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TiO$_2$ Nanotubes synthesised via Ti Electrochemical Anodization

*An investigation on phase transformation of anodized TiO$_2$ and the influences of grafted Cu (II) on morphology and photocatalytic ability.*

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Department of Chemical & Materials Engineering

July 2014
Abstract

Titanium dioxide is a relatively cheap, non-toxic, and environmentally safe material. Its properties as a photon semi-conductor allow it to be utilised in photocatalysis. This includes applications such as wastewater treatment, where it can break down organic contaminants into CO₂ and water. TiO₂ nanotubes produced via Ti electrochemical anodization combine its photocatalytic abilities with the high surface area to volume ratios inherent in nano-scale materials to produce a highly efficient photocatalyst.

Anodization was applied to produce amorphous TiO₂ nanotube arrays. Heat treatment was performed at various temperatures to study its crystallization it into various crystalline phase compositions. XRD analysis showed that the heat treatment resulted in mixture of two phases: anatase and rutile. Anatase phase began to transform into rutile at temperatures above 700 °C. However, at this temperature, due to the phase transformation, the tubular morphology collapses, which lowers the photocatalytic efficiency.

Because TiO₂ has a band gap greater than 3.0 eV, it can only utilize ultraviolet light, which accounts for only 5% of solar light. In this study, experiments were performed with the intent to develop a TiO₂ nanotube photocatalyst which can act efficiently under visible light by engineering the band gap in the form of copper grafting. Nanotube arrays synthesised via anodization and annealed at 450 °C were grafted with copper ions (Cu²⁺) in aqueous solution containing 0.2, 2, 20, and 200 ppm CuCl₂. Photocatalytic experiments were performed using these samples and showed that the most efficient photocatalyst in visible light was the 0.2 ppm grafted samples. But it was found that the efficiency decreases with increased grafting content from 0.2 ppm. A number of factors accounted for this trend, which are discussed within.

This study shows that copper grafting can successfully modify TiO₂ nanotubes to operate as a photocatalyst driven by visible light.
Acknowledgements

I would like to express my deep gratitude to my supervisor Professor Wei Gao for his academic guidance and support throughout the project.

Special thanks are given to PhD candidate Mr. Junye Dong and the lab technicians in the Department of Chemical & Materials Engineering for their advice and assistance. And also to my friends and family for their constant encouragement throughout this research.
Table of Contents

Chapter 1. Introduction ........................................................................................................... 1
  1.1. Background ..................................................................................................................... 1
  1.2. Research Objectives ..................................................................................................... 2
  1.3. Thesis Outline ............................................................................................................... 2
Chapter 2. Literature Review .................................................................................................... 3
  2.1. Nanotube Anodization Growth Mechanics/Parameters ......................................................... 3
    2.1.1 Effects of Voltage/Potential ....................................................................................... 5
    2.1.2 Effects of Electrolyte Composition ............................................................................. 7
    2.1.3 Effects of Electrolyte Temperature ........................................................................... 12
  2.2. TiO$_2$ Crystallographic Phases ..................................................................................... 14
  2.3. TiO$_2$ Based Photocatalysis .......................................................................................... 15
    2.3.1 Phase Influence ....................................................................................................... 16
    2.3.2 Band Gap Modification ............................................................................................ 18
  2.4. Conclusions .................................................................................................................... 21
Chapter 3. Experimental .......................................................................................................... 22
  3.1. Anatase & Rutile Phase Synthesis .................................................................................... 22
    3.1.1 Titanium Substrate Preparation .................................................................................. 22
    3.1.2 Anodization Process .................................................................................................. 23
    3.1.3 Crystallization of Amorphous Phase via Annealing ..................................................... 23
  3.2. Copper Grafting & Photocatalysis .................................................................................. 24
    3.2.1 Initial Copper Grafting Procedure .............................................................................. 27
    3.2.2 Final Copper Grafting Procedure .............................................................................. 27
    3.2.3 Photocatalysis .......................................................................................................... 28
  3.3. Characterisation ............................................................................................................. 29
    3.3.1 X-ray Diffraction ....................................................................................................... 29
    3.3.2 Scanning Electron Microscopy .................................................................................. 29
    3.3.3 Transmission Electron Microscopy ............................................................................ 29
Chapter 4. Results & Discussion ............................................................................................... 30
  4.1. Anatase & Rutile Phase Synthesis ................................................................................... 30
    4.1.1 SEM Characterisation .............................................................................................. 33
4.1.2 TEM Characterisation........................................................................................................40
4.2. Copper Grafting.........................................................................................................................42
  4.2.1 Initial Copper Grafted Samples ..........................................................................................42
  4.2.2 Final Grafted Samples .........................................................................................................43
  4.2.3 Photocatalysis Results .......................................................................................................46
4.3. Miscellaneous Observations ....................................................................................................51
  4.3.1 Oxide Colour .....................................................................................................................51
  4.3.2 Oxide Layer Durability ......................................................................................................52
Chapter 5. General Conclusions .....................................................................................................53
  5.5. Recommended Future Work ...............................................................................................54
Bibliography ....................................................................................................................................55
Appendix A: Chemicals & Materials Used ......................................................................................59
Appendix B: Calculations ..................................................................................................................60
Appendix C: XRD Diffractograms ..................................................................................................62
List of Figures

Figure 1: Depiction of a typical TiO$_2$ anodization setup. .................................................................3
Figure 2: Schematic representation of TiO$_2$ NT formation mechanics in fluoride based electrolyte. Reprinted with permission from TiO2 Nanotube Arrays: Growth and Application, in Encyclopedia of Nanotechnology, B. Bhushan, Editor. 2012, Springer Netherlands [1]......4
Figure 3: FESEM views of tapered nanotubes obtained: (a) by ramping the anodization voltage from 10 to 23 V over a 30 min period, 0.43 V/min, then holding the voltage at 23 V for 10 min, (b) by initially anodizing the sample at 10 V for 20 min then increasing the voltage at 1.0 V/min to 23 V then held constant at 23 V for 2 min, (c) straight nanotubes obtained by applying a constant 23 V for 45 min. ‘d’ denotes diameter of the conical apex, and ‘D’ diameter of conical base. Reprinted with permission from Fabrication of tapered, conical-shaped titania nanotubes. Journal of Materials Research, 2011 [9]............................6
Figure 4: FESEM images of multi-sectional TiO$_2$ nanotube arrays synthesised when the second stage (lower half) voltage is lower than that of the first stage voltage. The bamboo shaped tubes were synthesised using a square wave voltage (30 V for the second, 60 V for first). Reprinted with permission from Fabrication of multi-sectional TiO$_2$ nanotube arrays by anodization. Science China Chemistry, 2010 [11].................................................................6
Figure 5: FESEM image of NT array prepared with 1:7 acetic acid and 0.5 wt. % HF electrolyte at 10 V. Reprinted with permission from A room-temperature TiO$_2$-nanotube hydrogen sensor able to self-clean photoactively from environmental contamination. Journal of Materials Research, 2004 [12]........................................................................................................7
Figure 6: FESEM image of a nanotube array sample grown at 60 V in 0.25 wt.% NH$_4$F in ethylene glycol. Reprinted with permission from Anodic growth of highly ordered TiO$_2$ nanotube arrays to 134 micron in length. J Phys Chem B, 2006 [17]. .........................................................9
Figure 7: SEM image of bundles of high-aspect ratio titania nanotubes. Reprinted with permission from Anodic Formation of High-Aspect-Ratio Titania Nanotubes, in 208th ECS Meeting. 2005, The Electrochemical Society [23]...............................................................11
Figure 8: SEM image showing several individual nanotubes that were fabricated by anodization in a 0.5 M oxalic acid and 0.3 M KCl solution at 13 V for 8 min. Reprinted with permission from Titania nanotubes prepared by anodization in fluorine-free acids. J. Mater. Res, 2007 [24]....................................................................................................................11
Figure 9: FESEM images of 10 V NT arrays anodized at (a) 5 °C with an average wall thickness of 34 nm and (b) 50 °C with 9 nm. Reprinted with permission from Enhanced Photocleavage of Water Using Titania Nanotube Arrays. Nano Letters, 2004 [28].

Figure 10: Unit cells of (a) rutile, (b) anatase, (c) brookite. Grey and purple spheres represent oxygen and titanium respectively. Reprinted with permission from Nanostructured TiO$_2$ materials: properties, preparation, and applications. 2011, London, GBR: World Scientific Publishing [30].

Figure 11: Summary of the generation of photocatalytic reduction of pollutants in TiO$_2$. Original image from Figure 5 in Nanostructured TiO$_2$ materials: properties, preparation, and applications. 2011, London, GBR: World Scientific Publishing [30].

Figure 12: SEM photograph of a mixture of pure anatase and pure rutile powders. The large particles are rutile while the smaller agglomerates on them are fine anatase particles. Reprinted with permission from Morphology of a TiO$_2$ Photocatalyst (Degussa, P-25) Consisting of Anatase and Rutile Crystalline Phases. Journal of Catalysis, 2001 [39].


Figure 14: Grinding machine.

Figure 15: Heat treatment furnace.

Figure 16: Diagram of nanotubes before and after complete nanotube removal. After the nanotube removal, the base ‘dimples’ from the NT bottoms act as a template for further NT growth.

Figure 17: Samples annealed at 450 °C with (a) completely and (b) partially flaked off nanotube layer, whereas (c) is a successful intact sample.

Figure 18: XRD diffractograms of samples from 3.1 produced at 40 V and heat treated at (a) 300, 400, 500, 600, 700, and 800 °C and (b) 700, 725, 750, 775, 800 °C. The peaks marked by the black triangles, squares, and circles are titanium, anatase, and rutile peaks respectively.

Figure 19: SEM images of samples produced at 40 V for 4 h in ethylene glycol + NH$_4$F electrolyte annealed at 300 °C from 3.1.

Figure 20: SEM images of heat treated TiO$_2$ nanotubes produced at 60 V for 12 h. (a) and (b) show the side profile while (c) shows a top profile for the surface layer.
Figure 21: SEM images of the undersides of TiO$_2$ nanotubes produced at 60 V for 12 h. .....35
Figure 22: SEM images at 100,000x magnification of TiO$_2$ oxide layers prepared in 3.1 heat treated at (a) 300, (b) 400, (c) 500, (d) 600, (e) 700, and (f) 800 °C for 2 h. .........................36
Figure 23: (a) and (b): SEM images of a sample showing the cracks present in a TiO$_2$ nanotube layer heat treated at 700 °C. Nanotubes can be observed stretching across the cracks. (c): An 800 °C annealed oxide layer, note the lack of tubular structure. ..................37
Figure 24: Models representing the evolutions of morphology and crystallization of the TiO$_2$ nanotube arrays on Ti substrate (a) and the freestanding TiO$_2$ nanotube membranes.
Figure 25: TEM diffraction patterns and images of TiO$_2$ nanotubes synthesised at 60 V (a-b) pre, and (c-d) post heat treatment at 450 °C. .................................................................40
Figure 26: TEM images of the crystal structure of TiO$_2$ nanotubes heat treated at 450 °C. The red lines indicate grain boundaries. .................................................................41
Figure 27: (a): SEM images of Cu grafted TiO$_2$ NT layer from 3.2.1. (b): EDS results from locations 1 and 2 marked on (a). The particles observed in (a) are crystals of CuCl$_2$ used during the grafting procedures. The Pt peak is from the platinum coating used to prepare the samples for SEM. .................................................................42
Figure 28: SEM images of the samples annealed at 450 °C from 3.2.2 with (a) 0.05 ppm, (b) 0.5 ppm, (c) 5 ppm, (d) 50 ppm CuCl$_2$·H$_2$O grafting solution. .................................................................43
Figure 29: Possible model of how copper is grafted onto the surface of TiO$_2$ nanotubes where the blue shell layer is CuO. .................................................................44
Figure 30: EDS results from the samples annealed at 450 °C from 3.2.2 with (a) 0.05 ppm, (b) 0.5 ppm, (c) 5 ppm, (d) 50 ppm CuCl$_2$·H$_2$O grafting solution. .................................................................45
Figure 31: UV-Vis Spectroscopy results of 2 mg/mL RhB dye irradiated under blue light (a) with a TiO$_2$ NTA sample annealed at 450 °C without Cu grafting, and (b) without any samples. .................................................................46
Figure 32: UV-Vis Spectroscopy results of photocatalytic tests from 3.2.2 of TiO$_2$ NTA samples annealed at 450 °C with Cu (II) grafted at (a) 0.2, (b) 2, (c) 20, and (d) 200 ppm on Rhodaime B dye irradiated under blue light. .................................................................47
Figure 33: Photocatalytic effect of TiO$_2$ NTA samples annealed at 450 °C with varying amounts of copper grafting on RhB dye solution during irradiation under blue light...........48
Figure 34: TiO$_2$ nanotube samples heat treated at various temperatures. From upper left to right: 300, 400, 450, 600, 700, and 800 °C. The damaged/flaked off areas were caused by the sample mounting procedures for XRD. .................................................................51
Figure 35: Unit cell and tube dimensions of nanotube array (not to scale). .........................60
Figure 36: XRD Diffractograms of TiO$_2$ NTA annealed at 700 °C. .................................62
Figure 37: XRD Diffractograms of TiO$_2$ NTA annealed at 725 °C. .............................63
Figure 38: XRD Diffractograms of TiO$_2$ NTA annealed at 750 °C. .............................64
Figure 39: XRD Diffractograms of TiO$_2$ NTA annealed at 775 °C. .............................65
Figure 40: XRD Diffractograms of TiO$_2$ NTA annealed at 800 °C. .............................66

List of Tables

Table 1: Electrolyte pH and composition, anodization conditions and dimensions of the resulting nanotubes. Reproduced with permission from *The Effect of Electrolyte Composition on the Fabrication of Self-Organized Titanium Oxide Nanotube Arrays by Anodic Oxidation.* Journal of Materials Research, 2005 [16]. ..................................................................................................................8
Table 3: Semi-quantitative analysis on the XRD results on Figure 18 ...............................31
Table 4: List of Chemical & Materials Used ....................................................................59

List of Equations

Equation 1: Chemical etching reactions involved in nanotube formation .......................4
Equation 2: Redox reactions involved with photocatalysis with TiO$_2$. ........................15
Equation 3: Electron reduction reactions involved with photocatalysis with copper grafted TiO$_2$ .................................................................................................................................................20
Equation 4: Langmuir-Hinshel rate constant equations for heterogeneous photocatalytic degradation .............................................................................................................................................49
Chapter 1. Introduction

1.1. Background

Titanium dioxide today sees itself in a wide range of applications. It is commonly found in ore deposits around the world and is relatively cheap to process. Its earliest practical application was in the form of a whitening agent in pigments such as paints and sunscreens due to its high refractive index rating and opacifying power.

However, titanate as a nanomaterial has exponentially broadened its range of applications. Nanotechnology is a fast developing field in areas such as physics, chemistry, and materials engineering. Due to the nano-scale (≤100nm) sizes of nanomaterials, they have various properties which can be specifically engineered for specific purposes. These include a high surface area to volume ratio, thermal/mechanical/chemical properties, phase transition behaviour, optical, electrical, and magnetic properties.

Titanium dioxide is promising due to its natural abundance and potentially lower cost of production compared to other nanomaterials studied today. It is also non-toxic, biologically and chemically inert in the environment, and resistant to long term photo- and chemical corrosion. Nanostructured titanium dioxide (NS-TiO$_2$) can be synthesised into various forms such as spheroids, pores, tubes, sheets, or fibres/rods. They can be synthesised using a number of methods. They include sol-gel, chemical/physical vapour deposition, hydrothermal, sonochemical, seeded growth, and electrochemical anodization. The density and type of NS-TiO$_2$ is determined by the synthesis method and the parameters used. In turn, the properties and the performance of the nanomaterial are determined by the structure. Among these production techniques, electrochemical anodization to produce highly ordered, vertically orientated nanotube arrays is a relatively simple and cost-effective process.

NS-TiO$_2$ is utilised in a number of applications including photovoltaic cells, hydrogen production & storage, gas sensors, batteries, anti-microbial materials, self-cleaning surfaces, and as photocatalysts for wastewater treatment. Due to TiO$_2$’s property as an ‘n-type’ semiconductor with photon absorption and combined with the large surface area which comes with the small scale morphology of nanostructures makes it ideal for these applications.
However by itself, its photocatalytic applications are limited to working under ultraviolet irradiation due to its band gap size. There is undergoing research and development into methods to modify NS-TiO₂ to operate as an efficient photocatalyst under visible light.

1.2. Research Objectives

The aim of this study was to develop and research the synthesis of TiO₂ ordered nanotubes arrays (NTA) for the purposes of wastewater treatment via photocatalysis of organic chemical contaminants in wastewater. The factors being studied are the production of the different crystalline phases of titanate via heat treatment and modifications in the form of copper grafting with the intent to for photocatalysis to occur under visible light instead of only under ultraviolet light.

1.3. Thesis Outline

Chapter 2 covers the literature review performed prior and during the course of this Masters programme. This includes background on TiO₂ NTA synthesis via electrochemical anodization, the crystalline phases of TiO₂ and the influences these phases have, the mechanisms behind TiO₂ based photocatalysis, and past research into modifications made to TiO₂ to allow it operate under visible light.

Chapter 3 describes the experimental procedures used in this study and the characterisation methods used to analyse the samples produced.

Chapter 4 shows the results produced from the experimental procedures and includes discussions on the trends and details observed throughout the research programme.

Chapter 5 summarises the research performed in this thesis, describes the conclusions produced from the results, and recommended future work.
Chapter 2. Literature Review

2.1. Nanotube Anodization Growth Mechanics/Parameters

The subject of this research thesis is on the modification of TiO$_2$ nanotubes synthesised via anodization. Anodization typically involves the use of external applied electric current to produce a nanostructured oxide layer from a substrate metal (or modifying an existing metal oxide layer into a specific nanostructure). The substrate metal is connected to the positive terminal of a power supply as an anode and submersed in an electrolyte. The cathode is typically a rod or plate of platinum or carbon and also submersed in the electrolyte.

At the beginning of the anodization process, an initial passivating oxide layer (or barrier layer) forms on the titanium substrate with the interaction of Ti with O$_2^-$ or OH$^-$ ions. The anodization current experiences a large drop in the first few seconds with that formation. This barrier layer at this point only allows current to flow via ions. The O$_2^-$ anions travel through the oxide layer to the Ti/TiO$_2$ interface to react with the Ti. Ti$^{4+}$ cations are ejected by the applied electric field to the TiO$_2$/electrolyte interface. At the cathode, if the pH of the electrolyte is appropriate, hydrogen ions gain electrons and this is observable as hydrogen gas evolution as bubbles in the electrolyte solution. During this initial phase, the pH and diffusion gradient are established and growth begins as the oxide layer is converted into a NT structure while the Ti/TiO$_2$ interface grows deeper into the metal. Therefore, the thicker the initial
Chapter 2: Literature Review

oxide layer, the longer the resultant NT can be. The nanotube height finally reaches a steady state when the rate of the Ti/TiO₂ interface movement equals the rate of the chemical etching at the tube openings. This final nanotube length was also found to be independent of anodization time.

The anodic nanotube (NT) formation is a highly non-equilibrium process which involves three competing interactions: field-assisted oxide dissolution & cation migration, field-assisted oxidation of Ti, and chemical etching. These interactions are summarized in equations 1. The chemical etching reactions (dissolution of Ti⁴⁺ ions with HF acting as the acid) is the main cause of the synthesis of nanotubes rather than nanopores. This process can be enhanced with a greater concentration of H⁺ ions with self-induced local acidification due to the oxidation of elemental titanium [1-5].

\[
\text{Field-assisted oxidation: } \text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4\text{e}^- \\
\text{Field-assisted migration: } \text{Ti}^{4+} + 6\text{F}^- \rightarrow [\text{TiF}_6]^{2-} \\
\text{Field-assisted dissolution: } \text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow [\text{TiF}_6]^{2-} + 2\text{H}_2\text{O} \\
\text{Chemical dissolution: } \text{TiO}_2 + 6\text{HF} \rightarrow [\text{TiF}_6]^{2-} + 2\text{H}_2\text{O} + 2\text{H}^+ 
\]

**Equation 1: Chemical etching reactions involved in nanotube formation.**

![Figure 2: Schematic representation of TiO₂ NT formation mechanics in fluoride based electrolyte. Reprinted with permission from TiO₂ Nanotube Arrays: Growth and Application, in Encyclopedia of Nanotechnology, B. Bhushan, Editor. 2012, Springer Netherlands [1].](image)

One of the main advantages that nanotube arrays have over bulk (NS) TiO₂ powder is that it is easier to recover from solution after use as a photocatalyst. However, post-annealed NTA are limited in their applications due to that they are still attached to the metal substrate from which they were synthesised. To remove the TiO₂ films from the metal, there are a number of solutions. Wang (2008) separated the NT array by using solvent evaporation induced
delamination of the barrier layer between the oxide film and the metal [6], whereas Prakasam (2007) removed the NT film (>50 µm thick) from its Ti substrate by using ultrasonic cleaning [4]. Gentle mechanical bending may also be used to remove the NT film from the substrate [6].

The arrangements of the nanotubes are usually non-uniform. To remedy this, multiple anodization steps were performed by Sulka et al (2012). After the first anodization, the nanotube oxide layer was removed with adhesive tape leaving behind a substrate surface with non-uniform concaves from the remaining tube bottoms. These concaves then act as a template for subsequent anodization growth, improving the next arrangements. The repeated anodization and removals then produce an orderly array of nanopores/tubes. This improves the structural resilience of the overall NTA as well as photocatalytic efficiencies [7].

2.1.1 Effects of Voltage/Potential

By controlling the synthesis parameters, the structure of the resultant nanotubes can be engineered. Anodization voltage provides the driving force for tube growth. It affects the length of the nanotubes with the greater the voltage, the longer the resultant tubes. But after a certain voltage limit specific to the parameters, the nanotube structure breaks down and becomes sponge like [8].

If the applied voltage is repeatedly increased and decreased in a sweeping motion, conical-shaped tubes are produced [3, 5]. Mora et al (2011) demonstrated this with 0.5 wt. % HF solution and the voltage was ramped up from 10 to 23 V at rates between 0.43 and 2.6 V/min. Two sets of samples were prepared, the first being linear increase of voltage from 10 to 23 V and then held constant, and the other being held constant at 10 V and then increased ramped up to 23 V after 2 min. The reverse conditions of set one of a sweeping from 23 to 10 V followed by constant 10 V anodization for 40 min did not result in tapered nanotubes, but rather straight ones similar to those produced at constant 10 V. In nearly all samples, the average outer base diameters were at 166 nm, a figure similar to those tubes produced at a constant 23 V voltage. With Set 1, the average inner diameters of the tapered tube ends were 10, 80, 85, and 100nm for sweep rates of 0.43, 0.65, 0.87, and 2.6 V/min respectively. Sweeping rates faster than 1.0 V/min resulted in the collapse of the nanotube structure [9].

Yasuda et al (2007) demonstrated that if the applied current was completely cut off for a period of time then restarted, a break would occur in the nanotube, essentially allowing for
multilayer nanotube arrays [10]. Li (2010) produced ‘bamboo’ shaped nanotubes by using a square wave alternating current, this shape is explained by repeated tube growth initiations and cessations. Li also repeated Yasuda’s work, except with the second stage voltage (after cutting off the current for while) being greater than the first stage. This resulted in the second NT layer having tube diameters larger than that of the first. This NT diameter disparity and the abrupt increase in voltage cause significant structural damage to the layers as shown in Figure 4 [11]. Prakasam developed another method to produce double NTA layers up to 360 µm long each layer. Both sides of the substrate titanium foil was exposed to the electrolyte, and this allowed NT to grow on both sides resulting in a double layer [4].

Figure 3: FESEM views of tapered nanotubes obtained: (a) by ramping the anodization voltage from 10 to 23 V over a 30 min period, 0.43 V/min, then holding the voltage at 23 V for 10 min, (b) by initially anodizing the sample at 10 V for 20 min then increasing the voltage at 1.0 V/min to 23 V then held constant at 23 V for 2 min, (c) straight nanotubes obtained by applying a constant 23 V for 45 min. ‘d’ denotes diameter of the conical apex, and ‘D’ diameter of conical base. Reprinted with permission from Fabrication of tapered, conical-shaped titania nanotubes. Journal of Materials Research, 2011 [9].

Figure 4: FESEM images of multi-sectional TiO₂ nanotube arrays synthesised when the second stage (lower half) voltage is lower than that of the first stage voltage. The bamboo shaped tubes were synthesised using a square wave voltage (30 V for the second, 60 V for first). Reprinted with permission from Fabrication of multi-sectional TiO₂ nanotube arrays by anodization. Science China Chemistry, 2010 [11].
Chapter 2: Literature Review

2.1.2 Effects of Electrolyte Composition

The electrolyte is the solution in which the anode and cathode are submersed in during anodization. This solution provides the ionic species to transfer charge between the electrodes. The electrolyte composition affects the resultant product in various ways.

2.1.2.1 First Generation Electrolytes

Figure 5: FESEM image of NT array prepared with 1:7 acetic acid and 0.5 wt. % HF electrolyte at 10 V. Reprinted with permission from A room-temperature TiO$_2$-nanotube hydrogen sensor able to self-clean photoactively from environmental contamination. Journal of Materials Research, 2004 [12].

The first generation of electrolytes were aqueous solutions based on the method used in production of porous oxide films in aluminium. Most of these contain HF in varying concentrations. Gong, Grimes and co-workers (2001) produced nanotubes using 0.5 wt.% HF solutions at various voltages, resulting in pore diameters ranging from 25-65 nm with a constant tube length of 250 nm [5]. Grimes later produced more mechanically stronger nanotubes with the same shape and size by adding acetic acid in a 1:7 ratio to the 0.5 wt.% solution [12]. Others have used HNO$_3$/HF [13], H$_2$Cr$_2$O$_7$/HF [14], and H$_2$SO$_4$/HF [15] as their electrolytes and has successfully produced nanotubes.

2.1.2.2 Second Generation Electrolytes

The second generation pioneered by Cai et al used buffered electrolytes, where the desired pH was first obtained using sulphuric acid, NaOH, citric acid, or sodium hydrogen sulphate. Afterwards the KF was added to the solution. Electrolyte pH was found to affect the behaviour of both the chemical dissolution and the electrochemical etching due to the
hydrolysis of the titanium ions. The length of the produced NT was found to be longer in the higher pH electrolytes. As the electrolyte pH increases, the hydrolysis content increases, resulting in the rate of chemical dissolution slowing down. Although the produced NT lengths were longer, it was found that there was a lot of unwanted hydrous titanic oxide precipitates produced on the NT surface. In contrast, lower pH produced shorter but cleaner nanotubes. It was also discovered that at a certain pH the length also increases with applied potential. At another specific pH, the pore size increases with applied potential. However, the pore size was found to be independent of pH at a specific applied voltage [16].

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<th>t (h)</th>
<th>D (nm)</th>
<th>L (µm)</th>
<th>Q c</th>
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<tr>
<td>08</td>
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<td>20</td>
<td>1</td>
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<td>0.45 ± 0.03</td>
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<td>0.32 ± 0.03</td>
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<tr>
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<td>2.8</td>
<td>10</td>
<td>20</td>
<td>30 ± 5</td>
<td>0.59 ± 0.05</td>
<td>NT</td>
</tr>
<tr>
<td>11</td>
<td>0.1 1.0 ... 0.2</td>
<td>2.8</td>
<td>15</td>
<td>20</td>
<td>50 ± 5</td>
<td>1.00 ± 0.05</td>
<td>NT</td>
</tr>
<tr>
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<td>2.8</td>
<td>25</td>
<td>20</td>
<td>155 ± 10</td>
<td>1.50 ± 0.04</td>
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</tr>
<tr>
<td>13</td>
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<td>3.8</td>
<td>10</td>
<td>20</td>
<td>30 ± 5</td>
<td>0.80 ± 0.06</td>
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<td>3.8</td>
<td>10</td>
<td>60</td>
<td>30 ± 5</td>
<td>1.80 ± 0.06</td>
<td>NT</td>
</tr>
<tr>
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<td>10</td>
<td>90</td>
<td>30 ± 5</td>
<td>2.30 ± 0.08</td>
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</tr>
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<td>30 ± 5</td>
<td>1.05 ± 0.04</td>
<td>NT</td>
</tr>
<tr>
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<td>4.5</td>
<td>25</td>
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<td>4.40 ± 0.10</td>
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<td>5.0</td>
<td>10</td>
<td>20</td>
<td>30 ± 5</td>
<td>1.40 ± 0.06</td>
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<td>6.1</td>
<td>10</td>
<td>24</td>
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<td>...</td>
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</tr>
<tr>
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<td>2.0 ... ... ...</td>
<td>&lt;1</td>
<td>10</td>
<td>24</td>
<td>...</td>
<td>...</td>
<td>No NT</td>
</tr>
</tbody>
</table>

SO<sub>4</sub><sup>2-</sup> is from the addition of H<sub>2</sub>SO<sub>4</sub> or NaHSO<sub>4</sub>; PO<sub>4</sub><sup>3-</sup> is addition of potassium hydrogen phosphate K<sub>2</sub>HP<sub>2</sub>O<sub>7</sub>; Cit denotes citric acid from its salt, HO(CO<sub>2</sub>Na)(CH<sub>2</sub>CO<sub>2</sub>Na)<sub>2</sub>·2H<sub>2</sub>O.

Electrolyte components are in mol/L.

1 pH <1 represents a 1.0 or 2.0 mol/L H<sub>2</sub>SO<sub>4</sub> medium.

4 Q, quality of resulting nanotubes; NT, nanotubes uniformly across substrate; No NT, no nanotubes or partly developed nanotube/porous structures; Cit, citrate; t, time; D, inner diameter of nanotube; L, length of nanotube.

Table 1: Electrolyte pH and composition, anodization conditions and dimensions of the resulting nanotubes. Reproduced with permission from The Effect of Electrolyte Composition on the Fabrication of Self-Organized Titanium Oxide Nanotube Arrays by Anodic Oxidation. Journal of Materials Research, 2005 [16].

2.1.2.3 Third Generation Electrolytes

The third generation used polar organic based electrolytes. Grimes and co-workers used formamide (FA) based electrolytes to produce NT up to 70 µm long and with an average of
Chapter 2: Literature Review

180 nm pore diameter. Electrolyte compositions tested were formamide and/or N-methylformamide (NMF) with 1-5 wt. % deionized water and 0.3-0.6 wt. % NH$_4$F. It was found that keeping water content below 5% produced long NT arrays; this is due to the reduced water content decreases chemical dissolution of the oxide in the electrolyte. With NMF electrolytes, the tube length was found to be around 10% longer but with smaller diameters. Similarly to the first two generations, the diameters were proportional to anodization voltage. It was also noted that the range of voltages in which NT arrays could be successfully synthesised were significantly larger than those using aqueous KF or NaF electrolytes (10-50 V as compared to 10-29 V). The anodization duration is also important, tube lengths increase with time up to a certain limit, after which then they begin to shorten, possibly due to dissolution-induced cleaving of the nanotubes. The time to reach the maximum length appears to be a function of the anodization voltage, with the lower voltages reaching the maximum lengths quicker [17].

![Figure 6](image)

Figure 6: FESEM image of a nanotube array sample grown at 60 V in 0.25 wt.% NH$_4$F in ethylene glycol. Reprinted with permission from Anodic growth of highly ordered TiO$_2$ nanotube arrays to 134 micron in length. J Phys Chem B, 2006 [17].

Shankar investigated the effects of cationic species in the formation of NTA in formamide-water electrolytes. The shortest tubes produced were from those with only H$^+$ cations. The longest were those with tetrabutylammonium cations. The ammonium ions restrict the thickness of the barrier layer which forms between the substrate metal and the oxide layer. With a thinner barrier layer, NT growth is promoted due to increased ionic transformations. A
greater $F^-$ concentration results in thinner wall thicknesses with the increased chemical etching [18].

Other polar organic electrolytes used included ethylene glycol [4, 17], dimethyl sulfoxide [17], diethylene glycol [19], glycerol and NH$_4$F [20], and a methanol-water-HF solution [21].

2.1.2.4 Fourth Generation Electrolytes

All of the previous generations utilised fluorides in one form or another to act as an etching agent. However, hydrofluoric acids are extremely corrosive and it is difficult to safely handle and is costly dispose of after use [22]. Nakayama and co-workers (2005) managed produce bundles of nanotubes (rather than arrays) using anodization in perchloric acid solutions [23]. This lead to investigations to see whether non-fluoride based etchants in electrolytes could be feasible. Richter et al (2007) investigated various electrolytes with chlorines salts in a combination with oxalic, formic, trichloroacetic, gluconic, hydrochloric, or sulfuric acid. Voltages below 11 V yielded no nanotubes for all of the solutions. Past the 11 V limit, TiO$_2$ NT bundles formed for all of the combinations of electrolytes with no significant morphological differences between them. Unlike the regularly spaced arrays of the previous generations, the tube growth were irregularly spaced at locations were typically at edges or holes etched through the substrate Ti foil (pitting sites). The tube diameters did not appear to be dependent on anodization voltages. The rapidly formed bundles of nanotubes appeared to break off from the substrate quickly, indicating that the tube lengths were a function of where the bundles break off the substrate rather than that of acidity, anodization time, or voltage. All of the produced tubes contained a high carbon content of around 20% (trichloroacetic acid yielded tubes of around 45% carbon however) [24].

Titanate NT were successfully produced from 0.55 wt.% HCl (0.15 M) that had an average length of 30 µm, diameter of 40 nm, and wall thickness of 10 nm. Deviations on either side in the electrolyte concentrations increased the NT diameters, but produced less aligned structures [25]. Allam et al also investigated in the use of HCl as an electrolyte, and could not produce successful NT at voltages other than between 9-13 V and with HCl concentrations below 3 M. This limited working window may be due to the complex nature of the reactions between Ti and HCl [26]. Allan later widened this processing window by adding H$_2$O$_2$. Nanotubes were successfully produced with 0.5 M HCl + 0.1-0.5 M H$_2$O$_2$ at 5-25 V. Below 8 V however, nanostructures did not initially appear, but after a series of anodization treatments in new, unused electrolyte, NTA could be produced [27].
Chapter 2: Literature Review

Figure 7: SEM image of bundles of high-aspect ratio titania nanotubes. Reprinted with permission from Anodic Formation of High-Aspect-Ratio Titania Nanotubes, in 208th ECS Meeting, 2005, The Electrochemical Society [23].

Figure 8: SEM image showing several individual nanotubes that were fabricated by anodization in a 0.5 M oxalic acid and 0.3 M KCl solution at 13 V for 8 min. Reprinted with permission from Titania nanotubes prepared by anodization in fluorine-free acids. J. Mater. Res, 2007 [24].
2.1.3 Effects of Electrolyte Temperature

The anodic growth of TiO$_2$ NT is dependant of two major processes: the electrochemical etching and chemical dissolution of species. The temperature of the electrolyte bath will affect both these processes. Mor et al (2004) produced NT arrays at temperatures ranging between 5 and 50 °C at 10 V in acetic acid + 0.5 % HF electrolyte mixed in a 1:7 ratio. The results show a relatively constant pore size of 22 nm for all temperatures. However the wall thickness changes from 9 nm at 50 °C to 34 nm at 5 °C, showing increasing wall thickness with decreasing anodization temperature. The NT length also increases with decreasing temperature with 120 nm at 50 °C to 224 nm at 5 °C. FESEM images indicate that the interpore voids fill up, creating more interconnected tubes, resulting in a more porous nanostructure [28].

Wang et al (2009) compared the effects of temperature on NT formation in aqueous and non-aqueous based electrolyte. It was found that with anodization of Ti foil at 20 V in an aqueous electrolyte of 0.5 wt.% HF in DI water, its temperature had little effect on the NT morphology (only the inner tube diameter changed from 50 nm at room temperature to 60 nm in an ice bath). Whereas with a non-aqueous electrolyte of glycerol with ammonium fluoride, the nanotubes grown in an ice bath displayed smaller inner and outer diameters (20 and 50 nm respectively) than those that were grown at room temperature (90 and 110 nm). This is likely due to lowered fluoride ion mobility in the solution at low temperatures. This results in a slower etching of the formed titanate. In the aqueous solution, the difference in inner tube diameter was attributed to the increased TiO$_2$ formation at room temperature while the etching mechanism remained unaffected by temperature [29].
Figure 9: FESEM images of 10 V NT arrays anodized at (a) 5 °C with an average wall thickness of 34 nm and (b) 50 °C with 9 nm. Reprinted with permission from Enhanced Photocleavage of Water Using Titania Nanotube Arrays. Nano Letters, 2004 [28].
2.2. TiO$_2$ Crystallographic Phases

TiO$_2$ crystals come in three different phases: rutile, anatase, or brookite. Their basic structure is a titanium atom surrounded by six oxygen atoms in a distorted octahedral configuration with two TiO$_2$ formula units per unit cell. In all of these structures, these octahedra are stacked to result in three-fold co-ordinated oxygen atoms. Anatase has TiO$_6$ octahedrons which share four edges, whereas in rutile, TiO$_6$ octahedra form links by sharing an edge along the c-axis [30, 31].

![Figure 10: Unit cells of (a) rutile, (b) anatase, (c) brookite. Grey and purple spheres represent oxygen and titanium respectively. Reprinted with permission from Nanostructured TiO$_2$ materials: properties, preparation, and applications. 2011, London, GBR: World Scientific Publishing [30].](image)

<table>
<thead>
<tr>
<th>Crystal Structure</th>
<th>Density (kg/m$^3$)</th>
<th>System</th>
<th>Space Group</th>
<th>Cell Parameters (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$a$</td>
</tr>
<tr>
<td>Rutile</td>
<td>4240</td>
<td>Tetragonal</td>
<td>$D_{4h}^{14}$ − P4$_2$/mm</td>
<td>0.458</td>
</tr>
<tr>
<td>Anatase</td>
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<td>Tetragonal</td>
<td>$D_{4h}^{14}$ − I4$_1$/mm</td>
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</tr>
<tr>
<td>Brookite</td>
<td>4170</td>
<td>Rhombohedral</td>
<td>$D_{2h}^{15}$ − Pbca</td>
<td>0.544</td>
</tr>
</tbody>
</table>


Different TiO$_2$ crystallographic structures perform better at certain applications than others. The anatase phase is preferred for catalysts and charge separating devices such as in solar energy conversion, whereas the rutile phase is preferred in dielectric layers and gas sensors. After anodization, the synthesised TiO$_2$ nanostructures are in an amorphous state and have limited photocurrent efficiencies. But after annealing at elevated temperatures, it begins to transform into a more useful polycrystalline phase.

The temperatures at which the phases begin to appear depend on synthesis (and thus, structural) parameters, including impurities present, particle sizes, strain, and texture in the
structure. For samples produced using HF based electrolytes, anatase begins appearing at around 280 °C, then at 430 °C a portion of the anatase begins to transform into rutile. A transformation to complete rutile occurs at between 620-680 °C. In comparison, NT fabricated in a NH₄F⁺ glycerol electrolyte begins transformation into anatase at 400 °C, and then transitions into rutile at above 500 °C [2, 32, 33].

The gases in which the nanotubes are annealed were also studied, and it was found that it does have an influence on this phase transition temperature. This was likely due to the formation/presence of defects and vacancies introduced in the heat treatment. Phase transformation is promoted in gases such as Ar and CO, whereas it is inhibited in air or O₂ [34-36].

### 2.3. TiO₂ Based Photocatalysis

Honda and Fujishima first discovered the photocatalytic properties of TiO₂ in 1972 [37] and inspired a new direction in heterogeneous photocatalytic destruction of organic compounds in wastewater or gas. Photocatalysis involves an initial excitation of a catalyst via light with equal or greater energy than the catalysts’ band gap (the energy difference between the top of the valence band and the bottom of the conduction band). The catalyst’s valence band (VB) of electrons becomes excited and is ‘moved up’ into the conduction band (CB), leaving behind a positively charged hole. This results in ‘electron-hole pairs’ which can participate in oxidation and reduction reactions with species adsorbed on the photocatalyst. The holes in the valence band reacts with water to produce an oxidant in the form of a hydroxyl radical (•OH) with a high oxidation potential of 2.8 V. This radical can then attack organic compounds and reduce them to simpler and safer compounds such as CO₂ and H₂O. However, the photo-generated holes and electrons can ‘recombine’ again and reduce the overall photocatalytic ability [38].

This photocatalytic process can be summarized by Equations 2 and Figure 11 below.

\[
\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2(h)^+ + e^- \quad (1)
\]

\[
\text{TiO}_2(h)^+ + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+ + \text{TiO}_2 \quad (2)
\]

\[
\cdot\text{OH} + \text{Phenol} \rightarrow \text{intermediates} \quad (3)
\]

\[
\text{TiO}_2(h)^+ + \text{intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{TiO}_2 \quad (4)
\]

**Equation 2: Redox reactions involved with photocatalysis with TiO₂.**
2.3.1 Phase Influence

The standard TiO$_2$ photocatalyst in use today is the Degussa P-25, a powder containing both anatase and rutile particles in a ratio of 3:1. It was found that by having both phases present; the photocatalytic ability is greater than having only anatase or only rutile crystallites. This indicates a synergetic effect between the two phases when they are in contact with each other [39].

For pure phase compositions, it was found that anatase was more efficient than rutile [40]. However, there is no single generally accepted explanation behind the differences in photocatalytic ability between the phases. Possible explanations include:

- The surface properties and surface orientations may affect the photocatalytic abilities. The coordination structure can affect chemical adsorption of molecules [31], as well as the electronic structure of the titanate semiconductor surface [41].
- Anatase has a larger band gap than rutile. This means that it absorbs less light, but can also mean the valence band maximum will be of a higher energy level relative to adsorbed molecules. This results in the electrons having a stronger oxidation power [42].
- Anatase has a longer electron-hole pair life time compared to rutile, resulting for more surface reactions with adsorbents. This is evidenced by a study involving transient photoconductivity measurements on crystalline samples [43].
Fang and co-workers in 2011 performed photocatalytic tests on titanium substrate attached TiO$_2$ NTA heat treated at various temperatures. It was found that the samples heat treated to contain pure anatase showed significantly greater photo-degradation of methyl orange than samples heat treated at higher temperatures which contained rutile. It was theorised that with these nanotubes which were still attached to the substrate, defects at the nanotube/substrate interface acts as a nucleation site for rutile $[36]$. Although it was reported that a mixture of anatase and rutile particles showed a greater photocatalytic ability than that of pure anatase $[39]$, it is possible that this difference is attributed to rutile in the NT array samples existing at the compact base of the tubes and the anatase in the tubular section. This separation of the phases prevents the synergetic effects that occur with the mixture of phases.

Investigations were also made to investigate the photocatalytic potential of amorphous TiO$_2$ by Kaur in 2012. Using molecular dynamics simulations, multiple amorphous samples were prepared with different amount of atoms. The band gap characteristics of the amorphous titanate were compared with that of those of crystalline rutile and anatase. The analysis of the electronic properties indicated that the amorphous variant is a less efficient photocatalyst. But the due to the lack of heat treatment, amorphous TiO$_2$ may prove to be a cheaper alternative photocatalyst $[44]$. 
2.3.2 Band Gap Modification

TiO$_2$ has a large band gap of 3.2 eV for anatase and 3.0 eV for rutile. This band gap limits the photocatalytic response to the UV spectrum ($\lambda < 385$ nm) which only accounts for $\sim$5% of solar radiation [45]. UV light is costly and inefficient to artificially produce, so there has been research into methods to shift or widen this band gap to a more useful energy level such as visible light ($\lambda = 400 – 700$ nm) for more efficient photocatalysis.

The main method being studied is doping with foreign elements. Studies included doping transition metal Cr, Co, Bo, and Mg cations into Ti sites [45-48]; non-metal N, S, and C anions into O sites [49-51]. These studies include doping into TiO$_2$ bulk powder and nanostructures. Doping methods included annealing under CO gas flow [50], sputtering TiO$_2$ in a N$_2$/Ar gas mixture [51], and electrodeposition with the NT subjected to current in a H$_3$BO$_3$ electrolyte [48]. Other band gap modification methods other than doping include dye-sensitization [52], noble metal loading [53] and grafting [54-56].

The main principle behind the addition of foreign elements (via doping or grafting) is to extend the optical absorption edge. This is done by introducing impurity energy levels (IELs) into the forbidden band of TiO$_2$, allowing for a narrower gap between the IEL and the conduction band. In the case of substitutional N-doping, nitrogen ions replace oxygen ions in the lattice, with N (2p) states located above the valence band edge. The mix of O (2p) and N (2p) states leads to an overall reduction in the band gap of the N-doped TiO$_2$ [15, 51, 57]. However, the photo-generated holes in the dopant band decrease in oxidative power with irradiation, and also prevent the strong holes in the valence band of TiO$_2$ from being utilised. Metallic cation doping can also result in the formation of recombination centres in the carriers which causes reduced oxidative efficiencies [58, 59]. With Fe$^{3+}$ cation doping, concentrations below 0.5 mol% resulted in visible light responsive photocatalysis. But above 0.5 mol% cation concentration, Fe$_2$O$_3$ oxide molecules form and act as recombination centres [57].

Meng and co-workers (2013) attempted to solve these inadequacies by investigating the properties of TiO$_2$ co-doped with nitrogen and a transition metal using calculated models employing first-principles density functional theory (DFT). Systems with photocatalytic activities which occurred in the visible light region and with reasonable efficiencies included (V, N), (Mn, N), and (Cr, N) [45]. An earlier study by Long and English in 2011 also performed DFT calculations for Mg/Ca- and/or Mo/W mono- and co-doped anatase TiO$_2$. 
These systems also significantly narrow the band gap and also passivate the introduced impurity states, allowing for greater visible light harvesting. (Mg/Ca, Mo)-codoped TiO$_2$ was found to have a more narrowed band gap than that of (Mg/Ca, W). There was also a practical match in ionic radii between Ti$^{4+}$ (0.605 Å) and the dopants in the +6 chemical state (Mo$^{6+}$: 0.59 Å, W$^{6+}$: 0.60 Å) [47].

Irie and co-workers have attempted to solve the deficiencies caused by doping by grafting Cu(II) ions onto rutile TiO$_2$ bulk powder. CuCl$_2$·2H$_2$O powder was added to an aqueous suspension of rutile TiO$_2$ powder and heated at 90°C and stirred for 1 h. The resultant suspension was filtered and washed with distilled water and dried at 110°C for 24 h. It was then ground into a fine powder as the grafted photocatalyst. The product displayed greater apparent reaction rates (detected via CO$_2$ generation from 2-propanol degradation) than that of N-doped powder TiO$_2$ while under visible light. The mechanism of this increased efficiency is hypothesised to be due to interfacial charge transfer (IFCT) where electrons from the VB of TiO$_2$ are excited due to visible light and are transferred to Cu(II) which forms Cu(I). This leaves behind holes with strong oxidative power in the VB of TiO$_2$ which are free to decompose organics. The formed Cu(I) can also reduce O$_2$ through multielectron reduction as shown in equations 9-11 below. This also transforms the Cu(I) back into Cu(II), allowing
Chapter 2: Literature Review

for further IFCT to occur. This system thus has a catalytic function, producing oxidative decomposition activity.

Two electron reduction: \[2\text{Cu}(I) + \text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Cu}(II) + \text{H}_2\text{O}_2\] (1)

Four electron reduction 1: \[3\text{Cu}(I) + \text{O}_2 + 4\text{H}^+ \rightarrow 2\text{Cu}(II) + \text{Cu}(III) + 2\text{H}_2\text{O}\] (2)

Four electron reduction 2: \[4\text{Cu}(I) + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Cu}(II) + 2\text{H}_2\text{O}\] (3)

Equation 3: Electron reduction reactions involved with photocatalysis with copper grafted TiO$_2$.

K-edge X-ray absorption fine structure (XAFS) characterisation was performed on the grafted photocatalyst powder. These results and Fourier transforms of extended XAFS were compared with XAFS spectra of Cu(OH)$_2$, CuO, Cu$_2$O, and Cu. It showed that the grafted Cu species were in the 2+ state and in a distorted CuO amorphous structure where the apical oxygen approaches the Cu(II) in the form of a five-coordinate square pyramid. XAFS tests also further confirmed the role of the Cu(II) ions in photocatalysis [54, 55, 59].
2.4. Conclusions

Titanium dioxide nanostructures are a rapidly developing field with a wide range of practical applications. The combination of a large surface area to volume ratio inherent in nanostructures, band gap energy, and low cost/high abundance of TiO₂ makes it an attractive avenue of research.

The large surface area in nanostructures allow for increased reaction sites for chemical reactions. The small scales of these structures also cause interesting phenomena to occur with light absorbance/transmittance. Titanium dioxide’s band gap is the right size that when exposed to ultraviolet light; electrons are excited out, allowing for applications involving photocurrents and light induced redox reactions. Titanium dioxide is also a relatively cheap material and is inherent nontoxic and safe in the environment with a long service life.

NS-TiO₂ development started from synthesising elaborate nanostructures. Various parameters including voltage, anodization duration, and electrolyte composition/concentration were manipulated in order to understand the influence that they have on the anodization mechanics and on the resultant nanostructures.

The photochemical applications of pure titanate are limited to the ultraviolet spectrum, which is only a small portion of the light spectra. So research was done to modify the TiO₂ with other foreign elements in order to shift the band gap energy to the visible light spectrum. This allowed for more efficient application of the photocatalytic properties of TiO₂. The modifications include doping and grafting using a variety of methods such as heat treatment and sputtering. Although these attempts to allow for visible light applications have been successful, the oxidative power of these modified photocatalysts has been reduced. There is undergoing research into methods to solve these issues and make TiO₂ into an efficient photocatalyst for practical applications.
Chapter 3. Experimental

The experimental procedures performed in this study can be divided into two main sections:

- The initial synthesis of titanate nanotube arrays (NTA) via electrochemical anodization and subsequent heat treatment to identify the influence of phase composition on its morphology.
- The copper grafting procedures to modify synthesised titanate NTA so that they can perform photocatalysis under visible light.

3.1. Anatase & Rutile Phase Synthesis

There are two main phases of TiO$_2$ used in photocatalysts: anatase and rutile as mentioned in Section 2.2. Although past studies have identified the temperature ranges in which anatase and rutile appear, they can vary depending on factors such as the type of electrolyte used and in what form the TiO$_2$ is synthesised. So experiments were performed to identify the annealing temperature range in which these phases appear and transition from one into the other with nanotubes produced with the following synthesis method.

3.1.1 Titanium Substrate Preparation

The initial substrate for anodization used was titanium sheet (99.6% purity) of 0.2 mm thickness. It was cut into 10 x 20 mm pieces. One face of it was ground smooth with P220 SiC sandpaper and etched with 2% HF + 2% HNO$_3$ solution for 15s to remove the passive
oxide layer. It was then cleaned and degreased with distilled water, acetone and ethanol. The samples were stored in ethanol to minimise oxidation.

Before the anodization process, cellulose adhesive tape was applied to the sample so that only a 10 x 10 mm square area was exposed to the electrolyte solution for anodization.

3.1.2 Anodization Process

The anodization process involved a two electrode electrochemical cell. The electrolyte was 50 mL of ethylene glycol w/ 0.25 wt. % NH₄F and 2 vol. % distilled water. This was magnetically stirred at 450 rpm. The voltage used was DC 40 V using a Precision 9110 100W Multi Range 60V/5A DC power supply. Pure platinum foil was used as a cathode whereas the prepared substrate acted as the anode with the exposed titanium surface facing the cathode. The distance between the electrodes was set to 20 mm. The samples were anodized for 4 h at room temperature.

After the anodization, the samples were stored in ethanol for 24 h to relieve internal stresses caused by the volume expansion of oxide generation, before the adhesive tape was removed. Then the as-anodized samples were ultrasonically cleaned (Digitech ultrasonic cleaner) for 1 min to remove the surface debris. If there was any adhesive residue from the tape remaining on the sample surface, it was removed using acetone. The samples were then stored in ethanol until the next step.

3.1.3 Crystallization of Amorphous Phase via Annealing

The samples were heat treated to convert the amorphous structure to a crystalline one. Samples were placed into a furnace set to a certain temperature for 2 h in ambient air. The samples were left in the furnace to cool down to ambient temperature before being removed.
Chapter 3: Experimental

3.2. Copper Grafting & Photocatalysis

The samples prepared previously was found to be too small for effective photocatalytic tests, thus larger samples were prepared. These samples were prepared following the same method as before in Section 3.1 except with the following changes:

- Titanium foil was of 20 x 35 x 0.4 mm, and the anodised surface area was 20 x 20 mm. (For the purposes of SEM characterisation, smaller 20 x 10 mm samples were still produced.)
- The amount of electrolyte used was increased to 125 mL to account for the greater anodization area.
- Anodization duration of 6 h each.
- Heat treatment duration of 1 h.

Attempts were made with the same samples used in 3.1 (with a thickness of 0.2 mm), but after heat treatment, the nanotube layer flaked off the substrate metal. Examples are shown in Figure 17. This was likely due to the thermal expansion of the titanium substrate which differed from the expansion of the TiO$_2$ NT layer. To remedy this, a thicker substrate of 0.4 mm was chosen to reduce the strain produced by the thermal expansion. A number of other possible reasons for this could be due to the non-uniform distribution of NT layer, rapid
dehydration of the as-anodized TiO$_2$, or the internal stress produced by phase transformations within the sample.

However, even using the thicker substrate, some samples had significant portions of NT flaking off. It was theorised that this is due to a weak interfacial layer between the nanotubes and the substrate. In order to remedy this, a method similar to Sulka’s [7] was used. A more robust NT layer was produced by anodizing the substrate twice under the same parameters: After the first anodization, the nanotube layer was completely removed via a combination of mechanical bending of the substrate and ultrasonic cleaning. The substrate was then anodised again to produce a more uniform and stronger NTA.

Figure 16: Diagram of nanotubes before and after complete nanotube removal. After the nanotube removal, the base ‘dimples’ from the NT bottoms act as a template for further NT growth.
Figure 17: Samples annealed at 450 °C with (a) completely and (b) partially flaked off nanotube layer, whereas (c) is a successful intact sample.
Chapter 3: Experimental

3.2.1 Initial Copper Grafting Procedure

In order for photocatalysis to occur under visible light instead of only under ultraviolet light, copper ions (Cu\(^{2+}\)) were grafted onto the crystalline TiO\(_2\) NTA using a method similar to that used by Irie and co-workers [55, 59]. Unfortunately all the previous literature on grafting was based on TiO\(_2\) nanoparticles, so tests were required to see whether copper grafting in this manner was viable on NTA.

An initial trial copper grafting procedure was performed to observe the morphology of the samples. Heat treated samples were suspended in a solution of 10 mg CuCl\(_2\)·H\(_2\)O and 80 mL distilled water (125 ppm) for 1 h. The solution was heated to 90 °C in a water bath and stirred at 100 rpm. Afterwards, the sample was rinsed in distilled water and dried in an oven at 110 °C for 24 h.

After analysing the grafted samples under SEM/EDS and identifying possible issues with this method, changes were made to this procedure resulting in the section below.

3.2.2 Final Copper Grafting Procedure

Calculations were made to estimate the CuCl\(_2\)·2H\(_2\)O concentration of the grafting solution required relative to the surface area of TiO\(_2\). The concentration of CuCl\(_2\)·2H\(_2\)O in distilled water used in Irie’s work was around 270 ppm with 1 g of TiO\(_2\) powder with a total surface area of 90 m\(^2\). Using the dimensions of the nanotubes obtained from previous SEM characterisations, the surface area of these samples was estimated. Using the ratio of CuCl\(_2\)·2H\(_2\)O to surface area of Irie’s work, the grafting solution concentration appropriate for the surface area of the nanotube samples (20 x 35 mm) was estimated to be 0.2 ppm. (See Appendix X for calculations)

The purpose of this set of experiments was to vary the CuCl\(_2\)·2H\(_2\)O concentrations to observe the effects of grafting solution concentration on surface morphology and its photocatalytic properties. Samples were grafted at 200, 20, 2, and 0.2 ppm concentrations.

The samples to be examined under SEM are have a smaller dimension (10 x 20 mm), thus a smaller concentration of solution (four times more diluted – 50, 5, 0.5, 0.05 ppm) was used.

The grafting procedure used was similar to that of the previous section, but with the following changes:
Chapter 3: Experimental

- 200 mL of grafting solution instead of 80 mL.
- Sample is completely immersed in solution instead of suspended.
- Beaker containing grafting solution is covered to minimise evaporation.

3.2.3 Photocatalysis

Photocatalytic ability was tested with degradation of Rhodaime B (RhB) dye solution. 6 mL of 2 mg dye / mL deionised water solution was used. The sample was immersed into the solution in a glass beaker and irradiated. The irradiation was from filtered blue light from a Xenon lamp at 1 mWcm\(^{-2}\). This light wavelength was chosen because it does not contain the UV spectra. Before testing, the samples were kept in the dark for 30 min to reach adsorption/desorption equilibrium.

The measure of photocatalytic ability was measured using a UV-Vis Spectrometer (Perkin Elmer Lambda 35) on the dye solution at 0, 1, 2, 3, and 4 h. 3 mL of solution was tested each time and returned to the total solution afterwards. The absorbance peak values from the spectrometer of the tested solution were used as a measure of the concentration of dye in the solution.

The UV-Vis spectrometer parameters used were:

- Scanning range: 400 – 700 nm
- Scanning speed: 400 nm/min
- Ordinate mode A
- Slit size: 1 nm

After the photocatalytic tests, the samples were rinsed and stored in distilled water for 2 hours before being dried. This was to remove the remaining dye from the sample.

Although planned, due to a lack of time, experiments to compare across crystal phase compositions (i.e. heat treatment temperatures) and copper grafting concentrations on photocatalytic ability were not performed.
3.3. Characterisation

3.3.1 X-ray Diffraction

X-ray Diffraction (XRD, Bruker D2 phaser with LYNXEYE™ detector) with CuKα radiation characterisation was performed to determine the proportions of anatase and rutile phases present in the samples.

3.3.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM, FEI Quanta 200 F) with Energy Dispersive X-Ray Spectroscopy (EDS, SiLi Detector with super ultra-thin window) was performed to observe the morphology and elemental analysis of sample surfaces. Platinum was coated on the surface to provide conductivity and minimise beam damage.

3.3.3 Transmission Electron Microscopy

Transmission electron microscopy (TEM, Tecnai F20 200kV) was also performed to closer observe and characterise the morphology of synthesised nanotubes. Only nanotubes arrays removed from the substrate were analysed, as the large samples with titanium substrate are not appropriate for TEM.
Chapter 4. Results & Discussion

4.1. Anatase & Rutile Phase Synthesis

Figure 18: XRD diffractograms of samples from 3.1 produced at 40 V and heat treated at (a) 300, 400, 500, 600, 700, and 800 °C and (b) 700, 725, 750, 775, 800 °C. The peaks marked by the black triangles, squares, and circles are titanium, anatase, and rutile peaks respectively.
<table>
<thead>
<tr>
<th>Heat Treatment Temperature (°C)</th>
<th>Relative Phases (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Titanium</td>
</tr>
<tr>
<td>300</td>
<td>91.5</td>
</tr>
<tr>
<td>400</td>
<td>91.4</td>
</tr>
<tr>
<td>500</td>
<td>84.9</td>
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<tr>
<td>700</td>
<td>49.0</td>
</tr>
<tr>
<td>800</td>
<td>0.0</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Titanium</th>
<th>Anatase</th>
<th>Rutile</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>46.7</td>
<td>46.3</td>
<td>8.6</td>
</tr>
<tr>
<td>725</td>
<td>40.4</td>
<td>45.4</td>
<td>14.9</td>
</tr>
<tr>
<td>750</td>
<td>40.6</td>
<td>38.4</td>
<td>20.9</td>
</tr>
<tr>
<td>775</td>
<td>21.0</td>
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</tr>
<tr>
<td>800</td>
<td>0.0</td>
<td>32.0</td>
<td>68.0</td>
</tr>
</tbody>
</table>

Table 3: Semi-quantitative analysis on the XRD results on Figure 18.

Figure 18 (a) represents the initial tests performed to identify the variation in phases produced from the various heat treatment temperatures. After observing the appearance of rutile phase at 700 °C, further samples were prepared at 25 °C intervals between 700 and 800 °C to produce a more varied range of rutile and anatase phases as shown in (b). The results from (a) the results were from one sample per temperature; whereas in (b), they were from averaged results from three new samples at each annealing temperature. Individual XRD results can be found in Appendix C. Semi-quantitative analysis was performed to provide a numerical estimate of the relative amount of phases present in the samples. This is shown in Table 3 above.

The XRD results show the presence of the metallic titanium phase; this can be explained by the titanium substrate base in the sample. At heat treatment temperatures less than 700 °C, the crystalline phases present are only the titanium metal substrate and anatase. The proportion of anatase increases as the amorphous TiO₂ (undetectable by the XRD since it only characterises crystalline phases) becomes crystallised by the heat treatment. This is evident as the metallic Ti content decrease as more amorphous TiO₂ is crystallised, preventing the XRD from detecting the base Ti substrate. In a way, the Ti peak intensities can be used as a measure of the quantity of amorphous TiO₂ remaining in the sample.

In Figure 18 (a), the anatase peaks begin to become thinner in addition to growing higher. The peak width (at half maximum peak intensity) is inversely proportional to mean crystal
grain size via Scherrer’s relationship. This indicates the average crystal sizes are becoming larger and shows an increase in overall crystallinity. Beyond 700 °C, rutile peaks begin to appear as anatase begins its phase transformation to rutile, another crystalline form. It can also be noted that the rutile peaks, unlike the wide anatase peaks, first appear as narrow peaks. This confirms that the amorphous TiO$_2$ does not directly transform into rutile and suggests that it is the already crystalline anatase which transforms into rutile.

However in the 700 – 800 °C results in Table 3 (b), the anatase content appears to fluctuate. This may be due to the rate of amorphous TiO$_2$ transforming into anatase competing with the rate of anatase transforming into rutile. In Table 3 (a), the 800 °C phase composition is almost completely rutile, whereas in (b) the 800 °C phase composition has significantly less rutile. This is possible due to the Ti substrate used was from a new batch, and was prepared with slightly differences (i.e. degree of mechanical grinding and chemical etching). These factors can influence the phase transformation temperatures.
4.1.1 SEM Characterisation

Figure 19: SEM images of samples produced at 40 V for 4 h in ethylene glycol + NH$_4$F electrolyte annealed at 300 °C from 3.1.
Figure 20: SEM images of heat treated TiO₂ nanotubes produced at 60 V for 12 h. (a) and (b) show the side profile while (c) shows a top profile for the surface layer.
Chapter 4: Results & Discussion

Figure 20 shows the upper layer of nanotubes which were not ultrasonically cleaned. This surface layer is the result of the top sections of nanotubes intertwining with each other. Nanotube wall thicknesses are greater at the base as shown in Figure 21 below, and decrease higher up in the layer. This means that at the top of the nanotubes layer, the wall thickness become so thin that they become nanowires and entangle, resulting the ‘mat of wires’ shown in Figure 20 (c). Figure 19 shows significant amounts of debris on the surface, but most of the nanotubes are visible from the top. The remaining debris is the result of inadequate ultrasonic cleaning.

![SEM images of the undersides of TiO$_2$ nanotubes produced at 60 V for 12 h.](image)

Figure 21: SEM images of the undersides of TiO$_2$ nanotubes produced at 60 V for 12 h.
Figure 22: SEM images at 100,000x magnification of TiO$_2$ oxide layers prepared in 3.1 heat treated at (a) 300, (b) 400, (c) 500, (d) 600, (e) 700, and (f) 800 °C for 2 h.

As shown in Figure 22, the morphology of the annealed samples does not show significant changes between the heat treatment temperatures until 700 °C. Before that temperature, pore size remains constant at around 65 nm and tube wall thickness at 45 nm. After 600 °C, the nanotube morphology is lost as the anatase crystals begin their phase transformation into rutile. This is observed as the nanotube walls begin to become nodular in nature and the grains observed become larger. This drastic change in structure as well as the aggregation of the rutile crystals into large discrete grains (up to 330 nm) results in the change of the overall morphology from nanotubes to that of a porous structure.
Figure 23: (a) and (b): SEM images of a sample showing the cracks present in a TiO_2 nanotube layer heat treated at 700 °C. Nanotubes can be observed stretching across the cracks. (c): An 800 °C annealed oxide layer, note the lack of tubular structure.

The cracks observed in Figure 23 (a) is a result from the difference in thermal expansion of the Ti substrate and the NT oxide layer. Although the NT morphology has been distorted by the increase in crystal grain size and the presence of the rutile phase, discrete nanotubes are still present as shown in the cracks in the sample heat treated at 700°C in (b). However when heat treated at 800 °C in (c), the nanotube structure has completely disappeared, even in the side profile, and replaced by large particles of rutile instead.
Figure 24: Models representing the evolutions of morphology and crystallization of the TiO$_2$ nanotube arrays on Ti substrate (a) and the freestanding TiO$_2$ nanotube membranes. Reprinted with permission from Effect of heat treatment on morphology, crystalline structure and photocatalysis properties of TiO$_2$ nanotubes on Ti substrate and freestanding membrane. Applied Surface Science, 2011 [36].

Similar research performed by Fang et al supports the XRD characterisation results and the SEM images in this study and give a possible model of how the phase transformation between anatase and rutile destroy the nanotube morphology as shown in Figure 24. The nucleation of the rutile first begins at the interface between the nanotubes and the titanium substrate. As the temperature increases, the crystallites develop upwards along the nanotube axis. This wide range of phase transformation temperatures (400 - 1100 °C) can be influenced by a number of factors including particle size, shape, heat treatment atmosphere, and dopants. Defect sites produced by these factors can provide low energy mass transport routes and lower the transformation temperature. Oxygen vacancies produced at the nanotube-substrate interface due to reactions between the TiO$_2$ and Ti metal during annealing can act as nucleation sites for the rutile formation, explaining the above model. Other factors could also contribute to this phenomena, such as the temperature distribution throughout the entire substrate-NTA sample [36].

It was also discovered that with freestanding NT arrays (i.e. without the titanium substrate) heat treated at 800 °C consisted completely of anatase according to XRD characterisations, only at 900 °C did rutile peaks appear. SEM analysis of the 800 °C samples showed that the morphology was that of dense agglomerates of anatase nanoparticles, even without the presence of rutile. This suggests that the nucleation/ transformation mechanism of anatase to rutile is promoted by presence of the Ti substrate foil. The freestanding NT arrays, lacking
the oxygen vacancies at the substrate/NT interface, depended on the coarsening by grain growth to decrease the surface energy required for the anatase-rutile transformation [36].

Reidy et al demonstrated that the critical particle size was crucial to this phase transformation. Nanoparticles were produced via the sol-gel method and doped with various elements. Studies were performed to compare the effects of the doping on the transformation temperature. It was found that the phase transformation occurred when the grain size reached around 450 Å (45 nm) and this value was independent to the type and concentration of dopant used [60].

The critical grain size of 45 nm found by Reidy (although in nanoparticles produced via sol-gel) is similar to the wall thickness of our samples shown in Figure 22. In (e) most of the NT walls consist of grains with diameters the same or larger than 45 nm. Through a combination of rutile phase nucleation at the interface between the TiO$_2$ nanotubes and the Ti substrate, and the attainment of critical grain size via grain coarsening of anatase crystals resulted in the dramatic structural change observed between Figure 22 (d) to (f).

This destruction of ordered nanotube array morphology means that the overall surface area would be reduced and would be less efficient for applications such as photocatalysis and in DSSCs. Besides the loss in surface area, the structure no longer has the unique one-dimensional geometry that nanotubes possess. The arrangement of the highly ordered NTA perpendicular to the substrate surface allows for efficient charge transfer along the length of the nanotubes from the solution to the substrate. This pathway for charge transfer reduces the losses incurred when the charge has to transfer across nano-particle grain boundaries, allowing for excellent electrical properties [61]. This destruction of the one-dimensional geometry in the NTA also means that it is not recommended to perform heat treatment at high temperatures on TiO$_2$ based nanostructures engineered with complex architectures (i.e. multi-layer nanotube arrays).
4.1.2 TEM Characterisation

Figure 25: TEM diffraction patterns and images of TiO$_2$ nanotubes synthesised at 60 V (a-b) pre, and (c-d) post heat treatment at 450 °C.

TEM was performed on freestanding nanotubes produced from anodization at 60 V for 10 h to closer observe the tube surface morphology. Nanotubes with and without heat treatment at 450 °C were examined. The post anodized samples showed smooth nanotube walls and the TEM diffraction pattern showed that the structure was completely amorphous with no distinct diffraction rings. With samples exposed to heat treatment at 450 °C, the nanotubes do not have smooth walls as the amorphous structure becomes crystallized into anatase. The sharp distinct rings on the diffractogram on (c) coincide with peaks found in anatase. This structure seen in Figure 25 (d) supports that of the model proposed by Fang et al in Figure 24 (b).
Figure 26: TEM images of the crystal structure of TiO$_2$ nanotubes heat treated at 450 °C. The red lines indicate grain boundaries.

Figure 26 shows a close up of the crystal grains of the anatase TiO$_2$ present in the nanotubes. The striped areas are the crystals, and the non-striped areas are the background carbon substrate on which the samples were mounted on for TEM. The spaces between the fine lines give an indication of the crystal sizes and the directions of the lines show its preferred crystal orientation. Using the scale bar on the images and the spacing distance between the lines, the crystal size was estimated to be around 0.3 nm. This spacing distance remains constant throughout the samples. Grain boundaries can be discerned by where the lines change direction and are marked in red.
4.2. Copper Grafting

4.2.1 Initial Copper Grafted Samples

Figure 27: (a): SEM images of Cu grafted TiO\textsubscript{2} NT layer from 3.2.1. (b): EDS results from locations 1 and 2 marked on (a). The particles observed in (a) are crystals of CuCl\textsubscript{2} used during the grafting procedures. The Pt peak is from the platinum coating used to prepare the samples for SEM.

The EDS results of the Cu grafted sample in Figure 27 (b)-2 shows that the grafting procedure was successful in that copper peaks were detectable on the NTs surface. The Cu and Cl peaks on the EDS graph on (b)-1 clearly shows that the large crystals on (a) are the CuCl\textsubscript{2} crystal powder used in the grafting procedure. Around one particle of CuCl\textsubscript{2} was found in every 500 µm\textsuperscript{2}. The presence of these particles indicated that the 125 ppm CuCl\textsubscript{2}-2H\textsubscript{2}O solution used may be too concentrated. These large particles could have a detrimental effect to the catalytic abilities of the nanotubes due to physical obstruction of the tube morphology.
4.2.2 Final Grafted Samples

Samples grafted at 0.05, 0.5, 5, and 50 ppm were examined under SEM/EDS, and the results are seen above under Figure 27-28. There does not appear to be any significant morphological differences between these samples; the nanotube pore/wall sizes, tube lengths remain consistent. This means that the copper grafting with different concentrations did not have any effect on the morphology of the samples.

No large crystals like that seen in Figure 27 (a) could be found on any of the four samples. Although in the initial grafting trial, the grafting solution was of a lesser concentration (125 ppm) than that of the highest concentration sample in this set of samples (200 ppm); no CuCl₂ crystals could be found on the 200 ppm sample during the SEM session. This difference is likely due to the change of grafting solution quantity from 80 mL to 200 mL and the covering of the beaker containing the solution. This reduces the concentrating effect that results from the evaporation of the water content in the solution during the heating of the grafting solution.

There is a noticeable difference in tube morphology between that of Figure 22 and 28 which is that the tube wall is thinner in the latter. This is likely due to the NTA in Figure 22 being...
Chapter 4: Results & Discussion

affected more by ultrasonic cleaning than those in Figure 28, resulting in more of the higher level of nanotubes being removed.

Although Figure 27 with 125 ppm shows large discrete particles of CuCl₂ on the sample surface, SEM images of the samples grafted between 0.05 and 50 ppm in Figure 28 do not show any obvious particles containing copper or significance differences in tube morphology. Either the grafted CuO species is too small for SEM characterisation to detect and/or too rarely distributed across the NTA surface. It is also possible that the grafted CuO species exists as a very thin shell/layer on the nanotube surface like in Figure 29. High resolution TEM of copper grafted samples would need to be performed to clearly identify how the grafted species are attached to the titanate NTA.

![Figure 29: Possible model of how copper is grafted onto the surface of TiO₂ nanotubes where the blue shell layer is CuO.](image)
Figure 30: EDS results from the samples annealed at 450 °C from 3.2.2 with (a) 0.05 ppm, (b) 0.5 ppm, (c) 5 ppm, (d) 50 ppm CuCl$_2$·H$_2$O grafting solution.

The EDS results in Figure 30 were from general areas of around 6500 µm$^2$ on the sample surfaces. These results confirm that the amount of Cu found on the substrate surface is proportional to the grafting concentration. The copper peaks however, disappear below 5 ppm in the above figure. Below this concentration the copper content is too low for EDS to detect.
Chapter 4: Results & Discussion

4.2.3 Photocatalysis Results

Figure 31: UV-Vis Spectroscopy results of 2 mg/mL RhB dye irradiated under blue light (a) with a TiO$_2$ NTA sample annealed at 450 °C without Cu grafting, and (b) without any samples.

The RhB dye solution shows a negligible decrease in concentration when irradiated in visible light without any photocatalytic samples. This indicates that it is relatively stable under blue light and will not degrade by itself.

When exposed to a non-grafted sample, the dye shows degradation, indicating that the non-grafted sample shows a small degree of photocatalytic ability under blue light. Normally unmodified titanate should not be able to degrade anything under visible light, but this result
shows otherwise. A possible reason is due to the presence of oxygen defects in the NTA structure, introduced during the heat treatment process. These defects in the form of Ti$^{3+}$ (produced from the thermal reduction and removal of O$^{2-}$ anions) sites react with adsorbed O$_2$ molecules, producing superoxide O$_2^-$ radicals. These radicals participate as an oxidising agent on the RhB dye molecules in the solution and thus break them down [62, 63]. Or another simpler reason for this observed degradation may be during the transfer of the solution to and from the photocatalysis beaker to the UV-Vis spectrometer it was exposed to sunlight, which contains the UV spectrum. Thus it is possible that this short exposure of UV light combined with the above mechanisms resulted in the small level of photocatalytic ability observed.

Figure 32: UV-Vis Spectroscopy results of photocatalytic tests from 3.2.2 of TiO$_2$ NTA samples annealed at 450 °C with Cu (II) grafted at (a) 0.2, (b) 2, (c) 20, and (d) 200 ppm on Rhodamine B dye irradiated under blue light.
Figure 33: Photocatalytic effect of TiO$_2$ NTA samples annealed at 450 °C with varying amounts of copper grafting on RhB dye solution during irradiation under blue light.

Although the EDS results in Figure 30 show that beneath 5 ppm the copper concentrations were too low to detect, the 0.2 ppm grafted sample demonstrated the greatest photocatalytic ability out of the four samples. This confirmed that the copper grafting had a positive influence in photocatalysis even in such trace amounts. It is uncertain whether 0.2 ppm is the optimum grafting concentration for these samples. Unfortunately, there was not enough time to prepare and test samples with grafting concentrations between 0 and 0.2 ppm.

However, above 0.2 ppm, as the copper grafting concentration increases, the photocatalytic ability decreases. This phenomenon is similar to those experienced and explained in various past publications in regards to foreign element doping in titanate photocatalysts.

In Ganesh’s work in 2011, TiO$_2$ photocatalyst powder was doped with varying amounts of Ni (0.1, 0.5, 1, 5, and 10 %) and tested using the degradation of methylene blue (MB) solutions of various concentrations. Photocatalytic ability was shown to be greatest at 0.5 %. The results were analysed using the Langmuir-Hinshelwood rate constant equations. This equation described the relationship between the initial degradation rate ($r$) and the initial concentration of the organic substrate ($C$).
Chapter 4: Results & Discussion

\[ r = \frac{-dC}{dt} = \frac{kK_{ads}C}{1 + K_{ads}C} = k_{obs}C_t \]  \hspace{1cm} (1)

Where

\[ k_{obs} = \frac{kK_{ads}}{1 + K_{ads}C} \]  \hspace{1cm} (2)

\[ \frac{1}{k_{obs}} = \frac{1}{kK_{ads}} + \frac{C}{k'} \]  \hspace{1cm} (3)

\[ -\ln \frac{C_t}{C_o} = k_{obs}t \]  \hspace{1cm} (4)

**Equation 4: Langmuir-Hinshel rate constant equations for heterogeneous photocatalytic degradation.**

By plotting \(-\ln (C_t / C_o)\) against irradiation time from the degradation of MB, the \(k_{obs}\) values were estimated in the form of trend line gradients. When \(C_o\) was plotted against \(1/k_{obs}\), the rate constants \((k)\) and adsorption equilibrium constants \((K_{ads})\) were calculated using Equation 4-3. It can be identified as \(Y = mX + C\), where, \(C = 1/kK_{ads}, m = 1/k'Y = 1/k_{obs},\) and \(X = C_o\).

The results showed that \(r\) (calculated using Equation 4-1) and the \(K_{ads}\) decreased when Ni dopant concentrations in the TiO\(_2\) and the MB concentrations in the solution increased [64]. Unfortunately the experiments performed in this thesis did not test photocatalytic ability with differing initial dye concentrations, so the Langmuir-Hinshel adsorption equilibrium constants and initial degradation rate of RhB dye cannot be calculated with the data available in our results.

Cong (2007) produced Fe doped TiO\(_2\) nano-powder where its photocatalytic abilities increased with Fe\(^{3+}\) doping concentrations when the concentration remained below 0.5 atom %; above that value, the photocatalytic efficiency decreases. Fe\(^{3+}\) dopant serves as a charge trap to retard the recombination rate between electron-holes, and enhances the interfacial charge transfer (IFCT) required for photocatalysis. Cong theorised that when the dopant concentration is too high, the recombination rate will increase due to decreased distances between trapping sites [57].

Irie’s work mentions that due to how the interfacial charge transfer proceeds between the valence band of TiO\(_2\) and Cu (II), it is preferable for IFCT that the Cu (II) ions are atomically isolated on the TiO\(_2\) surface. It is possible that with excessive CuCl\(_2\) quantities grafted onto the sample, the grafted CuO atoms are no longer isolated on sample surfaces, reducing the photocatalytic efficiency [55].
In summary, past studies found that photo-reactivity of foreign doped TiO$_2$ is a complex function consisting of the dopant concentration, dopant energy level within the TiO$_2$ lattice, their electronic configuration, the dopant distribution, the electron donor distribution, and the light intensity [65]. This thus suggests that there is an optimum dopant concentration for photocatalysis. The principles behind photocatalysis via foreign metal doping and copper grafting are not dissimilar; both modify the band gap of TiO$_2$ by introducing ‘intermediate’ energy levels directly in the form of a metal cation impurity energy level or indirectly in the form of Cu(II) operating via interfacial charge transfer from the VB of TiO$_2$ to the Cu(II) ions. Both create electron-hole pairs which induce redox reactions which can decompose organic compounds into safer, simpler ones. It is possible that these photocatalytic results observed in our experiments can be explained by these mechanisms which drive photocatalysis under visible light with foreign metal cation doped TiO$_2$. 


Chapter 4: Results & Discussion

4.3. Miscellaneous Observations

4.3.1 Oxide Colour

Figure 34: TiO$_2$ nanotube samples heat treated at various temperatures. From upper left to right: 300, 400, 450, 600, 700, and 800 °C. The damaged/flaked off areas were caused by the sample mounting procedures for XRD.

When heat treating the samples, it was observed that the colouration of the nanotube oxide layer (and the titanium substrate) varied between the heat treatment temperatures. However, normally, TiO$_2$ is supposed to have a white/grey colour. The 300 °C sample has an orange/purple hue, and above that temperature the colour begins to darken and desaturate up to 600 °C. Above that the colour begins to whiten to a very light grey observed on the 800 °C sample.

This difference in colour is due possible reason, the presence of some remaining amorphous phases, or the presence of oxygen defects. These defects can be easily produced methods such as sputtering, electron bombardment, or in our case, thermal annealing. These defects are recognised to exist as oxygen vacancy sites located on the bridging oxygen rows of TiO$_2$ (110) surface. Upon annealing, on a macroscopic scale, this can be seen as the creation of colour centres. These defects have a significant effect on the electronic properties, and thus also the photocatalytic properties of the material [62, 66].
4.3.2 Oxide Layer Durability

Two in five samples produced via the single anodization method did not survive the heat treatment procedures and flaked off the substrate. This indicated a lack in strength in the nanotube/substrate interface. But approaching the end of the research year, the nanotube layers on the latest samples produced past anodization were mechanically more durable than previously produced samples. They were highly resistant to mechanical removal (mechanical bending of substrate and/or ultrasonic cleaning) from the titanium metal substrate. This proved to be a significant inconvenience due to the fact that samples were required to be anodised twice.

It is hypothesised that this increase in durability due to the influence of etching solution concentration during the substrate preparation. The available quantity of etching acid was approaching the last 10-20 mL. It is possible for the etchant to be more concentrated at the bottom of the container. This is confirmed as the duration of etching remained the same; the discolouration from etching became darker than previous samples prepared earlier. The more concentrated acid would have produced a stronger etch on the substrate surface. This would have produced a rougher surface on which the nanotubes would grow, producing a stronger interfacial layer between the nanotubes and the metallic substrate.
Chapter 5. General Conclusions

The purpose of this research thesis was originally to produce copper grafted TiO$_2$ nanotube arrays on titanium substrates via electrochemical anodization and identify an optimum phase composition for photocatalytic decomposition of organic compounds under the visible light spectra. Characterisation was performed on samples heat treated at various temperatures and the influence of copper grafting concentration on the morphology and photocatalytic ability of the modified NTA was studied. Although intended, due to a lack of time, photocatalytic tests were not performed to compare between grafted and non-grafted samples with different phase compositions.

A number of conclusions have been produced from this research:

- XRD analysis indicates that with TiO$_2$ nanotubes produced with electrochemical anodization using ethylene glycol + 0.25 wt. % NH$_4$F + 2 vol. % distilled water electrolyte at 40 V, the amorphous phase begins to crystallise into anatase at under 300 °C heat treatment, and anatase begins to transition to rutile at around 600-700 °C.
- SEM and TEM characterisation show that the as-anodised nanotubes are amorphous and have smooth tube walls. After heat treatment, the crystallisation of the TiO$_2$ transforms the smooth walls into that of a rougher one, where particles of crystals can be individually discerned within the walls. When the heat treatment temperatures reached to the point that rutile begins to appear, SEM images indicate that the nanotube structure begins to degrade as crystals grains agglomerate into large particles. Complete loss in nanotube morphology was observed at 800 °C. This transforms the once highly ordered nanotube structure into that of a random porous one.
- Samples grafted with copper showed greater photocatalytic degradation of RhB dye solution under visible light than that of non-grafted samples. This confirms that the copper grafting have successfully allowed the TiO$_2$ nanotubes arrays to perform photocatalysis under the visible light spectra. However, results showed that above a grafting concentration of 0.2 ppm CuCl$_2$·H$_2$O, the higher the copper grafting content, the less effective at photocatalysis the sample becomes.
5.5. Recommended Future Work

- TEM characterisation of TiO$_2$ NT samples with copper grafted at various concentrations in order to identify in what morphology the copper is grafted onto the NT.
- Characterisation using X-ray absorption fine structure (XAFS) techniques to confirm whether the atomic structure of the grafted copper species is the same as previous studies with grafting on nanoparticles. This would include X-ray absorption near-edge structure (XANES) and extended X-ray fine structure (EXAFS).
- More photocatalytic tests on samples grafted at concentrations between 0 and 0.2 ppm to find out whether is a grafting concentration which is more efficient than the 0.2 ppm tested.
- Photocatalytic tests to compare the photocatalytic ability of TiO$_2$ nanotubes across heat treatment temperatures (crystal phase compositions) and copper grafting solution concentrations.
- Photocatalytic tests to observe whether the photocatalyst ability decreases after repeated uses of the photocatalyst sample.
- Confirming if there is an influence of etching on nanotube layer morphology and adhesion to the titanium substrate. This would include comparisons between nanotube arrays produces from substrate prepared with different types of acids and concentrations.
Bibliography


22. MSDS: Hydrofluoric acid. 2011, SIGMA-ALDRICH.


Appendices

Appendix A: Chemicals & Materials Used

<table>
<thead>
<tr>
<th>Chemical/Materials</th>
<th>Purity (%)/Grade</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium Sheet</td>
<td>99.6</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Ethanol</td>
<td>99.4, LG</td>
<td>ECP-Laboratory</td>
</tr>
<tr>
<td>Acetone</td>
<td>≥99.5, LG</td>
<td>ECP-Laboratory</td>
</tr>
<tr>
<td>Nitric Acid</td>
<td>65</td>
<td>Merck Millipore</td>
</tr>
<tr>
<td>Hydrofluoric Acid</td>
<td>38-40</td>
<td>Merck Millipore</td>
</tr>
<tr>
<td>Mono Ethylene Glycol</td>
<td>&gt;95.0</td>
<td>ECP-Laboratory</td>
</tr>
<tr>
<td>Ammonium Fluoride</td>
<td>99.3</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Copper Chloride Dihydrate</td>
<td>&gt;99.0</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Rhodaime B Dye</td>
<td>&gt;95</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>

Table 4: List of Chemical & Materials Used
Appendices

Appendix B: Calculations

Surface area Calculations

Assumptions:

- Identical nanotube dimensions.
- Nanotube pores are circular.
- Nanotube bases are semi-spherical.
- Uniform nanotube distribution (i.e. Figure 22).
- Non-anodised areas are also grafted.
- Non-anodised areas of samples are perfectly flat.
- Ignoring sample edge surface areas.

Using SEM images for dimensions
Tube wall thickness: 45 nm
Tube pore radius: 32.5 nm
Tube length: 8 µm

![Diagram of nanotube array](image)

Figure 35: Unit cell and tube dimensions of nanotube array (not to scale).

Area of inner tube:

\[
\text{Tube wall} = 8000 \times (2\pi \times 32.5) = 1634000 \text{ nm}^2
\]

\[
\text{Tube base} = 0.5 \times 4\pi \times 32.5^2 = 6637 \text{ nm}^2
\]

\[
\therefore \text{Total inner tube surface area (SA) = 1634000 + 6637}
\]
Appendices

= 1640265 nm² ≈ 1.640 × 10⁻¹² m² per tube

Area of top surface wall:

Surface square – Tube circle = (65 + 45)² – π × 32.5²

= 8782 nm² ≈ 8.782 × 10⁻¹⁵ m² per unit cell

∴ Total SA per unit cell = Area of inner tube + Area of top surface wall

= 8.782 × 10⁻¹⁵ + 1.640 × 10⁻¹² ≈ 1.650 × 10⁻¹² m² per unit cell.

Number of unit cells in nanotube array:

Assuming an anodised area of 20 mm x 20 mm

Number of cells in one row = 20 × 10⁻³ / 110 × 10⁻⁹ = 181800 cells per row

∴ Total number of cells in nanotube array = 181800² = 3.306 × 10¹⁰ cells

∴ Total SA in nanotube array = 1.650 × 10⁻¹² × 3.306 × 10¹⁰ = 0.05451 m²

<table>
<thead>
<tr>
<th>Total SA in prepared 20 x 35 mm sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>= Total SA in nanotube array + Non-anodised area</td>
</tr>
<tr>
<td>= 0.05451 + (0.035 × 0.02) + (0.015 × 0.02) = 0.05551 m²</td>
</tr>
</tbody>
</table>
Appendices

Appendix C: XRD Diffractograms

700 °C Samples:

**700 °C Sample 1**

![XRD Diffractogram](image1)

**700 °C Sample 2**

![XRD Diffractogram](image2)

**700 °C Sample 3**

![XRD Diffractogram](image3)

Figure 36: XRD Diffractograms of TiO₂ NTA annealed at 700 °C.
Appendices

725 °C Samples:

Figure 37: XRD Diffractograms of TiO$_2$ NTA annealed at 725 °C.
Appendices

750 °C Samples:

750 °C Sample 1

750 °C Sample 2

750 °C Sample 3

Figure 38: XRD Diffractograms of TiO$_2$ NTA annealed at 750 °C.
Appendices

775 °C Samples:

Figure 39: XRD Diffractograms of TiO$_2$ NTA annealed at 775 °C.
Appendices

800 °C Samples:

Figure 40: XRD Diffractograms of TiO$_2$ NTA annealed at 800 °C.