FABRICATION OF TITANIUM DIOXIDE NANORODS ARRAYS FOR ULTRAVIOLET SENSOR APPLICATION

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This thesis was dedicated to my parents; Mohammad Mokhtar bin Mohammad, Rabiah binti Ibrahim, and my husband; Mohamad Najib bin Kammaludin
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LIST OF PUBLICATIONS


ABSTRACT

Pure rutile titanium dioxide nanorods thin film for ultraviolet sensor application was fabricated on top of bare FTO substrates using hydrothermal method. TiO$_2$ thin film was developed by optimizing amount of titanium butoxide (TBOT) as a precursor, amount of hydrochloric acid, and hydrothermal reaction time. Basically, there were four properties studied; surface morphology, structural, electrical, and optical properties. Surface morphology of the sample was analyzed by using FESEM. XRD and Raman spectroscopy were used to analyze the structural properties of the thin film. Electrical and optical properties were studied using 2-point probe and UV-vis-NIR spectrophotometer. The first optimization step was to vary the amount of precursor used. Surface morphology of the sample shows that the nanorods growth starts at 3.5 mL of TBOT, and as the precursors increased, diameter and the thickness of the nanorods also increased. Both XRD and Raman show the peaks of FTO and rutile TiO$_2$. Next, the hydrothermal reaction time was varied. Nanorods diameter and thickness increase with increasing reaction time. XRD and Raman depict FTO and rutile TiO$_2$ peaks produced. Lastly, the effect of using different amount of hydrochloric acid used was studied. The diameter and thickness of the nanorods decrease as the HCl used increased. Thin film produced was rutile TiO$_2$ confirmed by both XRD and Raman spectra. The optimized amount of precursor, reaction time, and amount of HCl were obtained at 4.0 mL of TBOT, 16 hour, and 130 mL of HCl, respectively. Study on the optical properties of the TiO$_2$ thin film shows absorption on ultraviolet wavelength and not on visible wavelength. Electrical analysis shows that the electron flows through TiO$_2$/FTO interface with conductivity of 0.167 S/m. The thin film was then tested as UV sensor using photoelectrochemical (PEC) method. The rise and decay time recorded was less than than 1 second, indicating a rapid photoresponse characteristics and the photocurrent gives acceptable differences with change in the supplied bias voltage.
ABSTRAK

### CONTENT

<table>
<thead>
<tr>
<th>TITLE</th>
<th>i</th>
</tr>
</thead>
<tbody>
<tr>
<td>DECLARATION</td>
<td>ii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF PUBLICATIONS</td>
<td>v</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>vi</td>
</tr>
<tr>
<td>ABSTRAK</td>
<td>viii</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xiii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xvii</td>
</tr>
<tr>
<td>LIST OF SYMBOL AND ABBREVIATIONS</td>
<td>xix</td>
</tr>
<tr>
<td>LIST OF APPENDICES</td>
<td>xx</td>
</tr>
</tbody>
</table>

**CHAPTER 1**  
**INTRODUCTION**  
1.1  Research background  
1.2  The properties of titanium dioxide  
1.3  Problem statement  
1.4  Research objective  
1.5  Scope of the study

**CHAPTER 2**  
**LITERATURE REVIEW**  
2.1  Introduction  
2.2  Titanium dioxide  
2.2.1  Titanium dioxide nanorods array  

CHAPTER 3 METHODOLOGY

3.1 Introduction

3.2 Substrate cleaning by sonicating method

3.3 Preparation of titanium dioxide solution for hydrothermal reaction

3.4 Fabrication of the titanium dioxide nanorods array via hydrothermal method

3.4.1 Fabrication of TiO\textsubscript{2} nanorods array using different amount of precursor

3.4.2 Fabrication of TiO\textsubscript{2} nanorods array using various reaction times

3.4.3 Fabrication of TiO\textsubscript{2} nanorods array using various amount of hydrochloric acid

3.4.4 Preparation of fabricated titanium dioxide nanorods array for two-point probe current-voltage (I-V) measurement

3.5 Nanostructured TiO\textsubscript{2} thin film characterization method

3.5.1 Field-emission scanning electron microscopy
3.5.2 X-Ray diffraction 32
3.5.3 Micro-Raman spectroscopy 34
3.5.4 Ultraviolet-Visible-Near-Infrared (UV-vis-NIR) spectrophotometry 35
3.5.5 Two-point probe I-V measurement 37
3.5.6 Ultraviolet photocurrent measurement system 39

CHAPTER 4 RESULTS AND DISCUSSION 41
4.1 Introduction 41
4.2 Study on the effect of using different amount of precursor solution on titanium dioxide nanorods array 42
4.3 Study on the effect of using different hydrothermal reaction time on titanium dioxide nanorods array 49
4.4 Study the effect of using different amount of hydrochloric acid on titanium dioxide nanorods array 56
4.5 Titanium dioxide nanorods ultraviolet sensor 63
   4.5.1 Electrical properties of the optimized sample 63
   4.5.2 Optical properties of the optimized sample 65
   4.5.1 Photocurrent properties of the optimized sample 66

CHAPTER 5 CONCLUSION 72
5.1 Introduction 72
5.2 Conclusion 73
5.3 Future works 73
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>REFERENCES</td>
<td>75</td>
</tr>
<tr>
<td>APPENDICES</td>
<td>84</td>
</tr>
<tr>
<td>VITAE</td>
<td>86</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1</td>
<td>Electromagnetic spectrum showing the wavelength of three types of ultraviolet that is UVA, UVB, and UVC</td>
<td>2</td>
</tr>
<tr>
<td>Figure 1.2</td>
<td>The primitive cell unit for rutile TiO₂</td>
<td>3</td>
</tr>
<tr>
<td>Figure 1.3</td>
<td>Schematic illustration of the formation mechanisms of the anatase and rutile crystal phase</td>
<td>4</td>
</tr>
<tr>
<td>Figure 2.1</td>
<td>TiO₂ nanorods fabricated by (a) sol electrophoretic and (b) sol-gel electrospinning methods</td>
<td>10</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>The mechanism of photoconduction in the TiO₂-based UV photoconductive sensor under both dark and UV illumination</td>
<td>22</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>Summarized of nanostructured TiO₂ thin film preparation and characterization</td>
<td>24</td>
</tr>
<tr>
<td>Figure 3.2</td>
<td>Summarized of cleaning substrate procedure</td>
<td>24</td>
</tr>
<tr>
<td>Figure 3.3</td>
<td>Autoclave used for hydrothermal process</td>
<td>26</td>
</tr>
<tr>
<td>Figure 3.4</td>
<td>FTO substrate before and after hydrothermal reaction</td>
<td>26</td>
</tr>
<tr>
<td>Figure 3.5</td>
<td>Summarized of preparation of TiO₂ solutions</td>
<td>27</td>
</tr>
<tr>
<td>Figure 3.6</td>
<td>The mask used for sputter-coater gold deposition</td>
<td>30</td>
</tr>
<tr>
<td>Figure 3.7</td>
<td>The auto-fine coater used to deposit gold on the sample</td>
<td>30</td>
</tr>
<tr>
<td>Figure 3.8</td>
<td>The FESEM equipment (JEOL-JSM 7600F) used to analyse the morphological and the cross-sectional images of the sample</td>
<td>32</td>
</tr>
<tr>
<td>Figure 3.9</td>
<td>Illustration of FESEM sample stage</td>
<td>33</td>
</tr>
<tr>
<td>Figure 3.10</td>
<td>FESEM’s (a) specimen stage control panel and (b) operation panel used to controlling screen sample images</td>
<td>34</td>
</tr>
</tbody>
</table>
Figure 3.11: XRD instrument (PANalytical X-Pert³ Powder) used to characterise the crystallinity of the samples
Figure 3.12: The Micro-Raman spectroscopy used to characterise the structural properties of the TiO₂ nanorods array
Figure 3.13: Illustration of typical Raman spectra system
Figure 3.14: The UV-vis-NIR spectrophotometers (Shimadzu UV-1800 240V) used to study the optical properties of the prepared nanorods arrays
Figure 3.15: Illustration of UV-Vis-NIR system
Figure 3.16: Two-point probe connected to the source meter used to identify the I-V characteristics of the sample
Figure 3.17: Close-up of the sample connected to the two-point probe
Figure 3.18: Electrochemical measuring unit used as a source of bias voltage
Figure 3.19: Photo-electrochemical instrument setup for measuring photocurrent
Figure 4.1: FESEM image of the commercial FTO as a reference
Figure 4.2: Surface morphology images of TiO₂ nanorods array fabricated using different amounts of precursor from (a) 0.5, (b) 2.0, (c) 3.5 (d) 4.0, and (e) 5.0 mL of TBOT
Figure 4.3: Cross-sectional images of TiO₂ nanorods array fabricated using different amounts of precursor from (a) 0.5, (b) 2.0, (c) 3.5 (d) 4.0, and (e) 5.0 mL of TBOT
Figure 4.4: Schematic diagram of TiO₂ nanorods in different amounts of precursor TBOT
Figure 4.5: XRD patterns of TiO₂ nanorods array fabricated using different amounts of precursor from (a) 0.5, (b) 2.0, (c) 3.5 (d) 4.0, and (e) 5.0 mL of TBOT
Figure 4.6: Raman spectra of TiO₂ nanorods array fabricated using different amounts of precursor from (a) 0.5, (b) 2.0, (c) 3.5 (d) 4.0, and (e) 5.0 mL of TBOT
Figure 4.7: Zoomed Raman spectra for TiO₂ nanorods array fabricated using (a) 0.5 and (b) 2.0 mL of TBOT
Figure 4.8: Surface morphology of TiO$_2$ nanorods array fabricated with different hydrothermal reaction times from (a) 4, (b) 7, (c) 16, and (d) 24 hours, cross-sectional images of (e) 4, (f) 7, (g) 16 and (h) 24 hours hydrothermal reaction time.

Figure 4.9: Growth mechanism of TiO$_2$ nanorods fabricated using different reaction time.

Figure 4.10: XRD patterns of TiO$_2$ nanorods array fabricated with different hydrothermal reaction time from (a) 4, (b) 7, (c) 16, and (d) 24 hour.

Figure 4.11: Raman spectra of TiO$_2$ nanorods array fabricated with different hydrothermal reaction times from (a) 4, (b) 7, (c) 16, and (d) 24 hour.

Figure 4.12: Zoomed Raman spectra for TiO$_2$ nanorods array fabricated with 4 hours reaction times.

Figure 4.13: Surface morphology of TiO$_2$ nanorods array fabricated with (a) 100, (b) 110, (c) 120, (d) 130, and (e) 140 mL of HCl.

Figure 4.14: Cross-sectional area of TiO$_2$ nanorods array fabricated with (a) 100, (b) 110, (c) 120, (d) 130, and (e) 140 mL of HCl.

Figure 4.15: Sketch diagram of TiO$_2$ nanorods in different amounts of hydrochloric acid.

Figure 4.16: XRD patterns of TiO$_2$ nanorods array fabricated with (a) 100, (b) 110, (c) 120, (d) 130, and (e) 140 mL of HCl.

Figure 4.17: Raman spectroscopy of TiO$_2$ nanorods array fabricated using (a) 100, (b) 110, (c) 120, (d) 130, (e) 140, and (f) 150 mL of HCl.

Figure 4.18: Current-Voltage (I-V) plots on TiO$_2$ surface and TiO$_2$/FTO interface of the optimized sample.

Figure 4.19: The (a) transmittance and (b) absorbance spectra of the optimized sample.

Figure 4.20: Indirect bandgap energy from Tauc’s plot.

Figure 4.21: Photocurrent of the optimized sample with different bias voltage.

Figure 4.22: Enlarged (a) rising and (b) decaying edges of the photocurrent.
Figure 4.23: Schematic energy band diagram and working principle of the UV photosensor
LIST OF TABLES

Table 2.1: Comparison of the method used to grow TiO$_2$ nanorods
10

Table 2.2: Evolution of hydrothermal technology with time
12

Table 2.3: Comparison of hydrothermal technique used to fabricate TiO$_2$ nanorods array
16

Table 3.1: Preparation of TiO$_2$ solution for hydrothermal reaction
24

Table 3.2: Preparation of TiO$_2$ solution for hydrothermal reaction with different amount of TBOT precursor
27

Table 3.3: Preparation of TiO$_2$ solution for hydrothermal reaction with different reaction time
27

Table 3.4: Preparation of TiO$_2$ solution for hydrothermal reaction with different amount of hydrochloric acid
28

Table 4.1: Summarised parameters used for optimization process
42

Table 4.2: Observed FESEM analysis with comparison to previous research
44

Table 4.3: Value of FWHM for TiO$_2$ nanorods array fabricated using different amounts of precursor
47

Table 4.4: Observed Raman shift with comparison to previous result
49

Table 4.5: Summarised parameters used for optimization process
50

Table 4.6: Observed FESEM with comparison to previous research
52
| Table 4.7 | Value of FWHM for TiO$_2$ nanorods array fabricated using different amounts of precursor | 54 |
| Table 4.8: | Observed Raman shift with comparison to previous result | 56 |
| Table 4.9: | Summarised parameters used for optimization process | 57 |
| Table 4.10: | Observed FESEM with comparison to previous research | 60 |
| Table 4.11: | Value of FWHM for TiO$_2$ nanorods array fabricated using different amounts of precursor | 62 |
| Table 4.12 | Observed Raman shift with comparison to previous result | 63 |
| Table 4.13 | The conductivity, resistivity, and sheet resistance value for different surfaces | 64 |
| Table 4.14 | Photocurrent value, as well as the rise rime and decay time of the photocurrent | 70 |
# LIST OF SYMBOL AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Cross sectional area</td>
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<tr>
<td>Au</td>
<td>Gold</td>
</tr>
<tr>
<td>CBD</td>
<td>Chemical bath deposition</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>d</td>
<td>Diameter</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized water</td>
</tr>
<tr>
<td>DSSC</td>
<td>Dye-sensitized solar cell</td>
</tr>
<tr>
<td>EMU</td>
<td>Electrochemical measuring unit</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>Field-emission scanning electron microscope</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine-doped tin oxide</td>
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<tr>
<td>GaN</td>
<td>Gallium nitride</td>
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<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>L</td>
<td>Length</td>
</tr>
<tr>
<td>O₂</td>
<td>Oxygen</td>
</tr>
<tr>
<td>R</td>
<td>Resistance</td>
</tr>
<tr>
<td>Rₛ</td>
<td>Sheet resistance</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>SiC</td>
<td>Silicon carbide</td>
</tr>
<tr>
<td>t</td>
<td>Thickness</td>
</tr>
<tr>
<td>TBOT</td>
<td>Titanium butoxide</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Titanium dioxide</td>
</tr>
<tr>
<td>TTIP</td>
<td>Titanium isopropoxide</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>V</td>
<td>Voltage</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zinc oxide</td>
</tr>
<tr>
<td>ρ</td>
<td>Resistivity</td>
</tr>
</tbody>
</table>
# LIST OF APPENDICES

<table>
<thead>
<tr>
<th>APPENDIX</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Gantt Chart</td>
<td>84</td>
</tr>
<tr>
<td>B</td>
<td>UV Lamp Datasheet</td>
<td>85</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Research background

TiO$_2$ has become known as a potential material to use in UV sensor applications. It can strongly absorb UV light because it has an indirect [1] and wide band-gap energy. Conductivity of TiO$_2$ rise when UV light is illuminated, making the electrons from valence band excited to the conduction band. A signal produced, due to the excitation that given increase in conductivity, that is used for UV light detection. There are several TiO$_2$ structures that can be produced such as microspheres, nanoflowers, nanotrees, and nanobelts [2] depending on the technique used. Example of the techniques include chemical bath deposition (CBD), hydrothermal method, sol-gel method, and RF sputtering. However, solution-based techniques are favored in producing high-quality TiO$_2$ as it is consuming low cost and therefore allowing the fabrication of UV sensors at minimal price. Moreover, by the addition of a stabilizer or surfactant, the growth of TiO$_2$ structure can be easily controlled. The solution-based can also promotes the growth of TiO$_2$ at low temperature with large-scale, simple processing methods [3]. Highly crystalline rutile TiO$_2$ has been intensively investigated due to its advantages such as easily controllable diameter and thickness [4], and higher electron mobility [5,6]. It also has advantages such as higher chemical stability, cheaper production cost [7] and thermodynamically stable [8].
Photo-detection in the ultraviolet (UV) area has attracted attention due to its numerous applications in industry, instrument, and our daily life. Ultraviolet light is defined as a portion of the electromagnetic spectrum that includes visible light, radio waves, X-rays and microwave, with wavelength ranging from 100 to 400 nm that can be further subdivided to: Vacuum UV (100-200 nm), UVC (200-280 nm), UVB (280-315 nm), and UVA (315-400 nm) [9]. It has wavelength that is shorter than visible light, but longer than X-rays as shown in Figure 1.1. Ultraviolet light is used in various applications, including cancer therapy, chemical synthesis, jaundice treatment for new-born babies [10], and drug detection. However, overly exposed to overdose radiations can gives harm to human health. For example, overexposure to UV radiation can causes skin burning and possible skin cancer [11]. Nowadays, research on higher performance UV light sensor are continuously being developed as many situations requiring the monitoring of UV irradiation. Ultraviolet sensor is a device that measures UV light from the sun. it is used in wide range of applications including fire detection, industrial manufacturing, biochemical research, and environmental health monitoring. The traditional electrical UV sensor, which consist of a sensitive photodiode that generates a photocurrent when exposed to UV light, is well established. The current is then converted into a voltage signal and amplified for easier detection. The sensing element of the traditional UV sensor is the photodiode, which is commonly based on silicon.

![Electromagnetic spectrum showing the wavelength of three types of ultraviolet that is UVA, UVB, and UVC](image)

Figure 1.1: Electromagnetic spectrum showing the wavelength of three types of ultraviolet that is UVA, UVB, and UVC
1.2 The properties of titanium dioxide

Titanium dioxide (TiO$_2$) is a compound that gained much attention for its uses in various applications including photocatalysis [12–14], photovoltaics [15–17], and photosensors [18]. Titanium dioxide, also known as titanium oxide or titania, is found in three natural crystalline phases that is anatase, rutile and brookite, which is thermally and chemically resistant [19], with melting point of 1825°C showing its strong chemical bonding. However, only the first two, which are anatase and rutile, play the role in industrial application because of the rareness and difficult preparation for brookite [20]. TiO$_2$ has been reported to be an intrinsically, n-type semiconductor due to its oxygen deficiency [21,22]. However, under certain growth condition, it can be found as p-type semi-conductivity behavior [23].

Structure of rutile and anatase are both tetragonal with different space groups. Rutile has space group of $P4_2/mnm$ with two TiO$_2$ formula units in one cell, while anatase belongs to group $I4/amd$ with four TiO$_2$ formula units in one cell [24]. The primitive cell unit for rutile is illustrated in Figure 1.2, where the large and small spheres represent the Ti and O atoms respectively. For all three TiO$_2$ polymorphs, the centre TiO$_6$ octahedra form their basic structural unit. The difference in these polymorphic structural is the number of edge-shared octahedra, which is two, three and four for rutile, brookite, and anatase, respectively [25]. Figure 1.3 shows the schematic illustration of the formation mechanisms of the anatase and rutile crystal phase [26].

![Figure 1.2: The primitive cell unit for rutile TiO$_2$][19]
Titanium dioxide is said to be an essential material because of its functional properties. It can absorb UV light and is transparent to visible light spectrum under certain conditions [27]. Additionally, TiO$_2$ is substantially less expensive than other materials and their reserve is abundant [28]. Its properties can also be altered chemically to enhance its properties, for example, through doping process, which can provide free carriers to increase its efficiency as a photo-catalyst depending on the type of dopants used as different dopant may not have the same effect on trapping electrons and/or hole [29]. It is also non-toxic and chemically inert [30]. The ability of TiO$_2$ to transmit light spectrum allows for their use in solar cell technology as transparent electrodes [31–33]. In nanomaterials, specific surface area and surface-to-volume ratio would increase as the size of nanomaterials decreases [34]. For TiO$_2$-based device, the high surface area from small particle size would be advantages. Thus, the performance of TiO$_2$-based devices was primarily impacted by the sizes of TiO$_2$ materials itself, particularly at nanometer scale.

Figure 1.3: Schematic illustration of the formation mechanisms of the anatase and rutile crystal phase [26]
1.3 Problem statement

Conventionally, narrow bandgap semiconductors such as silicon is widely used for UV photoconductive sensor applications [35]. However, these Si-based devices also reacted to visible light. Hence, to block the intervention of the visible light, a filters are required to be installed [36]. The necessity of this filter has indirectly increased the production cost. Enquiry on materials with wide band gap such as silicon carbide (SiC), gallium nitride (GaN), and TiO$_2$ have been made by researchers in order to tackle this problem. The use of filters can be entirely eliminated as these materials have a wide bandgap. Furthermore, devices with these materials give an effective detection of UV light. Additionally, in producing high-quality materials using GaN and SiC, high cost of the equipment and difficult fabrication process is required making it not cost effective. For instance, producing high-quality GaN is possible only if the fabrication process temperature is above 500°C [37].

Additionally, TiO$_2$ preparation using hydrothermal method is rarely reported for UV sensor application. Hydrothermal method has advantages to easily control the growth of the nanorods. Electrical properties such as low sheet resistance and high conductivity of TiO$_2$ nanorods thin film will enhance the TiO$_2$ thin film properties and also improve the efficiency of the sensing devices.

1.4 Research objectives

Because of their distinct properties, titanium dioxide nanorods are now one of the promising nanostructured materials to be applied in UV sensor application. Optimization of fabrication process is essential in order to achieve high performance value of UV-sensing device. For that reason, this work has been carried out with three main objectives that are:

I. To fabricate and optimize TiO$_2$ nanorods array via hydrothermal method on top of FTO as a substrate

II. To analyze the morphological, structural, optical and electrical properties of aligned TiO$_2$ nanorods array.

III. To investigate the photocurrent performance, rise time and decay time of aligned TiO$_2$ nanorods array as ultraviolet sensor.
1.5 Scope of the study

To achieve the objectives, the following scopes were investigated:

i. Several parameters were optimised to get the desired nanorod TiO$_2$ which are the amount of precursor, hydrothermal reaction time, and amount of the hydrochloric acid.

ii. The fabricated TiO$_2$ thin film were then analyzed using FESEM, XRD, Raman, 2-point probe, and UV-vis-NIR for its morphological, structural, electrical, and optical properties.

iii. The photocurrent performance, rise and decay time of the optimized nanorod was investigated using photoelectrochemical method for its sensing capabilities.
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, the history and past research work of hydrothermal and UV sensors were discussed. There are three subtopics that will be discussed including titanium dioxide, hydrothermal, and ultraviolet sensor.

2.2 Titanium dioxide

Titanium dioxide (TiO$_2$) exists in three known crystalline that is anatase, rutile, and brookite with polymorphs tetragonal for anatase and rutile, and orthorhombic for brookite [38]. TiO$_2$ have received significant notice these past few decades after the discoveries of photoelectrochemical cell (PEC) and dye sensitized solar cell. The wide range of application, chemical and biological inertness, low cost, eligibility for many experimental techniques and possibility of modifying its properties are the main forces for pursuing research on TiO$_2$. It is also used in heterogeneous catalysis, as a photocatalyst, a white pigment in all kinds of paints, in paper and cosmetics, antireflection coatings in silicon solar cells and thin films optical devices, as well as an anti-corrosion protective coating [39–42].

Major drawbacks of TiO$_2$ nanoparticles related to its recombination process during cell performance [43]. To overcome the drawback, TiO$_2$ nanostructures such as nanorods, nanoflowers, and nanowires, were introduced as its exhibit excellent
electron transport due to its well-defined crystalline structure and unique optical properties, which minimizes the recombination process and have been considered as a substitute in the solar cells and electronic devices.

2.2.1 Titanium dioxide nanorods array

The development of TiO$_2$ nanostructures in various applications has been progressively conducted [44–47]. Excellent carrier transport properties and large surface area availability makes an array of one-dimensional TiO$_2$ nanostructures such as nanowires, nanorods, and nanotubes appear to be as potential materials for device fabrication. Among these structures, nanorod or nanotube has been reported to be better in electron transport and recombination behaviour in liquid based analysis [48].

There have been numerous reports on the fabrication of TiO$_2$ nanorods array prepared by a variety of techniques. One of the techniques used is ‘dissolve and grow’ hydrothermal technique, where a rectangular bunched TiO$_2$ nanorods array was grown on carbon fibres from titanium foil by Wenxi Guo et al. [49]. After a corrosion process in a strong acid solution, every single nanorods is etched into a number of small nanowire. The diameter and length of the nanorods were found to be \( \sim 150 \) nm and \( \sim 3 \) \( \mu \)m, respectively.

The work by Zhang H et al has also been referred [50]. They grew a perpendicularly aligned and highly ordered nanorods/nanotubes (NR/NT) adjacent film by directly anodizing a modified titanium foil. The titanium foil substrate was modified with a layer of crystalline TiO$_2$ film via hydrothermal process in 0.05M \((\text{NH}_4)_2\text{S}_2\text{O}_8\). This resulted to the top layer consisting a highly ordered nanorod connected to array of nanotube at the bottom layer. The thickness of the top nanorod layer was \( \sim 90 \) nm with average nanorod diameter of 22 nm after 20 min of anodization. The thickness of the bottom nanotube layer was found to be 250 nm after 20 min of anodization, with an average outer and inner tubular diameter of 120 and 80 nm, respectively.

Bonil Koo et al. also fabricated TiO$_2$ nanorods and this time they used non-hydrolytic sol-gel reaction by continuously delivered two titanium precursor using two separate syringe pumps [51]. The length of resulting TiO$_2$ nanorods increased as
the injection decreased. First reaction was performed with an injection rate of 30 mL/h and the nanorods produced are 6 nm in thickness and 50 nm in length. When the injection rate was decreased to 2.5 mL/h, the nanorods produced are in the dimension of 25 nm to 9 nm in width and 200 to 100 nm in length. Nanorods with dimensions of 25 nm x 450 nm were synthesized when the injection rate was further decreased to 1.25 mL/h. In this experiment, the simultaneous phase transformation and length elongations of the TiO₂ nanorods were achieved.

Another method to grow TiO₂ nanorods was by using sol electrophoretic deposition that is done by Limmer et al [52]. They produced nanorods with a diameter size ranging from 45 – 200 nm in diameter and 10 – 60 μm in length after annealed it to 500 °C for 1 hour in a template membrane of polycarbonate and alumina with aluminium (Al) and Indium Tin Oxide (ITO) as a glass template, respectively. Their study shows that the growth occurs through the motion of charged nanoparticles from the bottom of the template pores, filling them up as time proceeds.

K. Fujihara et al fabricated nanorods by mechanically grinding the TiO₂ nanofibres in which the nanofibres was fabricated by combining sol-gel and electrospinning technique [53]. The average diameter of the composite nanofibers was 290 ± 90 nm which was decreased to 150±60 nm after sintering process to nanorod. Figure 2.1 shows FESEM image of TiO₂ nanorods fabricated by sol-electrophoretic and sol-gel electrospinning methods. A comparison of the method used to grow TiO₂ nanorods is summarised in Table 2.1.

![Figure 2.1: TiO₂ nanorods fabricated by (a) sol electrophoretic [52] and (b) sol-gel electrospinning methods [53]](image_url)
### Table 2.1: Comparison of the method used to grow TiO$_2$ nanorods

<table>
<thead>
<tr>
<th>Fabrication Method</th>
<th>Special Features</th>
<th>Structure (diameter (d)/length (l)/thickness (t) if notified)</th>
<th>Reference</th>
</tr>
</thead>
</table>
| Hydrothermal method      | Dissolve and grow  
  i. Hydrothermal of NR on carbon fibre (CF) using Ti foil  
  ii. CF ultrasonically cleaned  
  iii. Hydrothermal again for etching process  
  iv. immersed in TiCl$_4$ sol  
  v. Annealed to increase crystallinity | d: 150 nm /  
  l: 3 μm | [49] |
| Anodizing method         | Modified Ti foil using hydrothermal methods  
  i. To obtain crystalline TiO$_2$ film  
  ii. NR growth not highly ordered | d: 22 nm /  
  l: 90 nm | [50] |
| Non-hydrolytic sol-gel reaction | Length of NR can be controlled by controlling injection rate  
  i. 30 mL/h  
  ii. 2.5 mL/h  
  iii. 1.25 mL/h | i. 30 mL/h (d: 6 nm, l: 50 nm)  
  ii. 2.5 mL/h (d: 9 nm, l: 100 nm)  
  iii. 1.25 mL/h (d: 25 nm, l: 450 nm) | [51] |
| Sol electrophoretic deposition | Combination of sol-gel and electrophoretic deposition | d: 45 – 200 nm  
  l: 10 – 60 μm | [52] |
| Sol-gel and electrospinning | Mechanical grinding of TiO$_2$ nanofibres to nanorod | d: 150±60 nm | [53] |

### 2.3 Hydrothermal

There are many methods to produce nanostructured material or particles such as DC sputtering, pulse-laser deposition (PLD), and spray pyrolysis method. However, in this thesis, hydrothermal method will be used. Hydrothermal method is a non-
traditional way to obtain nanocrystalline inorganic material. In a self-explanatory word, “hydro” means water, and “thermal” means heat. According to Laudise, hydrothermal growth means growth from aqueous solution at ambient or non-ambient solution. Rabenau defined hydrothermal synthesis as the heterogeneous reactions in aqueous media above 100°C and 1 bar. Roy declares that hydrothermal synthesis involves water as a catalyst and occasionally as a component of solid phases in the synthesis at elevated temperature (>100°C) and pressure greater that a few atmospheres. Byrappa defines hydrothermal synthesis as any heterogeneous reaction in an aqueous media carried out above room temperature at a pressure greater than 1 atm. Yoshimura proposed the following definitions: reactions occurring under the conditions of high-temperature-high-pressure (>100°C, >1 atm) in aqueous in a closed system [30].

From all researchers mentioned above, it shows that hydrothermal method is one of the best methods for material synthesis at low temperature with high pressure in a closed system. By adjusting reactions conditions, many forms of ceramic materials can be synthesized such as fibre, powder, single crystals, nanoparticles, and thin films. This method also allows regulation of rate and uniformity of the nucleation, growth and aging process, which leads to improved size and morphology control.

2.3.1 History of hydrothermal

The term hydrothermal is solely geological origin. It is first described as the action of water at elevate temperature and pressure leading to emergence of different rocks and minerals in the earth crust by Sir Roderick Murchison [54]. Table 2.2 shows the decade-wise evolution of the hydrothermal with regards to its objective and apparatus used [30].
Table 2.2: Evolution of hydrothermal technology with time

<table>
<thead>
<tr>
<th>Period</th>
<th>Focus</th>
<th>Equipment</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1850-1900</td>
<td>Mineral synthesis, imitation of natural conditions</td>
<td>Simple reactors, glass reactors, digestors</td>
<td>Lower growth rate, tiny particles, geological interest</td>
</tr>
<tr>
<td>1900-1940</td>
<td>Mineral synthesis, improvement in PT conditions, German domination</td>
<td>Morey autoclaves, flat closure</td>
<td>Lower growth rate, silicates, carbonates, Germany, Russia, France, USA, geological interest</td>
</tr>
<tr>
<td>1940-1950</td>
<td>Large size and large scale production of quartz, beginning of zeolites, clays, and micas</td>
<td>Test-tube type (cold-cone-sealed), welded closure, modified Bridgman type</td>
<td>Cold-cone-seal type autoclaves made revolution, PVT diagrams systems</td>
</tr>
<tr>
<td>1950-1960</td>
<td>Phase diagrams for natural systems</td>
<td>Morey, Turtle-Roy, welded closures, modified Bridgman</td>
<td>The dawn of modern hydrothermal research</td>
</tr>
<tr>
<td>1960-1970</td>
<td>Synthesis of technological materials, new inorganic compounds without natural analogues</td>
<td>New designs from USSR, commercialization of the autoclaves, improved sealing, larger size of the autoclaves</td>
<td>Russian School dominated, Japanese labs appeared</td>
</tr>
<tr>
<td>1970-1980</td>
<td>A variety of new materials synthesis, ceramic processing in a bigger way, advanced materials</td>
<td>New designs, improved PT conditions, Grey-Loc sealing, large autoclaves</td>
<td>Appearance of many hydrothermal labs in several countries</td>
</tr>
<tr>
<td>1980-1990</td>
<td>Decline in interest on hydrothermal research. Importance of the technique in materials science, physical chemistry of hydrothermal solutions</td>
<td>-</td>
<td>Japan organized 1st Int. Conf. Hydrothermal Reactions. Beginning of the entry of physical chemist</td>
</tr>
<tr>
<td>&gt;1990</td>
<td>Diversification of hydrothermal technique, age of solvo-thermal, physical chemistry of hydrothermal solutions.</td>
<td>Design of new reactors to suit the specific applications: batch reactors, flow reactors, and so on</td>
<td>Entry of organic chemist, environmental scientist, fall in Russian domination and beginning of the Japanese domination</td>
</tr>
</tbody>
</table>
Hydrothermal synthesis is a non-conventional method of synthesizing nanocrystalline inorganic materials. The synthesis method use solubility in water of almost all inorganic substances at elevated temperature and pressure, performed in an apparatus consisting of a steel pressure vessel called an autoclave. These autoclaves are usually thick-walled steel cylinders with a tight seal which ought to withstand high temperature and pressure for prolonged times span. Furthermore, the autoclave material must be inert with the respect to the solvent. The autoclave closure is the most important element. Many designs have been progressed for seals, which the most famous being the Bridgman seal. To prevent corrosion of the internal cavity the autoclave, preservative inserts are generally used. Insert may be made of carbon-free iron, silver, gold, platinum, glass, or Teflon. In this research, the insert used is Teflon. Hydrothermal method is widely used for the production of small particles in the ceramics industry.

2.3.2 Fabrication of TiO$_2$ nanorods array using hydrothermal method

Nanostructured TiO$_2$ was synthesized by using hydrothermal processing of titanium alkoxides, such as Titanium Isopropoxide (TTIP) and Titanium Butoxide (TBOT). It has been widely studied and investigated as a photocatalyst and in dye-sensitize solar cell (DSSC). The morphology of the nanorods can be easily adjusted with different surfactants [55] or by changing the solvent compositions [56]. The hydrothermal method is widely used due to its simple processing, fast reaction velocity, and low cost [57]. At relatively lower temperature (~150$^\circ$) a high degree of crystallinity thin film can be obtained; it also offers a uniform composition, and control over the shape and the size of particles. The hydrolysis reaction between H$_2$O and TBOT are schematically given as [58]:

\[
Ti(CdH$_9$O)$_4$ + 4H$_2$O \rightarrow Ti(OH)$_4$ + 4CdH$_9$OH
\]  

(2.1)

Ti from the hydrolysis will then be used as a starting material for nucleation of TiO$_2$ nanorods. The hydrolysis reaction of hydrothermal process can be explained as follows [49]:
$$2\text{Ti} + 6\text{HCl} \rightarrow [\text{Ti}^{3+}] + 3\text{H}_2(\text{g})$$  \hfill (2.3) \\
$$[\text{Ti}^{3+}] + \text{H}_2\text{O} \rightarrow \text{TiOH}^{2+} + \text{H}^+$$  \hfill (2.4) \\
$$\text{TiOH}^{2+} + \text{O}_2^- \rightarrow \text{Ti} (\text{IV}) + \text{O}_2^- \rightarrow \text{TiO}_2$$  \hfill (2.5)

Ti species from TBOT precursor initially starts to react with H\text{+} ions from concentrated acidic solution. It is known that Ti\text{3+} are not stable in aqueous solution, thus it undergoes hydrolysis with H\text{2O} to form TiOH\text{2+}. It is then oxidized to Ti (IV) by reaction with dissolved oxygen. The Ti (IV) complex ions are thus used as the growth unit. The by-product from the reaction does not influence the sample as the sample was first rinsed with DI water before used.

Yawen Wang et al. reported that the synthesis of pure rutile nanorods is by hydrolysis of TiCl\text{4} ethanolic solution in water at 50°C [59]. By simply changing the molar ratio of TiCl\text{4}, ethanol or DI water, the assembly of rutile nanorods can be changed to flower and urchin-like morphologies. By playing around with the amount of ethanol and TiCl\text{4} used, the resulting rods seems becoming more complex with increasing amount of the solution. They also studied the effect of H\text{+}, Cl\text{−}, and ethanol on the morphologies by replacing TiCl\text{4} with TTIP and adding some additives such as KCl, HNO\text{3}, and H\text{2SO\text{4}}. It can be concluded that the strong acidic condition from H\text{+} and Cl\text{−} was crucial for the formation of rutile TiO\text{2} and ethanol is needed for the formation of rutile TiO\text{2} in the absence of seed nanocrystal or organic surfactant additives. Nanorods produced were of 10-15 nm in diameter and 50-70 nm in length. Doubling both amount TiCl\text{4} and ethanol gives diameter of the nanorods 4-7 nm while the length increased to 80-100 nm. When only the amount of TiCl\text{4} increase, the nanorods agglomerates to well-defined spheres with 200-600 nm in sizes.

Muhammad N. Tahir et al reported on the synthesis of in situ surface-functionalized, monocrystalline rutile TiO\text{2} nanorods using a hydrothermal method [60]. The rutile TiO\text{2} nanorods were prepared from TiCl\text{4} in aqueous solution under acidic conditions in the presence of dopamine and are in this study, they use 3-hydroxytyramine. With this amine group functionality on its surface, it offers an excellent prospect for TiO\text{2} nanobiocomposites and biotracers.

Large-scale, well aligned single crystalline TiO\text{2} on pre-treated glass substrate by hydrothermal method was prepared by Yuxiang Li et al [61]. The results demonstrated that the TiO\text{2} was well-aligned and grown along [001] direction with diameter and length of 15 to 25 nm and 300 to 500 nm respectively. The pre-
treatment of the substrate is done by coating the colloidal solution prepared onto the clean glass substrate. It has been shown that the nanorods grown on coated glass substrate has better growth orientation and uniform density.

Another hydrothermal synthesis is done by Yuan et al. on boron-doped diamond film with zinc oxide (ZnO) buffer layer [57]. It is shown that the ZnO buffer layer plays an important role in increasing the density and improving the morphologies of the TiO$_2$ nanorods. The ZnO buffer layer was so thin that it was not detected on XRD and some of the ZnO nanoparticles may be removed in the hydrothermal process.

Lingqing Dong et al. fabricated rutile TiO$_2$ nanorods film on titanium substrate via a hydrothermal method [62]. They used Tetra-n-butyl titanate as the source of Ti in the presence of hydrochloric acid. The Ti substrate did not only act as a substrate but also as the source of TiO$_2$. The nanorods thin film automatically formed even in the absence of a precursor when the thickness of the TiO$_2$ reached certain level. They also studied on the influence of metal chlorides on TiO$_2$ nanorods growth where chlorides such as LiCl, NaCl, and KCl were added into the mother solution. These chlorides affect the diameter and density of the nanorods by decreasing it when LiCl is added and increasing it in the presence of KCl and NaCl.

Hong En-Wang et al. used the hydrothermal method to prepare single-crystalline TiO$_2$ nanorods [63]. The average diameter and length of nanorods prepared are 60 nm and 400 nm respectively. They stated that this method shows great versatility and can be used to grow TiO$_2$ nanorods on large diversity of substrate including Si, Si/SnO$_2$, sapphire, and fluorine-doped tin oxide (FTO).

S. Venkatachalam et al. also used hydrothermal treatment to produce TiO$_2$ nanowires, nanorods, and nanoporous film [64]. By varying the amount of hydrochloric acid used and the annealing temperature, it is reported that nanorod size increased as the volume of HCl and the temperature in the reaction solution was increased. The nanorods produced have a range of 125 to 310 nm for diameter and 480 nm to 2.6 μm for length when the temperature was increased from 120°C to 160°C. Meanwhile, the nanorod size is in the range of ~150 nm to 200 nm when the HCl increased from 15 to 23 mL and DI water decreased from 45 to 30 mL. These studies shows that, solution-based synthesis generally, and hydrothermal fabrication method specifically, gives promising results in producing TiO$_2$ nanorods array. A
Comparison of hydrothermal technique used to fabricate TiO$_2$ nanorods array is summarised in Table 2.3.

Table 2.3: Comparison of hydrothermal technique used to fabricate TiO$_2$ nanorods array

<table>
<thead>
<tr>
<th>Additional features</th>
<th>Diameter (d) and Length (l)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Changing the molar ratio of TiCl$_4$, ethanol or DI water</td>
<td>d: 10 – 15 nm</td>
<td>[59]</td>
</tr>
<tr>
<td></td>
<td>l: 50 – 70 nm</td>
<td></td>
</tr>
<tr>
<td>NR was prepared from TiCl$_4$ under acidic conditions + dopamine</td>
<td>d: 15 – 16 nm</td>
<td>[60]</td>
</tr>
<tr>
<td></td>
<td>l: 40 – 100 nm</td>
<td></td>
</tr>
<tr>
<td>Pre-treated glass substrate; coating colloidal solution</td>
<td>d: 15 – 25 nm</td>
<td>[61]</td>
</tr>
<tr>
<td></td>
<td>l: 300 – 500 nm</td>
<td></td>
</tr>
<tr>
<td>Using boron-doped diamond film with ZnO as a buffer layer</td>
<td>d: 50 – 80 nm</td>
<td>[57]</td>
</tr>
<tr>
<td></td>
<td>l: 280 nm</td>
<td></td>
</tr>
<tr>
<td>Used Ti as a substrate where it also acts as a source of TiO$_2$. Study the effect of chlorides to NR growth</td>
<td>d: 10 – 20 nm</td>
<td>[62]</td>
</tr>
<tr>
<td></td>
<td>l: 800 – 900 nm</td>
<td></td>
</tr>
<tr>
<td>Using different types of substrate: Si wafers, Si/SiO$_2$ wafer, sapphire, Si pillars, and FTO-covered glass</td>
<td>d: 60 nm</td>
<td>[63]</td>
</tr>
<tr>
<td></td>
<td>l: 400 nm</td>
<td></td>
</tr>
<tr>
<td>Varying amount of hydrochloric acid</td>
<td>d: 150 – 200 nm</td>
<td>[64]</td>
</tr>
<tr>
<td></td>
<td>l: 480 nm – 2.6 µm</td>
<td></td>
</tr>
</tbody>
</table>

2.4 Ultraviolet Sensor

Flame detections, space communications, ozone layer monitoring, and UV astronomy are among the technology that are using UV photoconductive sensor [65]. Nowadays, fabrication of UV photosensor are gaining attention due to its applications in different fields. Among the materials that are being utilised in fabricating UV sensor is silicon (Si), gallium nitride (GaN), zinc selenide (ZnSe), silicon carbide (SiC) and diamond [65–68]. Using Si materials as a UV sensor have
caused several problems. First, Si has a low bandgap, which is 1.1 eV; causing low responsivity towards ultraviolet radiation and requiring a visible light filter if applied in the device structure [69]. Si is also not suitable to be used as it has limitation in harsh environmental conditions, for example UV detection at high temperature [70]. Meanwhile, GaN, SiC, and diamond shows a decent performance under high temperature conditions. However, the materials are not cost effective as they have high fabrication cost making it not fitting for large scale production [71].

2.4.1 Ultraviolet sensor using titanium dioxide nanomaterials

A number of materials, including TiO$_2$ nanostuctured have been proposed and studied intensively in order to fabricate a UV sensor with good stability and reliability at a reasonable prices. Among the TiO$_2$ nanomaterials that have been used for UV detectors are TiO$_2$ nanoflowers. For an example of fabrication of TiO$_2$ nanoflowers UV photoconductive sensors, the work by Xihong Zu et al. has been referred [72]. By using combined method of hydrothermal and in-situ multiple wet chemical depositions method, the successfully constructed structure was composed of heterostructured arrays of TiO$_2$ nanowires (NWs) and polyaniline nanoflowers (PANI NFs) in sandwiches form. With comparison to 254 nm, the resulting photodetector exhibits excellent UV sensitivity and fast response speed with UV illumination at 365 nm wavelength.

Another work by Huan Wang et al. also used the same structure of sandwiches layer of TiO$_2$ and PANI [73]. But this time, the TiO$_2$ are nanorods (TNRs) structure and the PANI layer are nanowires (PANI NWs). The fabrication method used for PANI NWs was the chemical oxidation method meanwhile TNRs are synthesized using hydrothermal method. This work has also been tested using two UV wavelengths that are 254 and 365 nm. The 365 nm UV photocurrent of the designed UV photodetector was as high as $3.5 \times 10^{-4}$ A, and 254 nm UV photocurrent was only $0.16 \times 10^{-4}$ A. This study can provide opportunities for developing devices that can recognize different wavelengths of UV light.

W. F. Xiang et al. fabricated two types of nanocrystalline TiO$_2$ films; porous (P-detector) and dense (D-detector), on FTO substrates by two step approaches that are hydrothermal and the adding of polyethylene glycol to form nanocrystalline TiO$_2$
solution [74]. They used two colloidal silver electrodes as top electrode for TiO$_2$ surface and bottom electrodes for FTO separated by about 3 mm. The rise time and decay time of the P-detector and D-detector are 19 and 136 ns, and 14 and 100 ns, respectively. By comparing these two types of detector, P-detector is found to give higher responsivity due to a light scattering effect.

Another solution-based technique that is spray pyrolysis deposition (SPD) is used by Masayuki Okuya et al for UV sensor application [75]. The measurement was carried out under the light intensity of 20 μW/cm$^2$ irradiated directly on the sensors. The fabrication process varied the solvent used among ethanol, 2-propanol, and 2-butanol in which the results showed that ethanol gives the higher intensity from photo response of UV sensors. The UV response of the photodiode became more sensitive with increasing porosity of TiO$_2$ layer deposited from ethanol solution. Sensitivity of the UV sensor can be improved in this study by doping a little amount of aluminium to reduce the depletion layer. The photo response of TiO$_2$ UV sensor fabricated with aluminium layer showed higher intensity than that fabricated without aluminium layer.

An ultraviolet sensor based on TiO$_2$ nanorods that are grown on a p-type substrate seeded with a TiO$_2$ layer and synthesized by radio frequency reactive magnetron sputtering was done by Abbas M. Selman et al [76]. The TiO$_2$ nanorods were grown by using chemical bath deposition (CBD) method. The device showed $3.79 \times 10^2$ sensitivity when it was exposed to 325 nm light at 5V bias voltage.

### 2.4.2 Ultraviolet sensor mechanism

The enhancement of TiO$_2$ conductivity during dark and UV illumination can be explained as follows [77]. Both intrinsic conductivity and the conductivity of TiO$_2$ in the dark can be described by equation 2.4:

\[
\sigma = en\mu
\]  

(2.4)
Where \( \sigma \) is the conductivity, \( e \) is the electronic charge, \( n \) is the charge carrier density, and \( \mu \) is the carrier mobility. Under a bias voltage across the metal contact gap, the current density, \( J \), can be found by equation 2.5:

\[
J = \sigma F \quad \text{where} \quad F = \frac{V}{x}
\]  

(2.5)

Here, \( F \) is the applied electric field, \( V \) is the bias voltage, and \( x \) is the distance. Under UV illumination, a change in photoconductivity, \( \Delta \sigma \), occurs either by a change in the carrier concentration, \( \Delta n \), or by a change in the carrier mobility, \( \Delta \mu \), as indicated by the equation 2.6:

\[
\Delta \sigma = \sigma_{\text{light}} - \sigma_{\text{dark}} = e(\mu \Delta n + n \Delta \mu)
\]  

(2.6)

Generally, the photocurrent density, \( J_{\text{photocurrent}} \), can be expressed as a function of time by equation 2.7:

\[
J_{\text{photocurrent}} = \mu(t) \Delta n(t) + n(t) \Delta \mu(t) \quad eF
\]  

(2.7)

In many semiconductors, the change in mobility can be entirely neglected because \( \Delta n \gg \Delta \mu \); therefore, the equation can be simplified as equation 2.8:

\[
J_{\text{photocurrent}} = \Delta \sigma F = e\mu \Delta n(t)F
\]  

(2.8)
From this equation, it can be concluded that the photoconductivity of TiO$_2$ UV sensor depends on the mobility, carrier concentration, and the electric field or the bias voltage. Thus, to increase the photocurrent of the device, these three parameters must be improved. For example, the mobility of TiO$_2$ can be enhanced by using highly crystalline TiO$_2$ nanostructures such as nanowires or nanorods. Additionally, the carrier concentration of TiO$_2$ can be increased by the doping process.

According to the previous study, the photoconduction of UV sensor is governed by oxygen adsorption and desorption on its surface, as shown in Figure 2.2 [78]. This mechanism is widely accepted as the cause of high photocurrent values under UV illumination as the lifetime of the photoexcited electron is increased. According to this mechanism, surrounding oxygen molecules can be adsorbed onto the nanorods surface by capturing the free electrons from the TiO$_2$ nanostructure, as shown in 2.9:

\[
O_2 + e^- \rightarrow O_2^-
\] (2.9)

Where O$_2$ is the oxygen molecule, e$^-$ is a free electron, and O$_2^-$ is adsorbed oxygen on the nanorod surface. This process is illustrated by Process 1 in Figure 2.2. The adsorption of oxygen onto the surface causes bend bending. When UV light is incident on the surface of the nanostructure, electron-hole pairs are generated according to the following equation 2.10:

\[
hv \rightarrow h^+ + e^-
\] (2.10)

Where $hv$ is the photon energy from the UV light, $h$ is a plank’s constant, $v$ is the photon frequency, $h^+$ is a photogenerated hole in the valence band, and $e^-$ is the photogenerated electron in the conduction band. Large surface area is needed as it facilitates fast surface reaction as the photogenerated hole reacts with negatively charged adsorbed oxygen, as shown by equation 2.11:

\[
O_2^- + h^+ \rightarrow O_2
\] (2.11)
This process releases oxygen molecules from the nanorods surface as shown by Process 2 in Figure 2.2. This will cause hole trapping phenomenon at the TiO$_2$ surface, as illustrated by Process 3 and Process 4, and leaves behind the electron of the pair, as indicated by Process 5 and Process 6, which results in increasing of the conductivity of the nanostructures. The unpaired e$^-$ will either collected at the metal contact or recombine with the holes when the oxygen is re-adsorbed on the TiO$_2$ surfaces, as shown by Process 7 in Figure 2.2. The maximum photocurrent can be achieved when the generation rate of the electron-hole pairs and recombination is equivalent. When illumination is removed, the oxygen molecule recombines with the electron, leading to the decrease in film conductivity.

**Figure 2.2: The mechanism of photoconduction in TiO$_2$-based UV sensor under dark and UV illumination conditions**
CHAPTER 3

METHODOLOGY

3.1 Introduction

In this chapter, preparation of the titanium dioxide (TiO$_2$) nanorods using hydrothermal synthesis is presented. Three main topics will be explained in this chapter including substrate cleaning, preparation of the TiO$_2$ solutions for nanorods array using hydrothermal methods, and the characterisation methods including surface morphology study, chemical composition, electrical, and optical properties. The experimental details are given in the subsequent chapter. Figure 3.1 shows the flow chart for nanostructured TiO$_2$ thin film preparation and characterization.

![Flow chart for nanostructured TiO$_2$ thin film preparation and characterization]

Figure 3.1: Summarized of nanostructured TiO$_2$ thin film preparation and characterization
3.2 Substrate cleaning by sonicating method

Before the fabrications, substrate used, that is fluorine-doped tin oxide (FTO) was cleaned in order to remove contaminants. The contaminations on the FTO might affect the material growth, thus affecting the properties of the material. FTO substrate is a substrate that is transparent, low cost, has high-temperature resistant, and chemically inert. Also, FTO substrate exhibit electrical conductivity and at the same time allows transmission of solar cell radiation on its active region[79]. The substrate cleaning procedure is summarized in Figure 3.2.

![Diagram of cleaning substrate procedure]

Figure 3.2: Summarized of cleaning substrate procedure

3.3 Preparation of TiO$_2$ solution for hydrothermal reaction

The TiO$_2$ hydrothermal were prepared by using titanium butoxide (TBOT) as a precursor (starting material), hydrochloric acid (HCl) as a chelating agent, and deionised water (DI) as a solvent. Chelating agent is ligand that can form bonds (covalent bondings) at more than one point. It is a substances whose molecules can form a several bonds to a single metal ion. Meanwhile, deionised water acts as a function of adding the oxygen (O$_2$) element into TBOT for hydrolysis process. 120 mL of concentrated hydrochloric acid (HCl) (36.5 % ~ 38 %) was dissolved in 120 mL of DI water as chemical solution for hydrothermal process. The mixture was vigorously stirred for 5 minutes on the hot plate stirrer and then TBOT was added drop wise using a capillary tube. After stirring for nearly 15 minutes, the solution was put into steel made autoclave with Teflon made liner (300 mL) for hydrothermal process in which the FTO glass substrate were put with the conducting FTO surface.
facing the walls of the Teflon. Nucleation of TiO$_2$ seed in the solution leads to the growth of nanoflowers [80,81]. The conductive side of the FTO was put facing the wall to avoid deposition of nanoflowers on top of the nanorods. The autoclave steel used was shown in Figure 3.3. The process was performed at 150°C with a variation of reaction time, volume of TBOT, and volume of hydrochloric acid used. After that, the autoclave was taken out from oven and cooled down in room temperature for 5 hours to allow the steel made autoclave to cool and touchable. The prepared samples were rinsed with DI water and left to dry at room temperature. Figure 3.4 shows the FTO substrate before and after the hydrothermal reaction. Summarised step for preparing the solution is shown in Figure 3.5 and the details experimental parameters are tabulated in Table 3.1.

Table 3.1: Preparation of TiO$_2$ solution for hydrothermal reaction

<table>
<thead>
<tr>
<th>Solution preparation</th>
<th>Materials</th>
<th>Precursor</th>
<th>Chelating agent</th>
<th>Solvent</th>
<th>Solution volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTO</td>
<td>Hydrothermal</td>
<td>Titanium butoxide</td>
<td>Hydrochloric acid</td>
<td>DI water</td>
<td>240 mL</td>
</tr>
</tbody>
</table>

Figure 3.3: Autoclave used for hydrothermal process
REFERENCES


2006.


2012.


