so the colour of Ti$_2$O$_3$ material is black, while TiO$_2$ only absorbs UV light ($< 400$ nm) and shows a white colour.

Ti$_2$O$_3$ was first synthesized by reducing TiO$_2$ with Ti metal in 1921. Most synthesis methods of Ti$_2$O$_3$ involve the reduction of TiO$_2$ at a high temperature of more than 1000°C. Apart from Ti metal and hydrogen gas, carbon, NaBH$_4$ and CaH$_2$ were also reported as reducing reagent in producing Ti$_2$O$_3$. Titanium alkoxides (titanium isopropoxide, titanium butoxide, etc.) were also used to synthesis Ti$_2$O$_3$ via sol-gel method or solvothermal method. Products of these synthesis route are reported as $\alpha$-Ti$_2$O$_3$, while other polymorphs were synthesized only by film-growth techniques. In previous studies, $\alpha$-Ti$_2$O$_3$ and $\gamma$-Ti$_2$O$_3$ thin films were fabricated using pulsed laser...
deposition (PLD) under high temperatures of 600-900°C, with α-Ti₂O₃ as the target. Hexagonal α-Al₂O₃ (001) single crystals were used as substrates of α-Ti₂O₃, while (001) SrTiO₃ and (001) LaAlO₃ were used as substrates of γ-Ti₂O₃.

1.4.2 Applications of Ti₂O₃, especially as an electrocatalyst

Benefitting from the high stability, ultranarrow bandgap and high conductivity, Ti₂O₃ has shown potential applications around energy conversion and storage, such as fuel cells,[76] Li-ion batteries[80][81], dye-sensitized solar cells (DSSCs),[79] electrochemical hydrogen/oxygen/NH₃/H₂O₂ evolution,[72][82][83][84] etc. Besides, Ti₂O₃ has an outstanding performance of light absorption, which makes it a promising material for photothermal conversion applied on water evaporation and dehydrogenation.[77][85]

Electrochemical nitrogen fixation at ambient conditions has been considered as an efficient and environmentally friendly method, and has attracted a lot of attention of researchers. Nitrogen reduction reaction (NRR) happens on electrocatalytic cathode and produces NH₃ in aqueous electrolyte. High-activity NRR electrocatalysts should have high efficiency of absorbing and activating N₂ molecules, along with a low selectivity of HER. Chen et al.[82] reported the application of Ti₂O₃ nanoparticle immobilized on carbon paper as an electrocatalyst of NRR. In an electrolyte of N₂-saturated 0.1 mol·L⁻¹ HCl, Ti₂O₃ nanoparticle electrocatalyst achieved the maximum faradaic efficiency (FE) (9.16%) and NH₃ yield (26.01 µg h⁻¹ mg_cat⁻¹) when the optimal potential is obtained at −0.25 V vs RHE. DFT calculation suggested that Ti³⁺ active site plays a crucial function in activating N₂ molecules, improving NRR selectivity and enhancing the electrocatalytic performance of NH₃ synthesis. The catalyst showed extraordinary stability after 40 h of electrolysis. In their further publication,[86] a plasma-etched Ti₂O₃ with oxygen vacancies has been reported as a more efficient electrocatalyst than pure Ti₂O₃, with a maximum NH₃ yield of 37.24 µg h⁻¹ mg_cat⁻¹ and the highest FE of 19.29% at −0.25 V vs.
RHE. More active sites were exposed on the surface of the material by introducing oxygen vacancies and NRR catalytic performance was enhanced.

Shi et al.\cite{Shi2019} reported a Ti$_2$O$_3$/reduced graphene oxide (rGO) composite as an electrocatalyst for oxygen reduction reaction (ORR). The material was produced by annealing a mechanical mixture of TiO$_2$, Si and rGO under Ar atmosphere at 800°C for 3 h. Electrochemical studies about the effect of mass ratios of Ti$_2$O$_3$ and rGO showed that the Ti$_2$O$_3$/rGO composite with a mass ratio of 0.07 (Ti$_2$O$_3$ to rGO) presents the most positive cathodic peak potential and the largest peak current density. Comparing with commercial Pt/C electrode, Ti$_2$O$_3$/rGO composite has similar onset potential and diffusion limited current density, which lead to a high ORR catalytic activity. Furthermore, Ti$_2$O$_3$/rGO composite has high stability in alkaline solution and high methanol resistance, which are limitations of Pt/C electrode.

Yao et al.\cite{Yao2020} investigated the in situ electrochemical reconstruction process of oxygen-deficient TiO$_2$ on the surface of Ti$_2$O$_3$ during the ORR process. HRTEM images showed that an oxygen-deficient TiO$_2$ layer of 3-4 atomic layer thick was formed on the surface of Ti$_2$O$_3$ after a 12h electrocatalytic test. During the electrocatalytic test, the selectivity of H$_2$O$_2$ production increased from 5% to over 90%, indicating a transition from the 4e$^-$ ORR pathway to the 2e$^-$ pathway driven by the surface oxygen vacancies. Ti$_2$O$_3$ with oxygen-deficient TiO$_2$ layer material was applied in an assembled membrane electrode flow cell, and showed a high efficiency of H$_2$O$_2$ production and a high stability after 100 hours.

1.5 Magnéli phase titanium oxides and their applications

1.5.1 Properties of Magnéli phase titanium oxides

Magnéli phase titanium oxides are a series of sub-stoichiometric titanium oxides with a general formula of Ti$_n$O$_{2n-1}$ ($n \geq 3$). Different from black TiO$_2$, the oxygen deficiency in Magnéli phase titanium oxides is described as changes of the crystal structures rather than oxygen atoms missing at specific lattice
Magnéli phase titanium oxides have been a popular research topic because of their interesting properties, especially their excellent electrical conductivity at room temperature.\textsuperscript{88}

Previous studies of the crystal structures of Magnéli phase titanium oxides have described that Magnéli phase structures are based on rutile TiO$_2$ crystal lattice. In rutile TiO$_2$, Ti and O atoms form edge-sharing TiO$_6$ octahedra. The coordination numbers of Ti and O are 6 and 3 respectively. Two-dimensional chains of edge-sharing octahedra are then linked by corner-sharing O atoms and packed to form rutile TiO$_2$ structure. In Ti$_n$O$_{2n-1}$, every nth layer has an oxygen deficiency, which leads to shear planes in the crystal structure. At the shear planes, the two-dimensional chains of octahedra become face-sharing to accommodate the deficiency in oxygen. Figure 1.6 showed the shear plane in Ti$_4$O$_7$ structures.\textsuperscript{87} This organization reduces the symmetry of the crystal system from tetragonal rutile TiO$_2$ to triclinic Magnéli phase Ti$_4$O$_7$.\textsuperscript{89} Ti$_2$O$_3$ can be seen as the limiting case of the graduated structure change, since TiO$_6$ octahedra in Ti$_2$O$_3$ face share with each other, and the coordination numbers of Ti and O are 6 and 4 respectively.\textsuperscript{69} Ti$_3$O$_5$ has multiple polymorphs including α, β, γ, δ and λ-Ti$_3$O$_5$. Phase transitions between these polymorphs happen with temperature or pressure change, leading to a change of electronic properties.\textsuperscript{90,91,92} Crystallographic data of some Magnéli phase Ti$_n$O$_{2n-1}$ along with anatase and rutile were listed in Table 1.2.
Table 1.2 Crystallographic data of some Magnéli phase Ti_{n}O_{2n−1}, anatase and rutile[^93]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space group</th>
<th>Cell parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase</td>
<td>I4_1/amd</td>
<td>a = 0.3785 nm, c = 0.9512 nm, α = β = γ = 90°</td>
</tr>
<tr>
<td>Rutile</td>
<td>P4_2/mnm</td>
<td>a = 0.4594 nm, c = 0.2959 nm, α = β = γ = 90°</td>
</tr>
<tr>
<td>Ti_5O_{17}</td>
<td>I1</td>
<td>a = 0.5524 nm, b = 0.7142 nm, c = 5.0030 nm, α = 66.41°, β = 57.20°, γ = 108.53°</td>
</tr>
<tr>
<td>Ti_5O_{11}</td>
<td>I1</td>
<td>a = 0.5552 nm, b = 0.7126 nm, c = 3.2233 nm, α = 66.94°, β = 57.08°, γ = 108.51°</td>
</tr>
<tr>
<td>Ti_5O_{9}</td>
<td>P1</td>
<td>a = 0.5600 nm, b = 0.7120 nm, c = 0.8870 nm, α = 97.60°, β = 112.30°, γ = 108.50°</td>
</tr>
<tr>
<td>Ti_4O_{7}</td>
<td>P1</td>
<td>a = 0.5600 nm, b = 0.7130 nm, c = 1.2460 nm, α = 95.10°, β = 95.10°, γ = 108.80°</td>
</tr>
<tr>
<td>γ-Ti_3O_{5}</td>
<td>l2/a</td>
<td>a = 0.9970 nm, b = 0.5075 nm, c = 0.7181 nm, α = 90°, β = 109.87°, γ = 90°</td>
</tr>
<tr>
<td>λ-Ti_3O_{5}</td>
<td>C2/m</td>
<td>a = 0.9826 nm, b = 0.3789 nm, c = 0.9969 nm, α = 90°, β = 91.26°, γ = 90°</td>
</tr>
<tr>
<td>α-Ti_2O_{3}</td>
<td>R3/c</td>
<td>a = 0.5157 nm, b = 0.5157 nm, c = 1.3610 nm, α = 90°, β = 90°, γ = 120°</td>
</tr>
<tr>
<td>TiO</td>
<td>Fm3m</td>
<td>a = b = c = 0.4293 nm, α = β = γ = 90°</td>
</tr>
</tbody>
</table>
The Goodenough theory reveals that the oxygen deficiency in the Magnéli phase results in delocalized d-electrons based on the Ti-Ti distance. A semiconductor-to-metal transition might occur at a certain temperature if the Ti$^{3+}$ ions come close to the shear plane and trap the d-electrons. Therefore, two d-electrons would be shared by two adjacent Ti$^{3+}$ ions. This results in crystallographic shear structures uniformly introduced in the rutile structure and acts as a good electron pathway. Therefore, Magnéli phase titanium oxides show surprisingly good conductivity comparable to carbon. Previous studies have reported that pure Ti$_4$O$_7$ material has the highest electrical conductivity of more than 1000 S cm$^{-1}$ among Ti$_3$O$_5$, Ti$_5$O$_9$, Ti$_6$O$_{11}$ and any mixed Magnéli phase materials.

Band structures of Magnéli phase titanium oxides have been studied by DFT calculations. The calculation results showed that Ti$_2$O$_3$, Ti$_3$O$_5$, Ti$_4$O$_7$ and Ti$_5$O$_9$ have similar defect levels close to the conduction band, which come from Ti d orbitals. All of them have been reported to have a narrow band gap, although different characterization methods and calculation methods give different values of band width ranging from 0.05 to 1.5 eV.
1.5.2 Synthesis methods of Magnéli phase titanium oxides

Similar with Ti$_2$O$_3$, Magnéli phase titanium oxides are mostly synthesized by reducing TiO$_2$. Reducing reagents that have been reported for synthesizing Magnéli phase titanium oxides include hydrogen gas, carbon, metals and metal hydrides. High annealing temperature of 950-1300 °C have been reported in reducing TiO$_2$ to Magnéli phase materials. Thermal plasma treatment has also been used for producing Magnéli phase titanium oxides.

Misal et al. and Lin et al. produced pure Ti$_4$O$_7$ powder by reducing TiO$_2$ powder in a tube furnace at 1050 °C for 6 h in the presence of 1.0 atm H$_2$. Smith et al. and You et al. mixed TiO$_2$ powder with water and isopropanol (1:1, v/v), followed by 5% (w/w) polyethylene oxide binder before compressing into a plate. The plate was sintered in air at a temperature of 1050 °C for 24 h, and then transferred into a furnace for reduction at H$_2$ atmosphere at 1050 °C for 4 h to form a monolithic porous Ti$_4$O$_7$ material. Liang et al. and Wang et al. reported a lower hydrogen reduction temperature of 950 °C. Kim et al. prepared TiO$_2$ nanotube arrays by Ti plate anodization, and then annealed it in an atmosphere of H$_2$/N$_2$ mixture (in the ratio of 1:5) at 108 cm$^3$/min at temperatures over 700 °C to form a series of Magnéli phase titanium oxide nanotubes.

Zhu et al. produced a series of Magnéli phase titanium oxides by ball-milling TiO$_2$ with 3.6–4.2 wt% carbon black and subsequent heat-treatment in vacuum furnace at 800–1100 °C for 2 h. XRD characterization showed that higher carbon content and higher temperature lead to further reduction of TiO$_2$, and Ti$_n$O$_{2n-1}$ with lower n values produced. High purity Ti$_4$O$_7$ powder was obtained when 4.0 wt% carbon was used and the mixture was annealed at 1025 °C for 2 h. Chai et al. used rutile TiO$_2$ coated by 1.0 wt% SiO$_2$ and 3.0 wt% Al$_2$O$_3$ as the precursor, mixing with 4.5 wt% carbon black before compressing to pellet, and annealling at 1050 °C for 3 h in the argon flow rate 0.5 L min$^{-1}$ to produce high purity λ-Ti$_3$O$_5$ powder.
Wang et al.\cite{104} ball-milled the mixture of TiO$_2$ and carbon black with the mole ratio of 4:1 before heating in a tube furnace at 900°C–1200°C for 2 h in an argon atmosphere. Wang et al.\cite{93} compared two carbothermal reduction route of producing Magnéli phase titanium oxides. Besides the typical TiO$_2$-carbon black ball milling mixture, polydopamine (PDA) coated TiO$_2$ was also prepared for annealing under Ar flow at different temperatures. For any Ti$_n$O$_{2n-1}$ with a specific n value, PDA coating reduced the heating temperature and heating time compared with ball milling TiO$_2$ and carbon. These two studies suggested that the phase evolution during the carbothermal reduction process followed the sequence of anatase TiO$_2$ → rutile TiO$_2$ → Ti$_9$O$_{17}$ → Ti$_8$O$_{15}$ → Ti$_7$O$_{13}$ → Ti$_6$O$_{11}$ → Ti$_5$O$_9$ → Ti$_4$O$_7$ → Ti$_3$O$_5$ → Ti$_2$O$_3$ → TiO. The reduction process was described as two steps; reaction between carbon and TiO$_2$ happened first to form Ti$_n$O$_{2n-1}$ shell and CO, then oxygen atoms diffuse from the core to the outer layer and react with CO.\cite{104,93}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{carbothermal_reduction.png}
\caption{Ideal schematic of the carbothermal reduction process during the synthesis of Ti$_4$O$_7$\cite{104}}
\end{figure}

Hydrogen reduction has been reported as a route of synthesizing pure Ti$_4$O$_7$ materials. Although carbothermal reduction is safer and costs less than hydrogen reduction, the products are usually mixtures of several Magnéli phase titanium oxides, which may affect further applications of the materials.
1.5.3 Magnéli phase titanium oxides as electrocatalysts

Due to the high chemical stability and high conductivity, Magnéli phase titanium oxides have been applied widely as electrodes in electrochemical systems, including fuel cells, batteries, cathodic protection, catalyst substrates and wastewater treatment.\[94][89][105]

Dimensionally stable anodes (DSAs), boron-doped diamond (BDD) electrodes and Magnéli phase $\text{Ti}_4\text{O}_7$ electrodes have been the most studied electrode materials of electrocatalytic water treatment. DSAs are a kind of electrode that consist of a corrosion-resistant base material, such as titanium or tantalum, coated with a layer of metal oxides (e.g., RuO$_2$, IrO$_2$, PbO$_2$, SnO$_2$). DSAs have been produced as commercial electrodes for around 30 years, and have excellent performance on electrochemical degradation of organic compounds, especially in the presence of chloride.\[17] However, DSAs contain noble metal oxides, which increases the cost of production. BDD electrodes have been considered as a promising choice of noble-metal free electrode for water treatment. Studies about BDD electrodes have reported that radical sites formed on the surface of BDD electrodes have a strong effect on charge transfer during the electrochemical oxidation. Produced by chemical vapor deposition (CVD) on metal substrates, BDD electrodes face a problem of physical and chemical stability.\[7][17] Compared with DSAs and BDD electrodes, Magnéli phase titanium oxide electrodes have higher stability and lower cost, with the performance of pollutant degradation at the same level.

Wang et al.\[19] synthesized $\text{Ti}_4\text{O}_7$ by carbothermal reduction, prepared bulk $\text{Ti}_4\text{O}_7$ electrodes and tested the degradation performance of methyl orange (MO). The removal rate of chemical oxygen demand (COD) reached 91.7% under current density of 10 mA cm$^{-2}$ and initial MO concentration of 100 mg L$^{-1}$ after 5 h electrolysis. Comparisons with other commercial electrodes including graphite and DSAs showed that $\text{Ti}_4\text{O}_7$ electrode had superior electrochemical MO oxidation performance under the same experimental conditions.
Liang et al.\cite{101} studied the performance of a Ti$_4$O$_7$ electrode on the degradation of tetracycline (TC). Degradation tests of 10 ppm and 50 ppm TC under different current densities were carried out, and based on the energy consumed per mole of TC removal, the optimum treatment condition was 0.5 mA cm$^{-2}$ at 50 ppm. Radical trapping tests suggested that reactions initiated by hydroxyl radicals dominate TC degradation.

Wang et al.\cite{22} compared the performance of BDD electrode and Magnéli phase Ti$_4$O$_7$ electrode in degrading perfluorooctanesulfonate (PFOS) with the presence of chloride. PFOS was effectively degraded by chlorine and hydroxyl radicals on both BDD and Magnéli phase Ti$_4$O$_7$ electrodes. In chloride-rich electrolyte, chlorine evolution reaction inhibited the evolution of hydroxyl radicals, however chlorine participated in oxidizing PFOS, leading to higher degradation efficiency than chloride-free electrolyte. Ti$_4$O$_7$ electrode showed slow rates of toxic ClO$_3^-$ and ClO$_4^-$ formation, which is superior to BDD in water treatment applications.

You et al.\cite{100} studied a porous Ti$_4$O$_7$ electrode in treatment of industrial wastewater. Dyeing and finishing wastewater (DFWW) containing 1042 mg L$^{-1}$ chloride ions was used for water treatment tests. Analysis of the mechanism suggested that electrochemical oxidation of organic pollutants in DFWW was proceeded by active species of ‗OH, HClO and ClO$^-$ under mass transfer control condition. 66.5% COD and 46.7% dissolved organic carbon (DOC) in DFWW were removed at current density of 8 mA cm$^{-2}$ after 2 h reaction.

Lin et al.\cite{106} successfully doped Ce$^{3+}$ in Ti$_4$O$_7$ structure and prepared (Ti$_{1-x}$Ce$_x$)$_4$O$_7$ electrode. It was reported that Ce$^{3+}$ doping effectively improved the electrochemical reactivity via enhancing the surface oxygen vacancies toward reactive sites. When the dopant amount of Ce$^{3+}$ is 3 at. %, the oxidation rate constant of PFOS increased to 2.4 times of that of pristine Ti$_4$O$_7$. (Ti$_{1-x}$Ce$_x$)$_4$O$_7$ (x = 3%) electrode exhibited a satisfactory durability over 20 cycles (60 min per cycle) of PFOS oxidation tests.
Wang et al.\cite{107} applied TiO$_7$ electrode to removal of antibiotics and multidrug resistant bacteria. Electrochemical oxidation process generates abundant OH that is effective in attacking the pathogen, resulting in cell damage and leakage of the cytoplasmic content. Multidrug-resistant Salmonella enterica serotype Typhimurium DT104 was completely deactivated with 6.2 log reduction in 15 min at the current density of 10.0 mA cm$^{-2}$, while tetracycline (TC) and sulfadimethoxine (SDM) were degraded 97.95 % and 93.42 % in the same electrooxidation treatment system within 3 h.

Magnéli phase titanium oxides, mainly TiO$_7$, have been reported effective for electrochemical degrading of a wide range of dyes, organic compounds and bacteria in wastewater. Magnéli phase electrodes showed high activity of producing active species in both chloride-rich electrolytes and chloride-free electrolytes. Table 1.3 showed some examples of pollutant degradation efficiencies of Magnéli phase titanium oxide electrodes in previous studies. In EAOPs water treatment system, pollutant degradation efficiencies in chloride-rich environment are relatively higher than that in chloride-free environment, which is due to free chlorine species participating in the oxidation of pollutant. This has been found not only on Magnéli phase titanium oxide electrodes but also DSAs and BDD electrodes.\cite{17} Further oxidation products of chloride, such as ClO$_3^-$ and ClO$_4^-$, were also discovered in EAOPs system containing chloride. These toxic byproducts can form under high current density or long treatment time, so lower current density and controlled reaction time may inhibit the formation of those byproducts.\cite{17}\cite{99} Although TiO$_7$ electrodes have been reported to have lower production rate of ClO$_3^-$ and ClO$_4^-$ than BDD electrodes,\cite{22}\cite{99} it is difficult to avoid the formation of these further oxidation products. In addition to its high stability, low cost and low byproduct production rate, Magnéli phase titanium oxide electrodes have a flexibility of being made to different shapes, including bulk plates, reactive electrochemical membranes and nanotube arrays.
Table 1.3 Examples of Magnéli phase titanium oxides applied in electrocatalytic water treatment

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Model Pollutant / Electrolyte</th>
<th>Current density</th>
<th>Degradation Measure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_4$O$_7$ bulk electrode$^{[19]}$</td>
<td>Methyl Orange / NaCl</td>
<td>10 mA cm$^{-2}$</td>
<td>99.3% in 120 min</td>
</tr>
<tr>
<td>Ti$_4$O$_7$ bulk electrode$^{[22]}$</td>
<td>perfluorooctanesulfonate / NaCl</td>
<td>10 mA cm$^{-2}$</td>
<td>98.8% in 20 min</td>
</tr>
<tr>
<td>Ti$_4$O$_7$ bulk electrode$^{[101]}$</td>
<td>Tetracycline / Na$_2$SO$_4$</td>
<td>3.0 mA cm$^{-2}$</td>
<td>98.4% in 120 min</td>
</tr>
<tr>
<td>Ti$_4$O$_7$ nanotube on Ti substrate$^{[102]}$</td>
<td>4-chlorophenol / Na$_2$SO$_4$</td>
<td>Not mentioned</td>
<td>~90% in 120 min</td>
</tr>
<tr>
<td>Ti$_4$O$_7$ on Ti substrate$^{[108]}$</td>
<td>p-Nitrophenol / NaCl</td>
<td>4 mA cm$^{-2}$</td>
<td>100% in 30 min</td>
</tr>
<tr>
<td>(Ti$_{1-x}$Ce$_x$)$_4$O$_7$ electrodes$^{[106]}$</td>
<td>perfluorooctanesulfonate / Na$_2$SO$_4$</td>
<td>20 mA cm$^{-2}$</td>
<td>&gt;99% in 60 min</td>
</tr>
<tr>
<td>Ti$_4$O$_7$ bulk electrode$^{[107]}$</td>
<td>Tetracycline / Na$_2$SO$_4$ sulfadimethoxine / Na$_2$SO$_4$ S. Typhimurium DT104</td>
<td>10 mA cm$^{-2}$</td>
<td>97.95% in 3 h 93.42% in 3 h completely deactivated in 15 min</td>
</tr>
<tr>
<td>Reactive Electrochemical Membrane</td>
<td>Treatment</td>
<td>Current Density</td>
<td>Efficiency</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>-----------</td>
<td>-----------------</td>
<td>------------</td>
</tr>
<tr>
<td>TiO\textsubscript{7}/TiO\textsubscript{9}</td>
<td>carbamazepine in secondary effluent</td>
<td>73 A m\textsuperscript{-2}</td>
<td>&gt;98% under flow rate of 1.34 m\textsuperscript{3} h\textsuperscript{-1} m\textsuperscript{-2}</td>
</tr>
<tr>
<td>O\textsubscript{3}-TiO\textsubscript{7}</td>
<td>Tetracycline / Na\textsubscript{2}SO\textsubscript{4}</td>
<td>2 mA cm\textsuperscript{-2} (2 mg min\textsuperscript{-1} O\textsubscript{3} dosage)</td>
<td>96.8% in 20 min</td>
</tr>
</tbody>
</table>
1.6 Summary

Black TiO$_2$ has a wider range of light absorption and a better charge separation than pristine TiO$_2$. The defect species in black TiO$_2$ greatly enhance the performance of TiO$_2$ as a photocatalytic material. However, the negative effect brought by those defect species shouldn’t be ignored. High concentration of defect species may bring too much disorder in the structure and charge recombination centres in black TiO$_2$ materials, which will lead to a poor performance in photocatalytic reactions. The relationship between concentration of defect species and photocatalytic efficiency still needs to be discussed.

Research to date still cannot give a clear understanding about the structure and morphology of black TiO$_2$ prepared via different routes. Further studies about how the synthesis method influences the crystal structure, the kinds and quantities of defects, the band structure and charge separation are still needed. If the structure and morphology of black TiO$_2$ material can be controlled by designing the synthesis route to reach a best performance, it will have a bright outlook for real world applications.

Ti$_2$O$_3$ and Magnéli phase titanium oxides have been applied as electrode materials because of their high electrical conductivity and high stability. Their characteristic crystal structures and band structures contribute to their excellent performance in electrochemical systems. However, the mechanism of reactions on the surface of these materials still needs further studies and discussions, especially reactions in EAOPs, including DET, production of -OH and free chlorine species. Besides, modifications of Ti$_2$O$_3$ and Magnéli phase titanium oxides, aiming to introduce more surface defects and increase electrochemical properties, have been reported by previous studies. This is also a topic that needs further discussions.

Magnéli phase Ti$_4$O$_7$ has been an attractive electrocatalytic material for wastewater treatment. However, research about applying Ti$_2$O$_3$ to electrocatalytic water treatment are still very few, and there are no studies
about CER on Ti$_2$O$_3$ materials yet. Work in Chapter 3 aimed to study the performance of a Ti$_2$O$_3$ thin film electrode in chlorine-driven wastewater treatment. The selectivity of OER and CER, chlorine evolution and model pollutants degradation of the Ti$_2$O$_3$ thin film electrodes were tested and discussed. This work aimed to expand the application of Ti$_2$O$_3$ to chlorine-driven water treatment in the real world.

Magnéli phase titanium oxides synthesized by carbothermal reduction methods usually contain a mixture of Magnéli phases. Research until now still don’t have a clear view of how the mixed phases affect the properties of the materials. Work in Chapter 4 aimed to synthesize a series of Magnéli phase titanium oxides by carbothermal reduction, to study their phase structures and electrochemical properties. They were also tested as electrodes applied in chlorine-driven wastewater treatment.

Work in Chapter 5 aimed to synthesize black TiO$_2$ materials via some easy and low-cost methods, to study their structure, morphology and defect species, and try to find some relationship between synthesis condition and properties of the products. Photocatalytic tests against model pollutants were carried out, and the relationship between material properties and photocatalytic performance were studied. This work aimed to produce some black TiO$_2$ materials which have potential applications in real world water treatments.

Technique of immobilizing material onto glass substrate and form thin film catalysts were applied in this work. Electrodes in wastewater treatment systems are usually bulk ceramic materials. Thin film electrode can decrease the cost of reactive materials while retaining a high performance. Powder photocatalytic materials for water treatment are difficult to be collected and recycled after using. Immobilized thin film photocatalysts can be simply removed from treated water and reused, which benefits their real world application.

The whole project aimed to explore the synthesis of high-stability and low-cost oxygen-deficient titanium oxide based materials, and their potential as
catalysts in small-scaled water treatment system, which can be applied in low-income areas.
References


Chapter 2  Experimental

2.1 Chemicals and materials

Ti$_2$O$_3$ (99.8%) and tris(hydroxymethyl)aminomethane were purchased from Alfa Aesar. P25 TiO$_2$, titanium tetrabutoxide (TTB), ethylene glycol (EG), fluorine-doped tin oxide (FTO) glass (15 Ω/sq), acetyl acetone, ethyl cellulose, terpinol, ethanol, potassium chloride, tetracycline hydrochloride (TC) and tert-butanol (TBA) were purchased from Sigma Aldrich. Sodium borohydride (NaBH$_4$), Triton X-100, Rhodamine B, N,N-Diethyl-p-phenylenediamine (DPD) sulfate and methyl orange (MO) were purchased from Acros organics. Dopamine hydrochloride and sodium sulfate were purchased from Fluorochem. Activated charcoal, ammonia (NH$_3$·H$_2$O), sodium hydroxide (NaOH) and plain microscope glass slides were purchased from Fischer Scientific. Silver conductive paint was purchased from RS PRO.

2.2 Sample preparation by doctor blading

Doctor blading is a simple method of immobilizing a thin layer of material onto a plain substrate surface, and has been applied in solar cell and photocatalytic systems.[1][2] In this work, glass slides including plain microscope glass and fluorine-doped tin oxide (FTO) glass were used as substrates. The glass slides were ultrasonically cleaned and treated by UV-Ozone ProCleaner before doctor blading.

Figure 2.1 shows the general steps of the doctor blading method. Scotch tape (thickness 0.060 mm) was placed on the glass slide as spacers, leaving the space for depositing materials. A paste containing the material was added between two spacers and then spread uniformly by a glass rod passed right above the spacers. The spacers can be removed when the paste has dried. The immobilized thin film material was then annealed under air at high
temperature, in order to burn the organic binder and allow the material to adhere well to the substrate.

![Figure 2.1 Schematic diagram of the process of doctor blading on glass surfaces](image)

### 2.3 Diffuse Reflectance, Kubelka Munk equation and Tauc plots

Diffuse reflectance is a technique used to obtain optical properties from solid samples, especially band gap values of semiconductor materials, where transmission absorption experiments are not viable.[3] The Kubelka-Munk function is related to the absorption (K) and scattering (S) of the sample as shown:

\[
F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} = \frac{K}{S}
\]

Where \( F(R_\infty) \) is the Kubelka-Munk function and \( R_\infty \) is the reflectivity of the sample (i.e. the outgoing flux divided by the ingoing flux) as a percentage,
assuming a sample thickness sufficient to behave as if it is infinite. Measuring the reflectivity of the sample at various wavelengths can therefore be used to obtain the Kubelka-Munk quantity as a function of wavelength.

This quantity can be applied in a Tauc plot to obtain the band gap as shown:

\[
(F(R_\infty)hv)\frac{1}{n} = A(hv - E_g)
\]

Where h is Planck’s constant, ν is frequency of incident light, A is the absorption constant, and \(E_g\) is the band gap. The band gap can be obtained by plotting \((F(R_\infty)hv)^{\frac{1}{n}}\) against energy, which is called a Tauc plot. The value of \(n\) depends on whether the transition is direct or indirect, with \(n = 0.5\) for direct transitions and \(n = 2\) for indirect transitions.[4] Extrapolation of the linear portion of the onset to the x-axis (where \((F(R_\infty)hv)^{\frac{1}{n}} = 0\)) gives the band gap \(E_g\).

2.4 X-ray Powder Diffraction and crystallite size from the Scherrer equation

X-ray diffraction is a convenient method for determining the phase and purity of a crystalline material, and also the mean size of nano crystallites in a nano crystalline bulk material.[5] Paul Scherrer introduced an equation for calculating crystallite size from XRD patterns in 1918, which became known as the Scherrer equation.[6] It is important to distinguish the fact that “crystallite size” is not synonymous with “particle size”, and X-Ray diffraction is sensitive to the crystallite size inside the particles. The Scherrer equation expresses the average crystallite size \(L\) as shown:

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

where \(\lambda\) is the X-ray wavelength in nanometer (nm), \(\beta\) is Full Width at Half Maximum (FWHM), the peak width of the diffraction peak profile at half
maximum height, resulting from small crystallite size in radians, and K is a constant related to crystallite shape, normally taken as 0.9. The value of $\beta$ in $2\theta$ axis of diffraction profile must be in radians, while $\theta$ can be in degrees or radians, since the $\cos \theta$ corresponds to the same number.

2.5 **Electrochemical methods**

2.5.1 **Mott-Schottky analysis and the Mott-Schottky equation**

Mott-Schottky analysis was performed using an Autolab PGSTAT30 with FRA software. A standard three electrode setup containing Ag/AgCl (3 mol·L$^{-1}$ KCl) reference electrode, Pt wire counter electrode and immobilized thin film as the working electrode were used, and the electrolyte used was 0.05 mol·L$^{-1}$ Na$_2$SO$_4$. Mott–Schottky analysis is a commonly applied technique used for determining the flat band potential ($E_{fb}$) of semiconductor materials.\textsuperscript{[7][8]} The Mott-Schottky equation can be represented as below:

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 A^2 e N_D} \left( E - E_{fb} - \frac{k_B T}{e} \right)$$

where C and A are the interfacial capacitance and area, $\varepsilon$ is the dielectric constant of the material, $\varepsilon_0$ is the permittivity of free space, $N_D$ describes the charge carrier density, E is the applied potential, $k_b$ is Boltzmann’s constant, T is the absolute temperature, and e is the electronic charge. From the linear portion of the Mott-Schottky plot, which is plotted by $1/C^2$ against E, $E_{fb}$ can be determined from the intercept on x axis. The value of $N_D$ can also be found from the slope, knowing $\varepsilon$ and A.

2.5.2 **General methods for water treatment experiments**

Linear sweep voltammetry (LSV) was measured by CV Autolab, using a 3-electrode, 1-compartment system with Ti$_2$O$_3$ thin film electrode as the working
electrode, platinum mesh as the counter electrode and Ag-AgCl (3 mol·L⁻¹ KCl) electrode as the reference electrode. All electrocatalytic tests, including free chlorine capture, model pollutant degradation, scavenger testing and repeated use testing, were carried out using an Ivium potentiostat V89102, in a 3-electrode, 2-compartment system. The anode compartment containing the Ti₂O₃ thin film electrode (working electrode) and the Ag-AgCl (3 mol·L⁻¹ KCl) electrode (reference electrode) was separated by a glass frit from the cathode compartment containing platinum mesh (counter electrode). The volume of electrolyte in the anode compartment was fixed to 25 mL. During all potentiostatic electrocatalytic tests the potential was fixed to 2.0 V.

N,N-Diethyl-p-phenylenediamine (DPD) reagent solution was prepared by dissolving 0.13 g DPD sulfate into 60 mL deionized water, followed by adding 1.5 mL 10% H₂SO₄ and 2.5 mL 0.8% EDTA before bringing the final volume to 100 mL with deionized water.

In all electrocatalytic tests, 0.4 mL aliquots of electrolyte in the anode compartment were removed every 30 min. For free chlorine capture, 0.4 mL of DPD reagent was mixed with 2.5 mL NaH₂PO₄/Na₂HPO₄ buffer (pH ~ 6.0) in a quartz cuvette before adding 0.4 mL of electrolyte aliquot. For model pollutant degradation, scavenging tests and recycling tests, 0.4 mL of electrolyte was mixed with 2.9 mL of deionized water in a quartz cuvette. UV-vis spectra were collected using a Shimadzu UV-1800 UV-Vis spectrometer.

2.5.3 Calculations of free chlorine capture tests

Data for the linear fit of DPD reagent UV-Vis absorption and NaClO concentration were collected by testing a series of standard NaClO solutions. The concentrations of NaClO solutions were determined by titration using Na₂S₂O₃ solution. The linear fit plot of UV-Vis absorption against NaClO concentration was showed in Figure 2.2, and the formula of linear fit is $y=2553.74x$. All of the concentration results from free chlorine capture tests were in the linear concentration range of the fit.
Faradaic yield is a ratio of the charge consumed by target reaction (free chlorine evolution in this work) and the total charge passed through the electrochemical system. An example calculation of Faradaic yield is as below:

The current during free chlorine capture test of sample 400EC30 was shown in Figure 2.3. Calculate the area under curve (0 ≤ x ≤ 3600 s) by integration. The value is the total charge which has gone through the electrode. For sample 400EC30, 5.29 C of charge have passed in 1 h.

The free chlorine concentration at the end of the test (5.56×10⁻⁴ mol·L⁻¹) was calculated from the UV-vis spectra data.

The amount of substance of free chlorine (calculated as ClO⁻): \n\[ n_{ClO^-} = c_{ClO^-} \times V_{cell} = 5.56 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \times 0.025 \text{ L} = 1.39 \times 10^{-5} \text{ mol} \]

Charge used to produce free chlorine: (F is Faraday constant)
\[ q_{\text{ClO}^-} = 2 \times n_{\text{ClO}^-} \times F = 2 \times 1.39 \times 10^{-5} \text{ mol} \times 96485 \text{ C} \cdot \text{mol}^{-1} = 2.68 \text{ C} \]

Faradaic yield:

\[ \gamma = \frac{q_{\text{ClO}^-}}{q} \times 100\% = 50.7\% \]

![Figure 2.3. Current during free chlorine capture test of sample 400EC30](image)

### 2.5.4 Degradation efficiency of model pollutants

Methyl orange, tetracycline, Rhodamine B and 4-chlorophenol was chosen as model pollutants in electrocatalytic or photocatalytic tests. The molecular structures and UV-vis spectra of these model pollutants are shown in Figure 2.4. Methyl orange and Rhodamine B are dye molecules, with a conveniently-monitored visible absorption, which have been frequently used as target molecules in testing photocatalytic and electrocatalytic materials. However, catalyst photo-sensitisation by dyes under visible light cannot be ignored when studying their degradation efficiency. For this reason, tetracycline and 4-
chlorophenol, colourless organic molecules which are common pollutants in industrial and pharmaceutical wastewater, were also used as model pollutants in this work.

Figure 2.4 Molecule structure and UV-vis spectra of (a) methyl orange, (b) tetracycline, (c) Rhodamine B and (d) 4-chlorophenol

The light absorption at the characteristic absorption peak of a certain model pollutant in UV-vis spectra is proportional to the concentration of the model pollutant. The degradation efficiency (percentage) is calculated by the ratio of concentration before and after the test.

$$\frac{C}{C_0} = \frac{A}{A_0}$$
where \( C_0 \) is the concentration before the test, \( C \) is the concentration after the test, \( A_0 \) is the absorbance before the test, \( A \) is the absorbance after the test.

Degradation efficiency (DE), the final overall degradation percentage, is calculated according to the following equation:

\[
DE = \left( 1 - \frac{C}{C_0} \right) \times 100\%
\]

DE is therefore the amount of model pollutant destroyed expressed as a percentage.

### 2.6 Instrumentation

Powder X-ray Diffraction (PXRD) patterns were measured by Bruker D2 phaser X-ray diffractometer in reflection geometry with CuKa radiation (1.54184 Å). Scanning electron microscope (SEM) images were taken by Carl Zeiss SIGMA HD VP Field Emission SEM, operated in SE2/InLens mode with a 5-10kV accelerating voltage. FT-IR spectra were collected by Shimadzu IRSpirit Fourier Transform Infrared Spectrophotometer. Thermogravimetric analysis (TGA) was carried out using a Netzsch STA 449 F1 thermal analyzer. UV-Visible diffuse reflectance spectra of the powder samples were measured by using a JASCO V-670 spectrophotometer with an integrating sphere attachment.
References

Chapter 3 Ti$_2$O$_3$ film electrode for water treatment via electrochemical chlorine evolution

3.1 Introduction

Electro-chlorination has proven to be one of the most reliable applications of electrochemistry in water treatment.[1] By electrooxidizing chloride ions which are already contained in wastewater, free chlorine species are produced and then contribute to the degradation of pollutants. Chlorine has been applied widely as an effective disinfection agent in water treatment.[2] Free chlorine species have been reported to help degrade a wide range of pollutants, including methyl orange, Rhodamine B, ceftazidime, bisphenol A, perfluorooctanesulfonate, etc.[3][4][5]

This chapter introduces a low-cost and earth-abundant Ti$_2$O$_3$ thin film electrode as the anode for chlorine-driven electrochemical water treatment. Ti$_2$O$_3$ is a semiconductor with a high stability, an ultra-narrow bandgap (≈0.09 eV) and a high conductivity ($\sigma = \approx 160$ S cm$^{-1}$).[6][7] Previous studies have proven that Ti$_2$O$_3$ remains stable after exposing to ambient air for a long time.[6][9] Ti$_2$O$_3$ has been applied as an electrode in fuel cells,[10] Li-ion batteries[11] and electrochemical ammonia evolution,[12] but its performance in chlorine-driven water treatment has not previously been studied.

Ti$_2$O$_3$ powder was immobilized on a conductive fluorine-doped tin oxide (FTO) glass slide by a simple method to form a thin film electrode. Morphology and crystal structure of the material before and after immobilization were characterized. Electrochemical properties of the Ti$_2$O$_3$ thin film electrode were tested in different electrolytes in order to study the selectivity of OER and CER. The thin film electrode was applied towards degradation of two different model pollutants in water solutions containing chloride ions. Mechanism of the degradation reaction was studied via scavenging tests and the performance of the Ti$_2$O$_3$ thin film electrode under repeated use was also tested.
3.2 Experimental

3.2.1 Ti$_2$O$_3$ paste preparation

0.4 g Ti$_2$O$_3$ powder was ground by pestle and mortar before stirring with 1 g mixture of ethyl cellulose and ethanol (10 wt% ethyl cellulose), 0.81 g terpineol and 1 mL ethanol overnight. The mixture was ultrasonicated by Toption ultrasonic homogenizer at a power of 400 W 3 times, 1 min each time. Excess ethanol was evaporated by rota-evaporation at 40 °C, 120 rpm.

3.2.2 Thin film electrode preparation

FTO glass was cut to 1 cm × 3 cm rectangle slides and cleaned by ultrasonication in detergent solution (Decon 90, ~ 5% in tap water), tap water, deionized water and ethanol for 15 min each step. Ti$_2$O$_3$ paste was doctor bladed on the conductive surface of FTO glass at an area of 1 cm × 2.5 cm spaced by scotch tape (thickness 0.060 mm). Thin films on the glass slides were dried at 100 °C under air for 30 min and annealed by programmable hotplate using the heating sequence in table 3.1. The heating ramp rate was 10 °C/min between every stage. After annealing, silver conductive paint was painted on the blank part of conductive surface of FTO glass slides to increase the conduction between electrode and clip. A schematic diagram of the Ti$_2$O$_3$ thin film electrode is shown in Figure 3.1. For control experiments, silver conductive paint was painted onto the same area of plain FTO glass as on the Ti$_2$O$_3$ thin film electrode to form a plain FTO electrode.
Figure 3.1 Schematic diagram of Ti$_2$O$_3$ thin film electrode

Table 3.1 Heating programmes of Ti$_2$O$_3$ thin film samples

<table>
<thead>
<tr>
<th>Sample name</th>
<th>400EC30</th>
<th>450EC60</th>
<th>500EC30</th>
<th>500EC60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rate:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 °C/min</td>
<td>325°C, 5 min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>375°C, 5 min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>400°C, 30 min</td>
<td>450°C, 60 min</td>
<td>450°C, 15 min</td>
<td>450°C, 15 min</td>
</tr>
<tr>
<td></td>
<td>500°C, 15 min</td>
<td></td>
<td>500°C, 45 min</td>
<td></td>
</tr>
</tbody>
</table>

3.3 Result and discussion

3.3.1 Characterization

In order to burn off organic binder, Ti$_2$O$_3$ thin film samples were heated under air, which risks the undesirable oxidation of Ti(III) to Ti(IV). FT-IR spectra of the sample 400EC30 (Figure 3.2) showed no peaks related to the presence of any
organic groups, suggesting that the organic binder was completely burned off at 400°C. SEM images of Ti$_2$O$_3$ powder, and Ti$_2$O$_3$ thin film before and after heating were taken and compared to each other (Figure 3.3). Particle size of the original Ti$_2$O$_3$ powder was about 1-2 μm, with grains apparently linked together. After film deposition and heating, the particles generally retained their shape and size, although some additional fusing of particles may have occurred. There was no obvious substantial morphology change after film deposition and heating of any of the thin film samples.

![Figure 3.2 FT-IR spectrum of 400EC30](image)

*Figure 3.2 FT-IR spectrum of 400EC30*
Figure 3.3 SEM images of (a) $\text{Ti}_2\text{O}_3$ powder, (b) $\text{Ti}_2\text{O}_3$ film before annealing, and (c) 400EC30 film sample, (d) 450EC60 film sample, (e) 500EC30 film sample, (f) 500EC60 film sample
To study the possible oxidation of Ti$_2$O$_3$ under different heating temperatures and times, PXRD patterns of all Ti$_2$O$_3$ thin film samples were collected and compared with standard patterns of possible products. All observed diffraction peaks in the patterns were found to fit well with the standard peaks of Ti$_2$O$_3$ (ICSD#1462), anatase TiO$_2$ (ICSD#9852) and rutile TiO$_2$ (ICSD#9161) (Figure 3.4). The intensity of the peaks assigned to anatase and rutile increased with the increase of annealing temperature and time. For 400EC30 however, only a negligible amount of TiO$_2$ was observed, while in 500EC60, most of the Ti$_2$O$_3$ was oxidized to TiO$_2$. According to the PXRD results, the oxidation progress of Ti(III) in Ti$_2$O$_3$ can be controlled by annealing temperature and time. As the sample annealed at 400 °C for 30 min is still almost entirely Ti$_2$O$_3$, with no detectable organic binder remaining, this material was used for all further electrochemical studies.

*Figure 3.4 PXRD patterns of Ti$_2$O$_3$-TiO$_2$ thin film samples*
3.3.2 Electrochemistry

LSV of sample 400EC30 and plain FTO glass were measured in 3 different electrolytes: chloride-rich electrolyte (4 mol·L\(^{-1}\) KCl), strong base electrolyte (1 mol·L\(^{-1}\) KOH) and neutral electrolyte (0.1 mol·L\(^{-1}\) Na\(_2\)SO\(_4\)) (Figure 3.5 a-c). The selectivity of CER and OER is affected by the concentrations of chloride and hydroxide ions.\(^{13}\) In chloride-rich electrolyte, CER was the dominant reaction, while in strong base electrolyte, OER was promoted and CER was minimised. OER in neutral environment can be studied by using Na\(_2\)SO\(_4\) solution as the electrolyte. Tafel plots and Tafel slopes of each electrode measured in different electrolytes are shown in Figure 3.5 (d). The Tafel slope is a critical parameter to evaluate the reaction kinetics and investigate the catalytic mechanism.\(^{14}\) It can be explained as the number of mVs required to increase the current by a factor of 10, and the unit of Tafel slope is mV/dec. A low Tafel slope value shows a high activity of catalyst, as a smaller overpotential is required to reach a higher current density. Kinetic information such as rate-determining step can be also extracted from the value of the Tafel slope.\(^{25}\) Comparing with plain FTO glass, Ti\(_2\)O\(_3\) film has a similar onset potential for OER in both base and neutral electrolytes. The difference of Tafel slopes may come from different mechanisms. Importantly, Ti\(_2\)O\(_3\) thin film has lower onset potential for CER than plain FTO glass in chloride-rich electrolyte, although Tafel slopes are similar. Ti\(_2\)O\(_3\) thin film can also have higher current density for CER at a certain potential comparing with plain FTO.

Comparisons of Tafel slope values of Ti\(_2\)O\(_3\) thin film and other similar electrocatalytic materials from previous studies are shown in Table 3.2. Mixed metal oxides electrodes were reported to have small Tafel slope values for both CER and OER, which suggested more favourable kinetics.\(^{14}\) However, these kind of electrodes usually need precious metal compounds and complex production processes, and the cost of these electrodes becomes high. Cheaper electrode materials were also studied, but the Tafel slope of these were larger than mixed metal oxides for both CER and OER. Further study of
the relationship between Tafel slope and mechanisms of reaction on the surface of electrocatalytic materials would be needed to further understand these differences. Furthermore, some literature introducing electrocatalytic materials doesn’t present Tafel plot and Tafel slope data, making the comparison of mechanism and kinetics harder among different materials. Overall however, it is clear from Figures 3.5a and 3.5c that CER is favoured over OER on Ti$_2$O$_3$ under neutral conditions, which is appropriate for water treatment applications. Research on widely used Ru/Ir-based water oxidation electrocatalysts suggests possible OER mechanisms that involve metal atom oxidation state change during adsorption and desorption of oxygen,$^{[15]}$ which may not operate readily for Ti(III), therefore OER may be less favoured on the surface of Ti$_2$O$_3$.

![Graphs](image)

**Figure 3.5.** LSV of 400EC30 and plain FTO glass, carried out in three kinds of electrolytes: (a) 4 mol·L$^{-1}$ KCl, (b) 1 mol·L$^{-1}$ KOH and (c) 0.1 mol·L$^{-1}$ Na$_2$SO$_4$, and (d) Tafel plot and Tafel slope calculated from LSV results.
Table 3.2. Tafel slope values comparing with literature

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrolyte</th>
<th>Reaction</th>
<th>Tafel slope mV/dec</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_2$O$_3$ thin film on FTO glass</td>
<td>4 mol·L$^{-1}$ KCl</td>
<td>CER</td>
<td>273</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>1 mol·L$^{-1}$ KOH</td>
<td>OER</td>
<td>218</td>
<td></td>
</tr>
<tr>
<td>Blue / Black TiO$_2$ nanotube (anatase phase)</td>
<td>1 mol · L$^{-1}$</td>
<td>OER</td>
<td>Blue 371</td>
<td>[16]</td>
</tr>
<tr>
<td></td>
<td>KH$_2$PO$_4$</td>
<td></td>
<td>Black 200</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Blue has higher selectivity for CER)</td>
<td></td>
</tr>
<tr>
<td>Co$_3$O$_4$ on FTO glass</td>
<td>Saturated KCl</td>
<td>CER</td>
<td>66</td>
<td>[14]</td>
</tr>
<tr>
<td></td>
<td>1 mol·L$^{-1}$ KOH</td>
<td>OER</td>
<td>101</td>
<td></td>
</tr>
<tr>
<td>RuO$_2$-TiO$_2$ @ Ti</td>
<td>Saturated NaCl</td>
<td>CER</td>
<td>39</td>
<td>[17]</td>
</tr>
<tr>
<td>RuO$_2$-TiO$_2$ @ Ti</td>
<td>5 mol·L$^{-1}$ NaCl</td>
<td>CER</td>
<td>41</td>
<td>[18]</td>
</tr>
<tr>
<td>La$_2$CoMnO$_6$</td>
<td>5 mol·L$^{-1}$ NaCl</td>
<td>CER</td>
<td>44</td>
<td>[19]</td>
</tr>
<tr>
<td></td>
<td>pH = 2.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 mol·L$^{-1}$ KOH</td>
<td>OER</td>
<td>115</td>
<td></td>
</tr>
</tbody>
</table>
### 3.3.3 Free chlorine capture

DPD method has been the most widely used method for quantitative analysis of free chlorine in water. DPD can be oxidized by chlorine and becomes a magenta-coloured compound known as a Würster dye at a near neutral pH. Before free chlorine capture tests, a series of standard NaClO solutions with different concentrations were made and tested by DPD reagent, and a linear fit of DPD reagent UV absorption and NaClO concentration was calculated (Figure 2.2). The linear fit was then used for calculating the concentration of free chlorine produced in electrocatalytic systems. All of the concentration results from free chlorine capture tests were in the linear concentration range of the fit.

Real raw waters, such as domestic and industrial raw waters, may contain quite different chloride concentrations ranging from 1.5 mmol·L⁻¹ to 1.5 mol·L⁻¹. A concentration of 0.1 mol·L⁻¹ was applied in all electrochemical oxidation tests in order to study the performance of electrodes in an environment which is similar to real raw waters. Samples 400EC30 and plain FTO glass were tested for free chlorine production in an electrolyte of 0.1 mol·L⁻¹ KCl, and the results are shown in Table 3.3. Preliminary experiments were carried out at different potentials, and at a potential of 2 V the working current can be kept above 1 mA, comparable with some previous studies that reported working currents ranging from 1-20 mA\(^{[14][16]}\), therefore 2.0 V was chosen as the fixed potential for later experiments. At the same fixed potential (2 V) and same time (1 h), both of them gave a good chlorine production efficiency of higher than 50% Faradaic yield. Higher current and more charge was passed by the Ti₂O₃ thin film electrode and more free chlorine was produced than plain
FTO glass. However, the plain FTO electrode had a slightly higher Faradaic yield of chlorine production. This indicates that slightly more charge is consumed by other reactions in the Ti$_2$O$_3$ electrocatalytic system than FTO glass.

Table 3.3. Results of free chlorine capture

<table>
<thead>
<tr>
<th>Test time: 1 h</th>
<th>400EC30</th>
<th>FTO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge</td>
<td>5.29 C</td>
<td>3.88 C</td>
</tr>
<tr>
<td>Chlorine concentration</td>
<td>5.56×10^{-4} mol·L$^{-1}$</td>
<td>4.54×10^{-4} mol·L$^{-1}$</td>
</tr>
<tr>
<td>Faradaic yield</td>
<td>50.7%</td>
<td>56.7%</td>
</tr>
</tbody>
</table>

3.3.4 Electrocatalytic test

Methyl orange (MO) and Tetracycline (TC) were chosen as model pollutants for electrocatalytic degradation tests. The former is an easily-tracked coloured dye and the latter is realistic model pollutant. The electrolytes used in the electrocatalytic tests are solutions of MO (4.6×10^{-4} mol·L$^{-1}$) or TC (2.08×10^{-4} mol·L$^{-1}$) along with 0.1 mol·L$^{-1}$ KCl. The degradation results of these two model pollutants over 1.5h is shown in Figure 3.6 alongside control experiments. Comparing with plain FTO glass, Ti$_2$O$_3$ thin film electrode had a higher degradation efficiency of MO (97.9% after 1.5h). Ti$_2$O$_3$ electrocatalyst also shows good performance on degrading TC via producing chlorine (78.0% after 1.5h). The performance of Ti$_2$O$_3$ thin film electrode in solutions containing
chloride was much better than that in solutions without chloride, suggesting that free chlorine took an important part of degrading model pollutants.

Figure 3.6. Electrocatalytic test result of degrading MO (a) and TC (b).

3.3.5 Mechanism study

Model pollutant molecules in an electrocatalytic system containing chloride ions can be degraded by three possible routes: degrading directly at the electrode (DET reactions), degrading by free chlorine and degrading by hydroxyl radical (·OH). Scavenging tests were carried out to study the roles of these three oxidation routes in the electrocatalytic system. Tert-butyl alcohol (TBA) was chosen as the scavenging reagent for hydroxyl radicals. The effective species in each electrolyte are listed in Table 3.4. The degradation percentages of each test are shown in Figure 3.7. The comparison between test 1 and 2 showed that approximately 75% of MO degradation was driven by free chlorine. The result of test 4 showed that 22.3% of MO was oxidized directly on the surface of electrode. Degradation percentages of test 2 and 4 are very similar, which may suggest that only a tiny amount of OH· took part in
the degradation of MO. This is likely because the electrolyte is at neutral pH and OH⁻ is difficult to be produced by the electrode, which has been shown in the LSV results above. The MO degradation in test 3 was lower than that in test 1 suggesting that TBA may react with some free chlorine and cause a decrease of MO degradation.

Table 3.4 Contents and effective species in each electrolyte of scavenging tests

<table>
<thead>
<tr>
<th>Test</th>
<th>MO (4.6×10⁻⁴ mol·L⁻¹)</th>
<th>KCl (0.1 mol·L⁻¹)</th>
<th>TBA (0.05 mol·L⁻¹)</th>
<th>Species for oxidation reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>√</td>
<td>√</td>
<td></td>
<td>Cl₂, HO⁻, electrode</td>
</tr>
<tr>
<td>2</td>
<td>√</td>
<td></td>
<td></td>
<td>HO⁻, electrode</td>
</tr>
<tr>
<td>3</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>Cl₂, electrode</td>
</tr>
<tr>
<td>4</td>
<td>√</td>
<td></td>
<td>√</td>
<td>electrode</td>
</tr>
</tbody>
</table>
3.3.6 Repeated use tests

Repeated use tests were carried out under the same conditions as the electrocatalytic test against MO for 6 cycles. Before the 4th, 5th and 6th cycle, the electrode was regenerated by a linear scan from 0V to -2V (vs. Ag/AgCl) in 0.1 mol·L⁻¹ KCl. Electrodes were rinsed by deionized water and dried under ambient air between each recycling and regeneration test. Fresh electrolyte was used in every test. The cell was ultrasonically cleaned by 0.1 mol·L⁻¹ HCl, water and ethanol between each test.

The current change during all test cycles is shown in Figure 3.8, while the degradation performances are listed in Table 3.5. For the cycles without regeneration of electrode, the current and charge dropped after the 1st cycle, which led to a decrease of MO degradation efficiency. No obvious change of
Current was found between the 2nd and 3rd cycles. After regeneration of electrode by negative potential sweep, the current and charge in the 4th cycle increased along with MO degradation efficiency. After several cycles of regenerating and recycling, the performance of recycled electrode returned to the same level as the fresh electrode. PXRD patterns of Ti$_2$O$_3$ thin film electrode before and after repeated tests were collected (Figure 3.9). No obvious change in phase composition and crystallinity of the electrocatalyst was found during the whole recycling test. The decrease of degradation efficiency may come from the destruction of active surface sites on the electrocatalyst for oxidation reaction during electrocatalytic reaction process. Previous research discovered that 3–4 atomic layers of oxygen-deficient anatase TiO$_2$ formed on the surface of Ti$_2$O$_3$ after electrolysis.$^{[22]}$ Ti$^{3+}$ on the surface may be oxidized to Ti$^{4+}$, along with additional oxygen coordinating with Ti atoms, possibly caused a structure rearrangement on the surface which cannot be detected by PXRD characterization. However, we have shown that the active surface sites can be regenerated by a quick linear scan to negative potential and the degradation efficiency will return to the same level as first usage. This may suggest that surface oxidation can be reversed. In summary, Ti$_2$O$_3$ thin film retained its crystallinity and structure during electrocatalytic tests, and the performance of Ti$_2$O$_3$ thin film electrode can be recovered by a simple regenerating method, which will extend the service life of the electrocatalyst.
Table 3.5 Results of recycling test; the 3rd, 4th and 5th cycles were followed by a sweep to negative potential before the subsequent test.

<table>
<thead>
<tr>
<th>cycle</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge / C</td>
<td>8.70</td>
<td>6.48</td>
<td>5.99</td>
<td>7.36</td>
<td>8.50</td>
<td>9.24</td>
</tr>
<tr>
<td>Degradation %</td>
<td>97.3</td>
<td>76.9</td>
<td>65.3</td>
<td>82.7</td>
<td>85.3</td>
<td>95.0</td>
</tr>
</tbody>
</table>

Figure 3.8 Current change during the recycling test
Figure 3.9 PXRD patterns of Ti$_2$O$_3$ thin film electrode before and after recycling test
3.4 Conclusions

A simple, low cost, earth abundant and stable Ti$_2$O$_3$ thin film electrode was prepared and its application was studied in chlorine-driven water treatment system. PXRD studies showed that by controlling the temperature and time of heating under air in the immobilizing procedure, the structure of Ti$_2$O$_3$ can be retained. The Ti$_2$O$_3$ electrode was found to be more effective for free chlorine evolution in neutral 0.1 mol·L$^{-1}$ chloride solution than plain FTO glass. It has a high efficiency in degrading MO (97.9% in 1.5h) and TC (78.0% in 1.5h) via free chlorine evolution. Mechanistic studies showed that free chlorine was the major species that oxidizes the organic pollutant molecules, while DET reactions also participated in the degradation of pollutants. The thin film electrode was able to be recycled and regenerated to keep a high performance in 6 cycles of usage.

Future work will focus on the detailed mechanism of the electrocatalytic system containing Ti$_2$O$_3$ thin film electrode and chloride, aiming to detect harmful side products like ClO$_4^-$ and halogenated organic compounds, which have been reported possible in previous studies. \cite{23,5} It is worth mentioning that plain FTO glass had a measurable performance during electrocatalytic tests, and all electrocatalytic tests were carried under ambient light. The role of FTO layer in the electrocatalytic system and possible photo-electrocatalysis would also be important to investigate in future studies. Modifications of Ti$_2$O$_3$ such as introducing oxygen vacancies on the surface have been reported in previous research,\cite{24} which is a possible way of enhancing activity of Ti$_2$O$_3$ electrocatalysts. Furthermore, we believe that Ti$_2$O$_3$ materials can be applied in complex wastewater treatment including organic compound degradation and microbe inactivation.
References


Chapter 4 Magnéli phase Ti\textsubscript{n}O\textsubscript{2n-1} film electrode for water treatment via electrochemical chlorine evolution

4.1 Introduction

Magnéli phase titanium oxides have been considered for a wide range of electrochemical applications, including electrochemical wastewater treatment. The commercial ceramic electrode Ebonex\textsuperscript{®}, which is usually a mixture of several Magnéli phase titanium oxides,\textsuperscript{[1][2]} has been applied in electrochemical water treatments in different forms, including powders, porous and non-porous three-dimensional solids.\textsuperscript{[1]} Ebonex\textsuperscript{®} electrodes have been proved effective in pollutant degradation in both chloride-riched and chloride-free model wastewater.\textsuperscript{[3][4]}

The special crystal structures of Magnéli phase titanium oxides contribute to their potential of electrochemical applications. Typically, for the formula Ti\textsubscript{n}O\textsubscript{2n-1}, shear planes are introduced by oxygen deficiency and appear at every nth layer of rutile-based TiO\textsubscript{6} octahedra chains.\textsuperscript{[1][5][6]} These shear planes act as electron pathways,\textsuperscript{[7]} and Magnéli phase titanium oxides show high conductivities.

Magnéli phase titanium oxides can be produced by reducing TiO\textsubscript{2} using a reducing agent, such as hydrogen, carbon, metal, metal hydrides, etc.\textsuperscript{[7][8]} Due to the methods used in manufacturing Magnéli phase materials, the product may contain a mixture of stoichiometries, and it is difficult to prepare the separate phases in a pure form.\textsuperscript{[1]} As one of the cheaper and safer synthesis method, carbothermal reduction of TiO\textsubscript{2} have been studied, and the products
formed are usually a mixture of different Magnéli phases.\textsuperscript{[5]}\textsuperscript{[9]}\textsuperscript{[10]} Literature introducing Magnéli phase titanium oxides synthesized by carbothermal reduction route seldom mentioned the electrochemical applications of those products. The electrochemical properties and possible applications in electrochemical system of those mixed Magnéli phase titanium oxide materials still need further study and comparison with existing data of Ebonex\textsuperscript{®} materials.

In this chapter, two carbothermal synthesis routes were used for producing Magnéli phase titanium oxides. The materials produced under different conditions were characterized and their morphologies and crystal structures were compared. Magnéli phase titanium oxide powder samples were immobilized on conductive FTO glass slides to form thin film electrodes by the same method as Ti_2O_3 film electrode (Chapter 3). Electrochemical properties of the Magnéli phase titanium oxide film electrodes were tested in electrolytes with and without chloride, in order to study their activity of chlorine evolution. Electrocatalytic tests against a model pollutant were carried out to study the performance of pollutant degradation via chlorine evolution.

\section{4.2 Experimental}

\subsection{4.2.1 Synthesis of Magnéli phase titanium oxides}

Two methods of mixing TiO_2 and carbon for carbothermal reduction reactions were used in this work, which were ball milling and polydopamine (PDA) coating. It has been reported that dopamine can form polydopamine by self-polymerization in weak basic environments such as in tris(hydroxymethyl)aminomethane (tris) buffer (pH \textasciitilde8.5), and can immobilize onto almost any type and shape of surface.\textsuperscript{[11]} Polydopamine can form a cover
layer on TiO$_2$ particles by simply adding TiO$_2$ powder into the self-polymerization system. Polydopamine acted as the carbon source in carbothermal reduction of TiO$_2$.

For the PDA coating route, 0.5 g P25 TiO$_2$ was dispersed in 80 mL tris buffer (pH ~8.5), then 0.5 g dopamine hydrochloride was added to the mixture under continuous stirring. The mixture was stirred under ambient temperature for 48 h, during which the colour gradually changed from orange to dark grey. The mixture was then centrifuged to collect solid product, washed by deionized water and ethanol, and finally dried in a vacuum oven at 65°C overnight.

For the ball milling route, 0.5 g P25 TiO$_2$ and 0.1 g activated charcoal were mixed and dispersed in 1.5 mL ethanol before transferred to a ZrO$_2$ planetary grinding jar. 6 ZrO$_2$ balls were added into the grinding jar. Ball milling was conducted using a planetary ball mill instrument for 24 h at 200 rpm. After ball milling the mixture was dried at 80 °C on a hotplate to remove ethanol.

After mixing P25 TiO$_2$ and carbon via the two routes above, the mixture was annealed in a tube furnace under Ar atmosphere at the temperatures listed in Table 4.1. The dwell time was fixed to 1 h, then the mixture was allowed to cool to room temperature under a flow of Ar.
Table 4.1 Annealing conditions of carbothermal reduction samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>CB1200</th>
<th>CB1150</th>
<th>CB1100</th>
<th>PDA1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing method</td>
<td>Ball milling</td>
<td></td>
<td></td>
<td>PDA coating</td>
</tr>
<tr>
<td>Heating temperature (°C)</td>
<td>1200</td>
<td>1150</td>
<td>1100</td>
<td>1200</td>
</tr>
<tr>
<td>Dwelling time</td>
<td></td>
<td></td>
<td>1h</td>
<td></td>
</tr>
</tbody>
</table>

4.2.2 Paste preparation

0.4 g of Magnéli phase titanium oxides powder was ground by pestle and mortar before stirring with 1 g mixture of ethyl cellulose and ethanol (10 wt% ethyl cellulose), 0.81 g terpineol and 1 mL ethanol overnight. The mixture was ultrasonicated using a Toption ultrasonic homogenizer at a power of 400 W 3 times, 1 min each time. Excess ethanol was evaporated by rota-evaporation at 40 °C, 120 rpm.

4.2.3 Thin film electrode preparation

FTO glass was cut to 1 cm × 3 cm rectangular slides and cleaned by ultrasonication in detergent solution (Decon 90, ~ 5% in tap water), tap water, deionized water and ethanol for 15 min each step. Magnéli phase titanium oxides paste was doctor bladed on the conductive surface of FTO glass at an area of 1 cm × 2.5 cm spaced by scotch tape (thickness 0.060 mm). Thin films
on the glass slides were dried at 100 °C under air for 30 min and annealed using a programmable hotplate with a program below: 325 °C, 5 min, 375 °C, 5 min, 400 °C, 30 min. The heating ramp rate was 10 °C/min between every stage. After annealing, silver conductive paint was painted on the blank part of conductive surface of FTO glass slides to increase the conduction between electrode and clip.

4.3 Result and discussion

4.3.1 Characterization of the phases formed

The morphology of the four Magnéli phase titanium oxide samples were analysed using SEM, as shown in Figure 4.1. Spherical and irregular shaped particles were found in all 4 samples. Comparison of the samples prepared using ball milling showed an increase of particle size from approximately 100 nm to 300 nm as the annealing temperature increased. For sample PDA1200, although the annealing temperature is high, the particle size was not as large as CB1200, which may suggested that PDA coating can inhibit the sintering of titanium oxides. Previous research using similar carbothermal reduction synthesis routes reported a similar increase of particle size when the annealing temperature was increased, and a smaller particle size of PDA-coated sample comparing with a ball milled sample at the same annealing temperature.[5]
Figure 4.1 SEM images of (a) CB1200, (b) CB1150, (c) CB1100 and (d) PDA1200

PXRD patterns of ball milled TiO$_2$-C mixture and PDA-coated TiO$_2$ before annealing were collected and compared with standard TiO$_2$ patterns (anatase TiO$_2$ ICSD#9852, rutile TiO$_2$ ICSD#9161) (Figure 4.2). Both of them showed a mixture of a large amount of anatase and a small amount of rutile, which is the content of P25 TiO$_2$ (approximately 80% anatase and 20% rutile). These PXRD pattern suggested that no Magnéli phase formed before annealing.
To identify the crystalline phases presented in carbothermal reduction products under different heating temperatures, PXRD patterns of all Magnéli phase titanium oxide samples were collected and compared with standard patterns of possible titanium oxide products (Ti$_2$O$_3$ ICSD#1462, α-Ti$_3$O$_5$ ICSD#26492, Ti$_4$O$_7$ ICSD#6098, Ti$_5$O$_9$ ICSD#9038, Ti$_9$O$_{17}$ ICSD#9042, anatase TiO$_2$ ICSD#9852, rutile TiO$_2$ ICSD#9161) (Figure 4.3). The phases identified as present in each sample are listed in Table 4.2. All samples showed a mixture of at least two titanium oxide (Ti$_n$O$_{2n-1}$) phases. Among the ball milled samples, further reduction happened at higher annealing temperatures, and Magnéli
phase titanium oxides Ti$_n$O$_{2n-1}$ with lower $n$ values were formed. The observed peak at 23.0°, in the PXRD pattern of CB1100, was reported as the most intense peak of the phase Ti$_6$O$_{11}$ by previous research.$^{[13]}$ However, the reduction in PDA coating sample was limited, a large amount of anatase TiO$_2$ and a small amount of rutile TiO$_2$ remained. A possible reason for this would be that during the PDA coating step, only a limited amount of dopamine formed the PDA covering on the TiO$_2$ powder, therefore carbon provided by the PDA layer on TiO$_2$ was not enough for further reduction. One point to note is that anatase TiO$_2$ did not completely transform to rutile TiO$_2$, which is more thermodynamically stable than anatase TiO$_2$. Previous studies have suggested that higher partial pressure of CO caused by the faster solid–solid reaction rate during the carbothermal reduction reaction, which will inhibit the anatase–rutile phase transformation.$^{[5]}$ In the reduction process of PDA1200, limited reduction happened, consumed all carbon available and formed Ti$_9$O$_{17}$, while the phase transition from anatase to rutile was inhibited. According to the PXRD results, the reduction from TiO$_2$ to Magnéli phase titanium oxide was affected by annealing temperature and the form of carbon contacting with TiO$_2$. 
## Table 4.2 Phases of Magnéli phase titanium oxide samples identified by PXRD patterns

<table>
<thead>
<tr>
<th>Sample</th>
<th>CB1200</th>
<th>CB1150</th>
<th>CB1100</th>
<th>PDA1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phases identified as present by PXRD</td>
<td>Ti$_2$O$_3$ + Ti$_3$O$_5$</td>
<td>Ti$_4$O$_7$ + Ti$_3$O$_5$</td>
<td>Ti$_5$O$_9$ + Ti$_4$O$_7$ + Ti$<em>6$O$</em>{11}$</td>
<td>Anatase + rutile + Ti$<em>9$O$</em>{17}$</td>
</tr>
</tbody>
</table>
Figure 4.3 PXRD patterns of Magnéli phase titanium oxides, with symbols showing the situation of standard peaks

(2: Ti$_2$O$_3$ ICSD#1462, 3: $\lambda$-Ti$_3$O$_5$ ICSD#26492, 4: Ti$_4$O$_7$ ICSD#6098, 5: Ti$_5$O$_9$

ICSD#9038, 9: Ti$_9$O$_{17}$ ICSD#9042, A: anatase TiO$_2$ ICSD#9852, R: rutile

TiO$_2$ ICSD#9161

* refers to the most intense peak of the phase Ti$_6$O$_{11}$')
4.3.2 Electrochemistry

LSV of all Magnéli phase titanium oxides film electrodes were measured in 2 different electrolytes: chloride-rich electrolyte (0.1 mol·L⁻¹ KCl) and neutral electrolyte (0.1 mol·L⁻¹ Na₂SO₄). Tafel plots and Tafel slopes of each electrode measured in the two electrolyte solutions are shown in Figure 4.4. All samples showed quite large Tafel slope values in both the chloride-rich and neutral electrolytes, about 3 times larger than it of Ti₂O₃ film electrode (Chapter 3, Figure 3.5 d). This suggested that both CER and OER have unfavourable kinetics on all Magnéli phase titanium oxides film electrodes. There was no obvious difference of Tafel slopes between each sample, suggesting that the efficiency of CER and OER on each electrode would be similar.
Figure 4.4 Tafel plots of Magnéli phase titanium oxides film electrodes, measured in 0.1M Na$_2$SO$_4$ (upper) and 0.1M KCl (lower)
4.3.3 Mott-Schottky plot

Mott-Schottky analysis is a frequently used method for determining the flat band potential and charge carrier density of semiconductor materials.\textsuperscript{[14]} In Mott-Schottky plot, the slope of linear fit relates to charge carrier density, and the intercept of linear fit to the x axis shows the value of flat band potential. A higher charge carrier density of the material suggests a better charge transfer efficiency, which links to the good performance as a electrode material. Mott-Schottky plots of all Magnéli phase titanium oxides film electrodes are shown in Figure 4.5, and the calculated slope and flat band potential are listed in Table 4.3. The measurements were carried out in 0.1 mol·L\textsuperscript{-1} Na\textsubscript{2}SO\textsubscript{4} electrolyte, and the data points were collected at a frequency of 2000 Hz. A previous study had given a range of the dielectric constant (\(\varepsilon\)) of Magnéli phase titanium oxides, which was \(10^5\text{-}10^6\).\textsuperscript{[15]} The accurate charge carrier density values of each sample were not able to be calculated, however, since they have similar dielectric constant and the same area, comparison of charge carrier density can be carried out by comparing the values of slope. According to the calculation results, the three ball milled samples showed similar charge carrier density and flat band potential, while PDA1200 showed a relatively larger slope and high flat band potential. This result matches well with the PXRD results, in terms of the performance of the phases identified as present in each of the samples. The PDA sample, which contains mostly low-conductivity TiO\textsubscript{2}, shows quite different electrochemical properties than the balled milled samples, which contain high-conductivity Magnéli phase titanium oxides. Data from previous study showed that Ti\textsubscript{4}O\textsubscript{7} has the highest conductivity among all Magnéli phase titanium oxides.\textsuperscript{[1]} However, the samples containing Ti\textsubscript{4}O\textsubscript{7} didn’t show obviously higher charge carrier density than other samples.
Figure 4.5 Mott-Schottky plots of Magnéli phase titanium oxides film electrodes

Table 4.3 Calculation results from Mott-Schottky plots

<table>
<thead>
<tr>
<th></th>
<th>CB1200</th>
<th>CB1150</th>
<th>CB1100</th>
<th>PDA1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>3.69x10^9</td>
<td>2.62x10^9</td>
<td>1.87x10^9</td>
<td>7.87x10^9</td>
</tr>
<tr>
<td>Flat band potential</td>
<td>-0.29</td>
<td>-0.75</td>
<td>-0.60</td>
<td>-0.025</td>
</tr>
</tbody>
</table>
4.3.4 Free chlorine capture and MO degradation

According to all characterization and test results above, it is hard to tell the difference between the electrochemistry performance of all Magnéli phase titanium oxide film electrodes. As the most reduced sample containing Ti$_2$O$_3$ phase, CB1200 was used for further electrochemical studies, in order to make a comparison with pure Ti$_2$O$_3$ film electrode.

CB1200 was tested for free chlorine production in an electrolyte of 0.1 mol·L$^{-1}$ KCl, and the results are shown in Table 4.4. At a fixed potential of 2 V and a reaction time of 1.5 h, the concentration of free chlorine produced on CB1200 electrode was much lower than that of Ti$_2$O$_3$ electrode in 1 h (5.56×10$^{-4}$ mol·L$^{-1}$). The Faradaic yield of chlorine evolution was also low (23%) comparing with pure Ti$_2$O$_3$ electrode (50.7%). This result suggested that over 3/4 of charge was consumed by other reactions instead of oxidizing chloride. Current change during the test is shown in Figure 4.6. The current going through CB1200 electrode remained low and gradually decreased with time to around 0.66 mA at 5000s. The low current may come from a high resistance of the material, which led to a low efficiency and low yield of free chlorine evolution.

Table 4.4 Results of free chlorine capture test

<table>
<thead>
<tr>
<th>Free chlorine concentration (mol/L)</th>
<th>Charge (C)</th>
<th>Faradaic yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.73×10$^{-4}$</td>
<td>5.727</td>
<td>23.0%</td>
</tr>
</tbody>
</table>
Figure 4.6 Current change during free chlorine capture test of CB1200
4.3.5 Electrocatalytic test

Methyl orange (MO) was chosen as the model pollutant for electrocatalytic degradation tests. The electrolyte used in the electrocatalytic tests is a solution of MO (4.6×10⁻⁴ mol·L⁻¹) along with 0.1 mol·L⁻¹ KCl. The degradation results of the model pollutant over 1.5h is shown in Figure 4.7 alongside control experiments using the electrolyte containing 4.6×10⁻⁴ mol·L⁻¹ MO and 0.1 mol·L⁻¹ Na₂SO₄. Comparing the results of the MO degradation with and without the help of free chlorine, the MO degradation efficiency with free chlorine was obviously higher (34.7% comparing with 23.9%). However, the total degradation was still much lower than that of Ti₂O₃ film electrode, which as found to be 97.9% under the same conditions. As shown in the free chlorine capture test, the low CER efficiency of CB1200 electrode (2.73×10⁻⁴ mol·L⁻¹ and 23.0% Faradaic yield in 1.5h) limited the chlorine-driven degradation of model pollutant.

PXRD patterns of CB1200 film electrode before and after the electrocatalytic test were collected and are shown in Figure 4.8. No obvious change in the phases present was found after electrocatalytic test.
Figure 4.7 Electrocatalytic degradation results of CB1200 electrode against MO, using electrolytes containing 0.1 mol·L⁻¹ KCl (black) or 0.1 mol·L⁻¹ Na₂SO₄ (red)
In summary, Magnéli phase titanium oxides produced by carbothermal reduction showed limited performance as an electrocatalyst for chlorine-driven water treatment. The low current going through the material and the unfavourable kinetics are proposed reasons for this limited performance. Since the materials are all mixed-phase, it is possible that the charge transfer between phases is an important limitation of the electrochemistry performance of Magnéli phase titanium oxides materials. Characterization results in this work cannot determine whether different phases were formed with interface structures between each other, or formed as separate crystallites. According to previous studies, lattice mismatch may occur at the interface between
different Magnéli phase Ti$_{n}$O$_{2n-1}$, especially between n≤3 and n≥4.$^{[5]}$ Electron pathways in different phases may not be well connected due to separated crystallites or lattice mismatch, which led to a result of poor electrochemical conductivity and poor electrochemical oxidation efficiency.

### 4.4 Conclusions

A series of Magnéli phase titanium oxide materials were produced via two synthesis routes based on carbothermal reduction. SEM images and PXRD patterns of ball milled samples showed that highly reduced phases (smaller n value) with larger particle sizes formed as the annealing temperature increases. Film electrodes of all samples were prepared and electrochemical tests were carried out on them. All film electrodes have similar high Tafel slopes, which may suggest unfavorable kinetics. Free chlorine capture and pollutant degradation tests of the CB1200 film electrode showed a low yield of chlorine evolution and low efficiency of pollutant degradation. A poor charge transfer between mixed Magnéli phases may influence the conductivity of materials, which then leads to the poor performance of electrocatalytic water treatment.

Future work will focus on the relationship between the detailed crystal structures of mixed phases Magnéli phase materials and the electrochemical performance of them. The high conductivity of pure Magnéli phase comes from the electron pathway based on regular shear planes. In the case of mixed phases materials, there is no information about how separated crystallites or lattice mismatch affect the electron pathway and electron transfer. HRTEM has already been used to study the intergrowths between phases of carbothermal reduced Magnéli phase titanium oxide products.$^{[5][10]}$ However, the results have
not been linked to electrochemical properties of the materials. Information about the electron pathway between different phases should be studied along with the electrochemical properties, in order to discover the structure that can achieve high electrochemical performance.

Mechanism of CER on the surface of pure Ti₄O₇ electrode have been studied by previous studies. Further study about the mechanism of CER on mixed Magnéli phases electrode is important to the comparison between single phase and mixed phase materials, and will help evaluate the application of mixed Magnéli phase TiₙO₂n₋₁ on electrocatalytic chlorine-driven water treatment.
References


Chapter 5  Low-cost black titanium dioxide preparation and application in photocatalytic water treatment

5.1 Introduction

Black titanium dioxide (TiO$_2$) is a semiconductor material which usually has a wider light absorption and lower charge recombination rate than pristine TiO$_2$. It has a potential for applications in photo-driven water treatment. Traditional synthesis methods of black TiO$_2$ require high temperature, high pressure and an active reduction reagent like hydrogen, which increases the risk and cost of synthesis.[1] In recent research, some low-cost synthesis routes to black TiO$_2$ have been reported, such as solvothermal method,[2] ‘one pot’ gel combustion method[3] and UV light-induced electron doping method.[4]

Previous studies reported that synthesis route of black TiO$_2$ played an important role in defining the morphology, optical and functional properties.[1] For black TiO$_2$ materials produced by traditional hydrogen reduction method, information about the relationship between synthesis condition and product properties have been reported by literature.[5][6] However, for the low-cost synthesis routes, there is still no clear explanation about how these synthesis routes affect the properties of materials. Mechanism of synthesis, defect species, and photocatalytic performance of black TiO$_2$ produced by these routes still need further study.

Work in this chapter aimed to synthesize black TiO$_2$ via some easy and low-cost methods, to study the samples’ morphology, structure and defect species, and aim to find some relationship between synthesis conditions and properties.
of the products. NaBH₄ reduction, solvothermal method and carbothermal reduction were chosen because these routes are safer and cost less energy than traditional methods. Irrespective of the actual colour, the literature term “black TiO₂” will be used to denote the products. The polymorphs/phases formed and light absorption of the black TiO₂ samples are studied using powder X-ray diffraction (PXRD) and diffuse reflectance spectra (DRS). Powder products were immobilized on glass substrates to form thin film photocatalysts when possible. Photocatalytic tests against model pollutants are carried out using black TiO₂ photocatalysts, and the photocatalytic performance and potential of applying in real-world water treatment are studied and discussed.

5.2 Experimental

5.2.1 P25 TiO₂ reduction using NaBH₄

A certain amount of NaBH₄ was dissolved into 100 mL 1 mol·L⁻¹ NaOH aqueous solution under vigorous stirring. 0.1 g P25 TiO₂ powder was then added into the solution. The mixture was then stirred for 2 h at different temperatures. For the sample undergoing ultrasonic treatment, the mixture of P25 TiO₂ and NaBH₄ solution was treated by Toption ultrasonic homogenizer at 300 W for 2 h, with a working cycle of 1 s vibration and 2 s rest. The temperature of the reaction system during ultrasonic treatment was around 30 °C. After vacuum filtering, the product was dried on a hotplate for 2 h at 60 °C. The samples were named as 0.1M-30, 0.2M-30, 0.2M-80 and 0.2M-sonic. The quantities of NaBH₄ and the reaction temperatures of preparing all samples are listed in Table 5.1.
Table 5.1 Synthesis conditions of NaBH$_4$ reduced black TiO$_2$ samples

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Quantity of NaBH$_4$ (g)</th>
<th>Reaction temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1M-30</td>
<td>0.38</td>
<td>30</td>
</tr>
<tr>
<td>0.2M-30</td>
<td>0.76</td>
<td>30</td>
</tr>
<tr>
<td>0.2M-80</td>
<td>0.76</td>
<td>80</td>
</tr>
<tr>
<td>0.2M-sonic</td>
<td>0.76</td>
<td>30 (in ultrasonic homogenizer)</td>
</tr>
</tbody>
</table>

5.2.2 Solvothermal method

A certain volume of titanium tetrabutoxide (TTB) (listed in Table 5.2) was added to 50 mL ethylene glycol under vigorous stirring. Then the pH of the solution was adjusted to 10 using an aqueous ammonia solution (1.8 vol%). After further stirring for 2 h, the solution was transferred into a 100 mL stainless steel autoclave. The autoclave was heated in a vacuum oven at 200 degrees for 24 h. After naturally cooled to room temperature, the solution was centrifuged and the gel was separated with the solvent. The gel was washed with ethanol and dried on a hotplate at 60 °C overnight. The samples were named as 0.5T, 2T and 3T, indicating the quantity of TTB added.
Table 5.2 Synthesis conditions of solvothermal method black TiO$_2$ samples

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Quantity of TTB (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5T</td>
<td>0.5</td>
</tr>
<tr>
<td>2T</td>
<td>2</td>
</tr>
<tr>
<td>3T</td>
<td>3</td>
</tr>
</tbody>
</table>

5.2.3 Carbothermal reduction

0.5 g P25 TiO$_2$ was dispersed in 80 mL tris buffer (pH ~8.5), then 0.5 g dopamine hydrochloride was added to the mixture under continuous stirring. The mixture was stirred under ambient temperature for 48 h, during which the colour gradually changed from orange to dark grey. The mixture was then centrifuged to collect solid product, washed by deionized water and ethanol, and finally dried in a vacuum oven at 65 °C overnight. The powder was annealed in a tube furnace under Ar flow at 1000 °C for 1h. with a heating rate of 5 °C/min. The product sample was named as P25-PDA-T.

5.2.4 Film formation

Deionized water (2 mL) was dropped into black TiO$_2$ powder (0.5 g) under stirring. Acetyl acetone (0.1 mL) and Triton X-100 (1 drop) were then added before stirring overnight to make the black TiO$_2$ paste.

Microscope glass slides were cut into 3.75 cm * 0.9 cm rectangles before ultrasonic cleaning in a solution of detergent (Decon 90, ≈5% in tap water) for
15 min. The substrates were then scratched by sand paper on one side and then ultrasonically cleaned with 5% detergent, tap water, deionised water and finally ethanol for 15 min each step. Finally, the glass slides were treated with UV-ozone cleaner for 15 min. The black TiO$_2$ paste was then doctor bladed in 3 cm * 0.9 cm strips onto the scratched surface of the glass slides by using scotch tape (3M) as a spacer. After drying under ambient air, the films were heated to 300°C in stages under vacuum in a vacuum oven to remove the organic templates and leave a highly porous TiO$_2$ film. The temperature profile of the heating regime was as follows: 250°C for 5 min, 275°C for 5 min, 300°C for 30 min. The heating ramp rate between each stage was 2.5°C min$^{-1}$.

5.2.5 Photocatalytic testing

Two systems for photocatalytic testing were used and are shown in Figure 5.1. Rhodamine B was chosen as the model pollutant for testing.

For thin film photocatalyst testing (Figure 5.1a), 3 cm * 0.9 cm black TiO$_2$ photocatalyst films were submerged into an aqueous solution of Rhodamine B (3 mL, 1.0×10$^{-5}$ mol·L$^{-1}$) in a standard UV-vis quartz cuvette. The films were stirred in the dark for 30 min to establish an adsorption equilibrium, then irradiated with a 370 nm or 410 nm LED (4 W applied power). The distance of LED and the film was fixed to 5 cm. The decolourisation of Rhodamine B was followed by measuring the absorption at 553 nm using a JASCO V-670 spectrophotometer. Measurement was done every 10 min during stirring in the dark and every 20 min during stirring under LED light.

For powder photocatalyst testing (Figure 5.1b), 0.1 g black TiO$_2$ photocatalyst powder was added into an aqueous solution of Rhodamine B (100 mL, 1.0×10^{-4} mol·L$^{-1}$) in a glass container under vigorous stirring. The mixture was stirred
in the dark for 30 min to establish an adsorption equilibrium, then irradiated with a 410 nm LED (4 W applied power). The distance of LED and the bottom of glass container was fixed to 10 cm. The decolourisation of Rhodamine B was followed by measuring the absorption at 553 nm using a JASCO V-670 spectrophotometer. 0.3 mL aliquot was taken out and diluted to 3 mL every 10 min during stirring in the dark and every 20 min during stirring under LED light. The diluted aliquots were centrifuged for 10 min at 4400 rpm before measuring the absorption.

Figure 5.1 Photocatalytic test set-ups: (a) thin film photocatalytic test, (b) powder photocatalytic test
5.3 Result and discussion

5.3.1 Black TiO$_2$ produced by NaBH$_4$ reduction

All samples prepared from NaBH$_4$ reduction were white powders and it was difficult to visibly observe any colour difference between NaBH$_4$ reduced TiO$_2$ samples and P25 TiO$_2$ samples. Thin films of 0.2M-sonicated material showed the same colour as the 0.2M-sonicated powder sample. PXRD patterns of original P25, 0.2M-30 and 0.2M-sonic are shown in Figure 5.2.

Comparing with the standard anatase (ICSD#9852) and rutile (ICSD#9161) calculated PXRD patterns, the typical peaks of anatase and rutile can be seen in patterns of 0.2M-30 and 0.2-sonic samples. Patterns of reduced TiO$_2$ samples are very similar to that of original P25 TiO$_2$, suggesting that the reduction didn’t change the structure of the TiO$_2$ phase. It is possible that NaBH$_4$ only reacted on the surface of powder TiO$_2$, forming a disordered layer that didn’t change the bulk structure.
Figure 5.2 PXRD patterns of NaBH$_4$ reduced TiO$_2$ samples compared to standard theoretical PXRD patterns of the TiO$_2$ polymorphs rutile and anatase
Diffuse reflectance spectra of NaBH₄ reduced TiO₂ samples were measured, and the Tauc plot of those samples are shown in Figure 5.3. Comparing with the Tauc plot of original P25 TiO₂ powder, the band gaps of all reduced samples (3.15 eV) were narrower than that of P25 TiO₂ (3.30 eV). The slight change of the band gap suggested that some defect species were produced by NaBH₄ reduction but the quantity is limited. There is no obvious difference between the Tauc plot of the different reduced TiO₂ samples, which may suggest that the quantities of defect species in those samples are similar. Taking the results of PXRD measurements into consideration, there may be limited defects on the surface of the powder samples produced by NaBH₄ reduction.

![Figure 5.3 Tauc plot of NaBH₄ reduced TiO₂ samples](image)

*Figure 5.3 Tauc plot of NaBH₄ reduced TiO₂ samples*
Thin films of the 0.2M-sonic material were made by the method described above and used for photocatalytic testing against Rhodamine B. According to the result in Figure 5.4, Rhodamine B shows little degradation after 3 h, which means the photocatalytic efficiency of 0.2M-sonic thin film under visible light is very poor.

![Graph showing absorbance over time](image)

*Figure 5.4 Testing NaBH₄ reduced TiO₂ thin film photocatalyst for degradation of Rhodamine B*

From the characterization results above, the poor photocatalytic efficiency of the sample possibly came from the limited reduction reaction in preparing the sample. The band gap of the material was 3.15 eV, which corresponds to a wavelength of 394 nm. Therefore, response to 410 nm light was negligible. The defect species produced by NaBH₄ reduction in this method are not
enough to give an improvement to the performance on degrading Rhodamine B under visible light.

5.3.2 Black TiO$_2$ produced by solvothermal method

Samples prepared by solvothermal methods were pale yellow powders. Thin films prepared from doctor-blading and annealing in vacuum oven became brown. PXRD patterns of the black TiO$_2$ samples prepared via the solvothermal method are shown in Figure 5.5. The PXRD patterns of the samples prepared via the solvothermal method match the standard anatase pattern (ICSD#9852), suggesting that all the samples contain anatase, and the peak widths suggested they all have similar crystallinities. Crystallite size of all samples were calculated by Scherr equation, and the results were listed in Table 5.3. All the samples were suggested to have similar crystallite size around 5.5~6 nm.

Table 5.3 Crystallite size of solvothermal method black TiO$_2$ samples

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5T</td>
<td>5.5(0)</td>
</tr>
<tr>
<td>2T</td>
<td>5.6(3)</td>
</tr>
<tr>
<td>3T</td>
<td>5.9(6)</td>
</tr>
</tbody>
</table>
Figure 5.5 PXRD patterns of solvothermal method black TiO$_2$ samples compared to standard theoretical PXRD patterns of anatase
SEM images of sample 2T and 3T were shown in Figure 5.6. Large bulk particles with a size of over 10 μm were found in both 2T and 3T, along with some smaller particles. The crystallite size is much smaller than the particle size, suggesting that small nanoparticles have aggregated into a bulk, which caused a decrease of surface area. This was expected to affect the surface photocatalytic reaction efficiency.

Diffuse reflectance spectra of black TiO$_2$ samples prepared by solvothermal methods were measured, and the Tauc plot comparing these samples is shown in Figure 5.7. The calculated band gap data of the three black TiO$_2$ samples prepared from the solvothermal method are listed in Table 5.4. The band gaps of 3 samples are slightly narrower than P25 TiO$_2$ (3.30 eV). All 3 Tauc plots of the 3 samples have an additional absorption tail in visible area, showing that some visible light can be absorbed by the materials. A previous study on black TiO$_2$ produced by a similar solvothermal route also reported some additional light absorption in visible area determined by UV-vis absorption spectrum.[2] The additional absorption tails in Tauc plots may suggest that the defect species in the material introduced some localized state between the
conduction band and valence band, therefore the material can absorb some visible light.

![Figure 5.7 Tauc plot of solvothermal method black TiO$_2$ samples](image)

**Table 5.4 Band gap of solvothermal method black TiO$_2$ samples**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5T</td>
<td>3.15</td>
</tr>
<tr>
<td>2T</td>
<td>3.21</td>
</tr>
<tr>
<td>3T</td>
<td>3.23</td>
</tr>
</tbody>
</table>
Thin films of solvothermal method black TiO$_2$ samples were prepared using the same method above and used in photocatalytic tests. However, the film was found to crack and fall from the glass substrate during the photocatalytic test. According to SEM images, the powder samples had quite large particles, which made the material difficult to stay firm on the glass substrate.

Instead of thin film, powder sample 3T was used for carrying out the photocatalytic test against Rhodamine B under 410 nm LED light. According to the test result shown in Figure 5.8, powder 3T had 48.8% Rhodamine B degradation efficiency in 3 h. Although the solvothermal method black TiO$_2$ powder has the ability of absorbing visible light and degrading the model pollutant, failure of immobilizing on glass substrate makes the material hard to be separated from the system, which has limited its real-world application.
Black TiO$_2$ materials synthesized by solvothermal method were able to absorb some visible light and help degrading pollutants in water, which may suggest that defect species were introduced to the crystal structure of TiO$_2$ and contributed to the photocatalytic reaction driven by visible light. However, the large particle size of the material affected the surface area and the combination between particles and glass substrate, and its application on real-world wastewater treatment became difficult.

5.3.3 Reduced TiO$_2$ prepared via carbothermal reduction

P25-PDA-T appears as a black powder, and the black colour was retained after forming a thin film on glass substrates using the same method above. A PXRD
pattern of P25-PDA-T was collected and compared with standard patterns of anatase (ICSD#9852) and rutile (ICSD#9161) (Figure 5.9). The result showed that P25-PDA-T has the phase structure of both anatase and rutile, and rutile has much higher intensity than anatase in the pattern. Comparing with the PXRD pattern of the precursor P25 TiO$_2$, the different peak intensity indicates that anatase has transformed to rutile during the reaction. There is no other peaks observed from structures other than anatase and rutile.

Figure 5.9 PXRD pattern of P25-PDA-T comparing with rutile and anatase

Diffuse reflectance spectrum of P25-PDA-T powder was measured and the Tauc plot is shown in Figure 5.10. From the Tauc plot, P25-PDA-T showed a high absorption of light across the whole range of measurement, covering both UV and visible light. A linear fit to the mid-region of the Tauc plot gives a value
of band gap of 1.51 eV. Previous researches about black TiO$_2$ reported similar UV-vis absorption spectra or diffuse reflectance spectra, with the band gap value around 2.0 eV.$^{[7][8][9]}$ However, P25-PDA-T showed high absorption at the whole range of measurement (200 nm – 800 nm). It is possible that many defect states appeared in the band structure, and the band gap is hard to define from the full-range high absorption spectrum.

Figure 5.10 Tauc plot of P25-PDA-T powder
In order to study whether Ti$^{3+}$ and carbon are present in the carbothermal reduction product, TGA data of P25-PDA-T powder heated under air was collected. Pure Ti$_2$O$_3$ was used as a reference of oxidizing Ti$^{3+}$. According to the results in Figure 5.11, pure Ti$_2$O$_3$ started to gain weight at around 500 °C, which was taken to be the process of Ti$^{3+}$ oxidizing to Ti$^{4+}$ and combining with oxygen atoms. However, P25-PDA-T started to lose weight at around 500 °C. The decrease of mass may be considered as burning off carbon that may be present on the surface. It is therefore not able to determined whether Ti$^{3+}$ is present only by TGA results.

*Figure 5.11 TGA results of P25-PDA-T*
Photocatalytic test of P25-PDA-T thin film against RhB was carried out using LEDs of 370 nm and 410 nm. P25 TiO$_2$ film was also tested under the same condition as a control test. P25-PDA-T thin film was found to have high absorption of RhB molecules, and the system was kept in dark overnight to obtain a stabilised absorption before the test. The system was stirred in dark for 60 min before exposure to LED light, during which some absorbed RhB molecules went back to the solution, and led to a rise of concentration in the dark (Figure 5.12). According to the result showed in Figure 5.12, in the 1 h test, P25-PDA-T only degraded 17.8% and 2.2% RhB respectively under 370 nm and 410 nm light, both lower than P25. Degradation testing of 4-chlorophenol was also tested using P25-PDA-T thin film, however, no degradation was found under 410 nm and 370 nm LED light.
Figure 5.12 Testing P25-PDA-T thin film photocatalyst for degradation of Rhodamine B

Black TiO₂ sample produced by carbothermal reduction had very high visible light absorption, but the photocatalytic efficiency of degrading RhB was lower than white TiO₂. Carbon was found remained in the sample, and the characterization above couldn’t determine the existence of defect species. A possibility reason for the poor photocatalytic efficiency may be a quick charge recombination caused by many defect states in band structure (if exist) or carbon in the material.

5.4 Conclusions

Black TiO₂ samples were prepared via 3 different low-cost routes. NaBH₄ can produce a limited quantity of defect species on the surface of P25 TiO₂ at low temperatures and in aqueous conditions. The band gaps of NaBH₄ reduced
TiO$_2$ samples were found to be slightly narrower than that of P25 TiO$_2$, but the samples were found to hardly absorb visible light and have poor photoactivity. Black TiO$_2$ samples prepared via a solvothermal route were shown to form the anatase polymorph, as confirmed by PXRD, and have some additional absorption in the visible region, as confirmed by diffuse reflectance spectra. Powder sample of solvothermal method black TiO$_2$ showed some efficiency on degrading model pollutant, however, thin films of them poorly adhered to glass substrates, which led to a failure of the thin film photocatalytic test. Black TiO$_2$ samples prepared via a carbothermal method were shown to form a mixture of anatase and rutile polymorph, as confirmed by PXRD. Despite the high absorption of UV and visible light, carbothermal method black TiO$_2$ showed poor performance on degrading model pollutants.

Future work for black TiO$_2$ synthesized by these easy and low-cost routes will be further characterization, including HRTEM, XPS etc. HRTEM images give a clear view of lattice, surface defects and possible core-shell structure of samples, while XPS can suggest the existence of defect species. We aim to learn more about the relationship between the concentration of defect species, band structure and photocatalytic performance of the black TiO$_2$ material. Furthermore, mechanism studies of these routes are also helpful on controlling defect species in the product and design the materials for better performance and wider application.

Previous research suggests that testing a new photocatalyst with only one kind of molecule as the model pollutant may lead to an incomplete picture of the photocatalytic performance.$^{[10]}$ Therefore, organic molecules, inorganic compounds and bacteria will also be chosen as substrates in future photocatalytic tests. Tests of multiple use and recycling of immobilized
photocatalysts will also be carried out. Results of these tests will give important information about whether the photocatalyst can be applied on real-world wastewater treatment, especially in low-income areas.
References

Thesis conclusion and outlook

Wastewater treatment has been, and will continue to be, an important topic over the world, relating to environmental protection and water scarcity. Photocatalytic and electrocatalytic water treatment have been regarded as suitable techniques applied in small scale wastewater treatment facilities for low-income areas. Titanium oxides containing Ti$^{3+}$, including Ti$_2$O$_3$, Magnéli phase Ti$_n$O$_{2n-1}$, and Ti$^{3+}$-doped TiO$_2$ (black TiO$_2$), are a series of abundant, stable and non-toxic materials, and have attracted the attention of researchers for decades.

In this work, Ti$_2$O$_3$, Magnéli phase Ti$_n$O$_{2n-1}$, and black TiO$_2$ were studied for destruction of pollutants in wastewater. Ti$_2$O$_3$ and Magnéli phase Ti$_n$O$_{2n-1}$ were applied to electrocatalytic system due to their high conductivity, while black TiO$_2$ was applied to a photocatalytic system due to its wider light absorption range compared with pristine TiO$_2$. Ti$_2$O$_3$ showed a high degradation efficiency in chlorine-driven electrochemical pollutant degradation reaction. However, materials comprising several Magnéli phases Ti$_n$O$_{2n-1}$ didn’t show a good performance in electrochemical oxidation of chloride for degrading pollutants. Thin film black TiO$_2$ synthesized by NaBH$_4$ reduction and carbothermal reduction showed poor performance on photocatalytic pollutant degradation, while black TiO$_2$ synthesized by solvothermal method was difficult to form thin film on substrates.

The high conductivity of Ti$_2$O$_3$ and Magnéli phase Ti$_n$O$_{2n-1}$, and the wider light absorption of black TiO$_2$, all arise from their crystal structures and electronical band structures. Different synthesis methods of these materials introduce different stoichiometries, which lead to differences in their crystal structures.
including phase structures and defect species, and finally affect their properties. For traditional synthesis method like hydrogen reduction, the relationship between synthesis condition, crystal structure and material properties has been studied and reported by many researchers. On the other hand, energy-efficient and low-risk synthesis method such as solvothermal method and carbothermal reduction under lower temperature have been reported, but we are still lacking of information about the relationship among synthesis condition, crystal structure and material properties.

Black TiO$_2$ and Magnéli phase Ti$_{n}$O$_{2n-1}$ have already been applied in water treatment systems, but the studies about mechanisms of oxidation reaction on the surface of these catalysts still cannot give a clear view. In this work, some mechanistic studies have been carried out on Ti$_2$O$_3$, which have been applied as electrocatalyst of chlorine-driven water treatment for the first time. We hope this study will contribute to the further development of titanium oxide electrocatalysts. Improving the selectivity of reactions that help degrading pollutants, enhancing the efficiency of surface reactions and inhibiting possible harmful side products would be the future aims for this topic.

Titanium oxide materials studied in this work were synthesized by simple and low-cost methods, and were immobilized on glass substrates. Different types of model pollutants were used in degradation testing. These research methods were designed for studying the materials’ potential for application in real world wastewater treatment, which may require small-scale, limited cost, effectiveness to multiple pollutants and ease of recycling. We believe that results from this work will benefit the development of low-cost and energy-saving decentralized wastewater treatment facilities.
It would be a long way from a high efficiency catalyst in lab to a product for real world water treatment. Field tests are the conditions where catalysts face realistic problems, such as wastewater with a wide range of pollutants, bad weather with low light (for photocatalysts) and unstable electricity (for electrocatalysts). We hope that based on our work on mixed-valence titanium oxide materials, future photocatalysts and electrocatalysts can be more adaptable to field conditions, taking one step closer to real world applications.
Published work

Publications included in this thesis:

Ti$_2$O$_3$ film electrode for water treatment via electrochemical chlorine evolution

Yishu Zhang, Caroline Kirk and Neil Robertson, Materials Advances, 2024, 5, 1631-1638