IN VITRO BIOACTIVITIES OF ANODISED TITANIUM IN MIXTURE OF β-
GLYCEROPHOSPHATE AND CALCIUM ACETATE FOR BIOMEDICAL
APPLICATION

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A thesis submitted in
fulfilment of the requirement for the award of the
Doctor of Philosophy of Mechanical Engineering

Faculty of Mechanical and Manufacturing Engineering
Universiti Tun Hussein Onn Malaysia

AUGUST 2016
Special thanks to **my beloved family**,  
LEE ING KUANG, LOW CHIEW CHOO, LEE CHING SHEN, LEE CHING JUI,  
LEE TE HSIANG and also to my family members,  
for the love, care, and moral support. Thanks for continuous support for the  
encouragement toward the success of this study  

**My inspirational supervisor and co-supervisor,**  
ASSOC. PROF. DR MAIZLINDA IZWANA BINTI IDRIS &  
ASSOC. PROF. DR HASAN ZUHUDI BIN ABDULLAH  
for their understanding, support and encouragement during this research  

**All my friends,**  
for their concern, encouragement and knowledge.  

*All the support, enthusiasm and sacrifice in giving me assistance and strength to complete this thesis will never be forgotten.*
ACKNOWLEDGMENT

First of all, I would like to thank God for being my strength and courage to do this research.

Secondly, I would like to express my sincere appreciation to my supervisor, Assoc. Prof. Dr. Maizlinda Izwana Binti Idris and co-supervisor, Assoc. Prof. Dr. Hasan Zuhudi Bin Abdullah who gave me a good opportunity to do this meaningful research and the support given during this PhD’s project. Apart from that, I would like to express my special thanks to Dr Pramod Koshy, lecturer from University of New South Wales, Sydney, Australia, who helps me for proofreading my thesis.

Last but not least, I would like to thank my parents, relatives, and friends for always being supportive of my education especially during this research duration. Thanks again to all who helped me.
ABSTRACT

Anodic oxidation has been widely used to modify the surface properties of titanium in order to improve the biocompatibility after implantation. In this study, high purity titanium foils were exposed in a mixture of β-glycerophosphate disodium salt pentahydrate (β-GP) and calcium acetate monohydrate (CA). The parameters for anodic oxidation method such as applied voltage (50-350 V), current density (10-70 mA.cm⁻²), electrolyte concentration (0.02 M β-GP + 0.2 M CA, 0.04 M β-GP + 0.04 M CA), anodising time (5-10 mins), agitation speed (300-1500 rpm), ultrasonic amplitude (20-60 μm) and bath temperature (4-100 °C) were varied to investigate the impact on the surface properties of titanium. The results showed that surface of the titanium foil appeared to be highly porous and demonstrated high crystallinity as well as high hydrophilic properties especially when the parameters of anodic oxidation have been varied. This study also proposes two novel methods particularly to accelerate the bone-like apatite formation on the anodised titanium in a shorted time: (1) UV irradiation during in vitro testing and (2) adding additives in electrolyte. After soaked and irradiated with UV in simulated body fluid (SBF) for 7 days, highly crystallised bone-like apatite was fully covered on the anodised surface. Interestingly, the smooth and partially porous surface of the anodised titanium was observed to be fully covered by the bone-like apatite layer, which contradict previous research results. The mechanism for growth of bone-like apatite was developed and involved several stages from the existence of hydroxyl groups (•OH) under the UV irradiation has been disclosed thoroughly. Further, additives such as sulphuric acid (H₂SO₄), hydrogen peroxide (H₂O₂) and sodium hydroxide (NaOH) were added into the electrolyte were also able to accelerate the formation of bone-like apatite because of the presence of (•OH), tricalcium phosphate (Ca₃O₈P₂), calcium diphosphate (Ca₂O₇P₂), calcium titanate (CaTiO₃) or sodium titanate (Na₂Ti₅O₁₇) on the anodised surface, which able to induce the nucleation site of bone-like apatite.
**ABSTRAK**

Pengoksidaan anod telah digunakan secara meluas untuk mengubahsuai sifat-sifat permukaan titanium bagi memperbaiki keserasian bio selepas implitisasi. Dalam kajian ini, kerajang titanium berketulenan tinggi telah didedahkan di dalam campuran garam pentahidrat dinatrium β-gliserofosfat (β-GP) dan kalsium asetat monohidrat (CA). Parameter-parameter bagi langkah pengoksidaan anod seperti voltan gunaan (50-350 V), ketumpatan arus (10-70 mA.cm⁻²), kepekatan elektrolit (0.02 M β-GP + 0.2 M CA, 0.04 M β-GP + 0.04 M CA), tempoh penganodan (5-10 mins), kelajuan agitasi (300-1500 rpm), amplitud ultrasonik (20-60 μm) dan suhu elektrolit (4-100 °C) telah diambil kira bagi mengkaji kesan terhadap sifat-sifat permukaan titanium. Permukaan kerajang titanium didapati mempunyai liang yang banyak dan menunjukkan kekrystalan serta sifat hidrofilik yang tinggi terutama semasa parameter-parameter pengoksidaan anod telah diubah-ubah. Kajian ini turut mencadangkan dua kaedah baru bagi mempercepatkan pembentukan apatit tulang pada titanium yang sudah dianodkan dalam masa yang singkat: (1) penyinaran UV semasa ujian in vitro dan (2) peletakan bahan tambahan dalam campuran β-GP + CA. Setelah direndam dan didedahkan dengan UV di dalam SBF selama 7 hari, didapati apatit berbentuk tulang tinggi kekrystalan telah dilitupi pada permukaan titanium yang sudah dianodkan. Permukaan titanium tersadur yang licin dan sebahagianya berliang didapati telah dilitupi sepenuhnya dengan lapisan apatit berbentuk tulang bertentangan dengan dapatan yang. Mekanisma bagi pertumbuhan apatit berbentuk tulang telah dibangunkan dan melibatkan beberapa peringkat bermula dari kewujudan kumpulan hidroksil (•OH) di bawah sinaran UV telah dilampirkan. Bukan itu sahaja, bahan tambahan seperti asid sulfuric (H₂SO₄), hidrogen peroksida (H₂O₂) dan natrium hidroksida (NaOH) ke dalam elektrolit juga berkemampuan untuk mempercepatkan pembentukan apatit berbentuk tulang disebabkan oleh kewujudan kumpulan hidroksil (•OH), trikalsium fosfat (Ca₃O₈P₂), di-kalsium difosfat (Ca₂O₇P₂), kalsium titanat
(CaTiO₃) atau natrium titanat (Na₂Ti₃O₇) yang berkebolehan untuk mendorong pembentukan tapak penukleusan apatit berbentuk tulang telah dianodkan pada permukaan titanium.
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7.32 GAXRD patterns of anodised titanium obtained at 350 V and 70 mA.cm$^{-2}$ for 10 minutes at various volume fraction of 1 M NaOH (12.5-50 vol %) after soaking in SBF for 7 days
# LIST OF SYMBOLS AND ABBREVIATIONS

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<th>Abbreviation</th>
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<tr>
<td>•OH</td>
<td>- Hydroxyl group</td>
<td></td>
</tr>
<tr>
<td>AFM</td>
<td>- Atomic force microscopy</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_4$O$_2$</td>
<td>- Acetic acid</td>
<td></td>
</tr>
<tr>
<td>CA</td>
<td>- Calcium acetate monohydrate</td>
<td></td>
</tr>
<tr>
<td>Ca$_2$O$_3$P$_2$</td>
<td>- Calcium diphosphate</td>
<td></td>
</tr>
<tr>
<td>Ca$_3$O$_8$P$_2$</td>
<td>- Tricalcium phosphate</td>
<td></td>
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<tr>
<td>Ca-P</td>
<td>- Calcium Phosphate</td>
<td></td>
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<tr>
<td>CaTiO$_3$</td>
<td>- Calcium titanate</td>
<td></td>
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<tr>
<td>Cp-Ti</td>
<td>- Commercially pure titanium</td>
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<tr>
<td>DSLR</td>
<td>- Digital single-lens reflex camera</td>
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<tr>
<td>FESEM</td>
<td>- Field emission scanning electron microscope</td>
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<tr>
<td>FIB</td>
<td>- Focused ion beam</td>
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</tr>
<tr>
<td>FTIR</td>
<td>- Fourier transform infrared spectroscopy</td>
<td></td>
</tr>
<tr>
<td>GAXRD</td>
<td>- Glancing angle X-ray diffraction</td>
<td></td>
</tr>
<tr>
<td>h</td>
<td>- hour</td>
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</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>- Hydrogen peroxide</td>
<td></td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>- Sulphuric acid</td>
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</tr>
<tr>
<td>HAp</td>
<td>- Hydroxyapatite</td>
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<tr>
<td>HCL</td>
<td>- Hydrochloric acid</td>
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<tr>
<td>JCPDS</td>
<td>- Joint Committee on Powder Diffraction Standards</td>
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<tr>
<td>Na$_2$Ti$_3$O$_7$</td>
<td>- Sodium titanate</td>
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<tr>
<td>NaOH</td>
<td>- Sodium hydroxide</td>
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</tr>
<tr>
<td>SBF</td>
<td>- Simulated body fluid</td>
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</tr>
<tr>
<td>Ti</td>
<td>- Titanium</td>
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</tr>
<tr>
<td>TiO$_2$</td>
<td>- Titanium dioxide</td>
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</tr>
<tr>
<td>UV</td>
<td>- Ultraviolet</td>
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</tr>
<tr>
<td>Acronym</td>
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<tr>
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</tr>
<tr>
<td>UVA</td>
<td>Ultraviolet light type C</td>
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<tr>
<td>UVC</td>
<td>Ultraviolet light type A</td>
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<tr>
<td>β-GP</td>
<td>Beta-glycerophosphate disodium salt pentahydrate</td>
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CHAPTER 1

INTRODUCTION

1.1 Background

Titanium and its alloys are the most popular implant material due to its superior properties such as biocompatibility, good mechanical properties, low modulus of elasticity, and high corrosion resistance compared to other metals (Liu et al., 2004; Geetha et al., 2009 & Mohammad et al., 2012). There has been increased use of titanium, particularly as dental implants, cochlear replacements, screws for orthodontic surgery, bone fixation, artificial heart valves, and surgical instruments (Patel & Gohil, 2012). Figures 1.1 and 1.2 show the applications of titanium within the biomedical industry. However, titanium is a bio-inert material and does not allow significant bone apposition after implantation (Mohammad et al., 2012). The formation of a thin and passive titanium dioxide (TiO$_2$) layer occurs upon exposure of titanium to atmospheric conditions (Park et al., 2013).

TiO$_2$ is the most popular photocatalytic material due to its outstanding properties such as low cost, high stability, high photocatalytic performance, and strong oxidation ability (Augugliaro et al., 2010). Titanium dioxide (TiO$_2$) exists as three main crystalline phases, namely anatase, brookite, and rutile, of which rutile is the most common and stable form (Diebold, 2013). The band gaps for anatase and rutile TiO$_2$ are 3.20 eV and 3.02 eV, respectively (Hanaor & Sorrell, 2011). Hence, a number of research had been conducted on photocatalytic performance of TiO$_2$ due
to its wider band gap energy. Most research has been conducted on the photocatalytic properties of anatase and rutile TiO$_2$ compared to those on brookite TiO$_2$ (Diebold, 2013 & Koelsch et al., 2004).

Figure 1.1: Artificial bone screw (Liu et al., 2004).

Figure 1.2: Artificial hip joint (Liu et al., 2004).

The surface of the implant plays a crucial role in promoting osseointegration. Osseointegration is important to ensure the implants integrated into bone for long-term successful clinical outcome. Properties such as porous, rough, high crystallinity, and high hydrophilicity are ideal to enhance the osseointegration process (Elias, 2010; Ehrenfest et al., 2010 & Kim et al., 2012). A number of efforts have been undertaken using anodic oxidation, alkaline treatment, gel oxidation, and plasma spraying in order to enhance the bioactivity of the titanium (Liu et al., 2010). Among these, anodic oxidation is the simplest and cost-effective method. The anodic oxidation of
titanium is categorised by solid state diffusion in the oxide and/or by dissolution deposition in the electrolyte. Anodic oxidation combines electric field-driven metal and oxygen ion diffusion to form an oxide layer on the anode surface (Liu et al., 2004; Kim & Ramaswamy, 2009). This process thus enhances the adhesion and bonding, improves crystallinity, and increases the corrosion resistance of the inherent oxide layer (Liu et al., 2004). Post implantation, anodised titanium forms a bone-like apatite layer on the surface that bonds to living bone tissue. The composition and structure of bone-like apatite that is formed is very similar to human bone (Kasuga et al., 2002).

In this study, a mixture of β-glycerophosphate disodium salt pentahydrate and calcium acetate monohydrate (β-GP + CA) was used as the electrolyte. For biomedical applications, this solution provides phosphorous and calcium ions that promote bone tissue growth and thereby enhance the anchorage of the implant to the bone (Lee et al., 2015a & Abdullah et al., 2014). The in vitro bioactivities of the implant are normally evaluated by using simulated body fluid (SBF). The SBF solution is prepared by following the recipe of Kokubo & Takadama (2006) in order to study the precipitation of bone-like apatite as well as prediction of natural bone growth on the implant.

This study investigates the effect of processing parameters such as applied voltage, current density, anodising time, electrolyte concentration, stirring methods during anodic oxidation, bath temperature, UV light treatment condition and type of additive in electrolyte to improve the biocompatibility of the material as well as to improve the bonding time and reduce the healing time once the material is placed in the body.

1.2 Problem Statements

To date, anodic oxidation of titanium with a mixture of β-GP + CA requires a longer time (more that 300 days) to form bone-like apatite on the surface. This is due to the lack of sufficient nucleation sites on the oxide layer (TiO$_2$) for the growth of bone-like apatite (Abdullah, 2010). Using a mixture of β-GP + CA as the electrolyte for
preparing anodised titanium, Ishizama and Ogino (1995) observed that bone-like apatite was not formed on the surface of anodised titanium even after soaking in SBF for 300 days. Han et al. (2008) also noted the absence of bone-like apatite on the surface of anodised titanium after soaking in SBF for 90 days, and similar results were observed by Huang et al. (2007) and Abdullah (2010) after soaking in SBF for 50 days and 7 days, respectively.

In order to address the issues, this research was conducted to explore the effective ways to shorten the time for the growth of bone-like apatite on the surface of anodised titanium and improve the biocompatibility of the titanium. The tendency of the oxide layer to may exhibit bone-like apatite forming ability could be enhanced upon exposure to ultraviolet (UV) irradiation (Han et al., 2008). Therefore, UV light treatment after anodic oxidation and UV irradiation during in vitro testing were conducted to elucidate the effect of UV irradiation on the bone-like apatite forming ability. Apart from that, additives such as sulphuric acid (H₂SO₄), hydrogen peroxide (H₂O₂), acetic acid (C₂H₄O₂) and sodium hydroxide (NaOH) were used in order to activate the nucleation sites of bone-like apatite.

1.3 Objectives

The present research has the following objectives:

(a) To investigate the anodic oxidation behaviour of titanium surface in a weak organic acid mixture (β-glycerophosphate + calcium acetate).
(b) To propose and access a new approach of in vitro bioactivation of the anodised titanium in SBF with UV irradiation.
(c) To explore the effect of stirring methods and bath temperature during anodic oxidation on the surface properties of anodised titanium.
(d) To investigate the effect of UV light treatment after anodic oxidation on the bone-like apatite forming ability of the anodised titanium.
(e) To characterise the growth of bone-like apatite on the surface of anodised titanium in SBF.
(f) To investigate the effect of additives in mixture of β-GP + CA electrolyte on the bone-like apatite forming ability of anodised titanium.
1.4 Scope of Study

The scope of this study is as follows:

(a) Oxide layers on titanium were produced via anodic oxidation in mixtures of β-GP + CA. The parameters used are as follow:
   • Applied voltage : 50-350 V
   • Current density : 10-70 mA/cm²
   • Anodising time : 5-10 min
   • Concentration of β-GP + CA : 0.02 M + 0.2 M and 0.04 M +0.4 M
   • Temperature : ~25°C

(b) SBF was used to conduct the in vitro testing by following Kokubo's recipe. In vitro testing were conducted in three different conditions:
   • Without UV irradiation
   • With short wavelength (254 nm) UV irradiation
   • With long wavelength (365 nm) UV irradiation

(c) Different stirring methods and varying bath temperatures were used to investigate the effect of these parameters on the resultant surface properties of the anodised titanium. The parameters used are as follows:
   • Stirring Method : Magnetic, Ultrasonic, Water Bath
   • Agitation speed : 300-1500 rpm
   • Ultrasonic amplitude : 20-60 μm
   • Bath temperature : 4-100°C

(d) UV light treatment was conducted after anodic oxidation. The parameters used for UV light treatment are as follows:
   • pH of solution during UV light treatment : 1-11
     **pH of solution was adjusted using H₂SO₄ and NaOH
   • Duration of UV light treatment : 4-12 hours
   • Wavelength of UV irradiation : 365 nm

(e) UV-treated anodised titanium was soaked in SBF for 7 days. The samples were analysed each day in order to investigate the growth mechanism of bone-like apatite.

(f) Additives were added to the mixture of β-GP + CA electrolyte to explore
the effect on bone-like apatite forming ability of anodised titanium.

Parameters in this part of the study are as follows:

- Types of additives: \( \text{H}_2\text{SO}_4, \text{H}_2\text{O}_2, \text{C}_2\text{H}_4\text{O}_2 \) and \( \text{NaOH} \)
- Molarity of additive: 1 M
- Volume fraction of additives: 12.5-50.0 vol %

**The characterisation of anodised titanium were carried out using the following techniques:**

- Digital camera - colourisation
- Colourimeter - colourisation
- Field emission scanning electron microscopy (FESEM) - surface morphology
- Focus ion beam (FIB) - cross sectional image
- Glancing angle X-ray diffractometer (GAXRD) - surface mineralogy
- Laser Raman microspectroscopy - surface mineralogy
- Atomic force microscopy (AFM) - surface topography
- Fourier transform infrared spectroscopy (FTIR) - structural characteristic
- Goniometer - surface wettability and surface energy
- UV-VIS spectroscopy - optical properties

### 1.5 Significance of Study

This section briefly describes the significances of this project with regard to helping in faster recover from injury and aging, and surface modification technology of the biomedical implant.

(a) **Injury and aging**

Kovan (2008) reported that the most common causes for bone fracture are vehicles accident, severe assault and falls. Meanwhile, Farr & Khosla (2016) claimed that aging is the most significant risk factor for osteoporosis and fractures. This research can assist in helping in the growth of new bone on the implant surface and help the patients experienced bone fracture caused by
accident and osteoporosis to replace fractured bone. Anodisation of titanium in mixture of calcium acetate and β-glycerophosphate will enhance the osseointegration of tissues and bones with the implant titanium and shorten the recovery time of patient suffered injury.

(b) Surface medication technology

This research can show the potential of anodised titanium for biomedical uses. Furthermore, the new approach of in vitro testing under UV irradiation on anodised titanium can provide information on the effect of UV irradiation during immersion in SBF.

1.6 Novelty of study

The present work reveals novel methods (UV irradiation and additives addition in β-GP + CA) to enhance the rate of growth of bone-like apatite on the surface of titanium metal anodised in a mixture of β-GP + CA.

Previous researchers (Ishizama & Ogino, 1995; Huang et al., 2007) observed absent of bone-like apatite on anodised surface even after soaking in SBF for more than 300 days. Han et al. (2008) and Gao et al. (2013) proved that UV irradiation is able to enhance the bioactivity of anodic films. However, better understanding of the effect of UV irradiation on growth of bone-like apatite need to be elucidated due to absent of studies on investigating the effect of UV irradiation during in vitro testing.

Therefore, the study was carried out was also able contribute new knowledge in biomaterials research field and propose novel methods to accelerate the growth of bone-like apatite. In this study, highly crystallised bone-like apatite was fully covered on the anodised surface after soaking in SBF with UV irradiation for 7 days.

Moreover, there are no available study and literature with regards to effect of additives addition in β-GP + CA electrolyte on bone-like apatite forming ability of anodised titanium. In this study, H₂SO₄, H₂O₂, C₂H₄O₂ and NaOH were added in mixture of β-GP + CA. It was found that addition of additives in β-GP + CA electrolyte is capable to accelerate the formation of highly crystallised bone-like apatite on anodised surface in 7 days only.
Titanium and its alloys have been widely used in biomedical applications as implant materials due to its good biocompatibility with hard tissue. However, titanium and its alloys do not facilitate osseointegration since the surface of machined titanium is smooth, low in crystallinity, hydrophobic, and poor in bioactivity. Consequently, machined implants do not promote significant better bone apposition (Liu et al., 2004). Therefore, it is necessary to conduct surface modification though anodic oxidation in order to produce micro-rough, highly crystalline, hydrophilic, and bioactive surfaces. This particular mechanism will enhance the process of osseointegration. Anodic oxidation is a simple and low-cost surface modification method for titanium-based implants and has been widely used for dental implants and medical fastener (Kim & Ramaswamy, 2009). In vitro and in vivo tests proved that anodised titanium implants showed a considerable improvement in their osseointegration capability as compared to the machined titanium implants (Kim & Ramaswamy, 2009).
2.2 Biomaterials

2.2.1 Overview of Biomaterials

Biomaterials can be defined as “any substance (other than a drug) or combination of substances, synthetic or natural in origin, which can be used for any period of time, as a whole or as a part of a system which treats, augments, or replace any tissue, organ, or function of the body” (Boretos & Eden, 1984).

Biomaterials in the form of implants are widely used to replace, repair and restore the damaged organs or tissues and thus improve the life quality of the patient. For blood contact applications, biomaterials are inserted into blood vessels or devices that are permanently implanted to remove and return the blood from the body. For soft tissue applications, biomaterials are implanted to augment or redefine the damaged tissue. On the other hand, for orthopaedic and dental applications, biomaterials are implanted to repair the defective parts of the body (Nascimento et al., 2007). Figure 2.1 presents the human anatomy and organs where biomedical materials are used. Biomaterials are very important for improving the quality and longevity of human life (Manivasagam et al., 2010).

Basically, biomaterials can be divided into three categories which are metals, ceramics and polymers. Each biomaterials has its own unique functions whether for hard or soft tissue implants. The selection of biomaterials is important in order to provide true biological and mechanical match for living tissue. Table 2.1 shows the comparison among metals, ceramics and polymers biomaterials. Table 2.2 shows the biomedical application of metals, ceramics and polymers biomaterials (Bauer, 2013).
Figure 2.1: Implants in the human body (Patel & Gohil, 2012).

Table 2.1: Advantages and disadvantages of metals, ceramics and polymers for biomedical applications (Nallaswamy, 2008)

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<tr>
<th>Materials</th>
<th>Advantages</th>
<th>Disadvantages</th>
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<tbody>
<tr>
<td>Metals</td>
<td>High strength, high ductility, biocompatibility</td>
<td>Low corrosion resistance, may disrupt the interfacial attachment.</td>
</tr>
<tr>
<td>Ceramics</td>
<td>Biocompatibility, minimal thermal and electrical conductivity; modulus of expansion, colour and chemical composition are similar to bone.</td>
<td>Low mechanical, tensile and shear strength under fatigue loading, low attachment strengths for some coatings with the substrate interface.</td>
</tr>
<tr>
<td>Polymers</td>
<td>Low term experience, biocompatibility, ability to control properties through compositional means</td>
<td>Porous polymers undergo elastic deformation and lead to closing and opening of regions intended for tissue growth, difficult to clean contaminations</td>
</tr>
</tbody>
</table>
Table 2.2: Example of metal, ceramic, and polymer biomaterial use for biomedical applications (Bauer, 2013)

<table>
<thead>
<tr>
<th>No</th>
<th>Material</th>
<th>Medical applications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Metals</strong></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Cobalt – chromium alloys</td>
<td>Artificial heart valves, dental prosthesis, orthopaedic fixation plates, artificial joint components, vascular stents</td>
</tr>
<tr>
<td>2</td>
<td>Stainless steel</td>
<td>Dental prostheses, orthopaedic fixation plates, vascular stents</td>
</tr>
<tr>
<td>3</td>
<td>Titanium alloys</td>
<td>Artificial heart valves, dental implants, artificial joint components, orthopaedic screws, pacemaker cases, vascular stents</td>
</tr>
<tr>
<td>4</td>
<td>Gold or platinum</td>
<td>Dental fillings, electrodes for cochlear implants</td>
</tr>
<tr>
<td>5</td>
<td>Silver–tin–copper alloys</td>
<td>Dental amalgams</td>
</tr>
<tr>
<td></td>
<td><strong>Ceramics</strong></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Aluminium oxides</td>
<td>Orthopaedic joint replacement, orthopaedic load-bearing implants, implant coatings, dental implants</td>
</tr>
<tr>
<td>7</td>
<td>Zirconium oxides</td>
<td>Orthopaedic joint replacement, dental implants</td>
</tr>
<tr>
<td>8</td>
<td>Calcium phosphates</td>
<td>Orthopaedic and dental implant coatings, dental implant materials, bone graft substitute materials</td>
</tr>
<tr>
<td>9</td>
<td>Bioactive glasses</td>
<td>Orthopaedic and dental implant coatings, dental implants, facial reconstruction components, bone graft substitute materials</td>
</tr>
<tr>
<td></td>
<td><strong>Polymers</strong></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Polyethylene</td>
<td>Orthopaedic joint implants, syringes</td>
</tr>
<tr>
<td>11</td>
<td>Polypropylene</td>
<td>Heart valves, sutures, syringes</td>
</tr>
<tr>
<td>12</td>
<td>Polydimethylsiloxane</td>
<td>Breast implants, contact lenses, knuckle replacements, heart valves, artificial hearts</td>
</tr>
<tr>
<td>13</td>
<td>Polyethylenterephthalate</td>
<td>Vascular grafts, sutures, blood vessels</td>
</tr>
<tr>
<td>14</td>
<td>Polyethylene glycol</td>
<td>Pharmaceutical fillers, wound dressings</td>
</tr>
<tr>
<td>15</td>
<td>Polytetrafluoroethylene</td>
<td>Vascular grafts, sutures</td>
</tr>
<tr>
<td>16</td>
<td>Collagen</td>
<td>Orthopaedic repair matrices, nerve repair matrices, tissue engineering matrices</td>
</tr>
<tr>
<td>17</td>
<td>Hyaluronic acid</td>
<td>Orthopaedic repair matrices</td>
</tr>
<tr>
<td>18</td>
<td>Elastin</td>
<td>Skin repair matrices</td>
</tr>
<tr>
<td>19</td>
<td>Fibri</td>
<td>Haemostatic products, tissue sealants</td>
</tr>
<tr>
<td>20</td>
<td>Chitosan</td>
<td>Wound dressing</td>
</tr>
<tr>
<td>21</td>
<td>Alginate</td>
<td>Wound dressing</td>
</tr>
</tbody>
</table>
2.2.2 Important Properties of Biomaterials for Implants

The biomaterials used for implant must possess important properties such as biocompatibility, good mechanical properties, and non-toxicity for a long term usage in human body without any negative effects. Table 2.3 briefly describes the important properties of biomaterials (Patel & Gohil, 2012).

Table 2.3: Important properties of biomaterials for use as implants (Patel & Gohil, 2012; Basu & Nath, 2009)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Brief Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Host Response</strong></td>
<td>Response of the host organism either local or systemic to the implanted material. There are 3 types of host response:</td>
</tr>
<tr>
<td></td>
<td><em>Bioinert / biantletant</em></td>
</tr>
<tr>
<td></td>
<td>- Unable to induce any interfacial biological bond between implant and bone.</td>
</tr>
<tr>
<td></td>
<td>- Examples: alumina, titanium and zirconia.</td>
</tr>
<tr>
<td></td>
<td><em>Bioactive</em></td>
</tr>
<tr>
<td></td>
<td>- Able to attach directly with body tissues and form chemical and biological bonds during early stages of the post implantation period.</td>
</tr>
<tr>
<td></td>
<td>- Examples: 45S5 bioglass and calcium phosphates.</td>
</tr>
<tr>
<td></td>
<td><em>Bioresorbable</em></td>
</tr>
<tr>
<td></td>
<td>- Gradually resorbed before they finally disappear and are totally replaced by new tissue in vivo.</td>
</tr>
<tr>
<td></td>
<td>- Examples: bone cement and tricalcium phosphate.</td>
</tr>
<tr>
<td><strong>Biocompatibility</strong></td>
<td>Ability of a material to perform without any adverse host response in a specific application implies harmony with the living system.</td>
</tr>
<tr>
<td><strong>Biofunctionality</strong></td>
<td>Ability to withstand load transmission and stress distribution, allowing for movement, controlling of fluid flow of blood, ability to provide space filling, electrical stimuli, light and sound transmission.</td>
</tr>
<tr>
<td><strong>Functional Tissue Structure and Pathobiology</strong></td>
<td>Ability to govern the structure of normal and abnormal cells, tissues and organs.</td>
</tr>
<tr>
<td><strong>Non - toxicity</strong></td>
<td>Toxicity of biomaterials will cause cell and human death</td>
</tr>
<tr>
<td><strong>Sufficient Mechanical Properties</strong></td>
<td>Biomaterials should possess high tensile strength, yield strength, elastic modulus, surface finish, creep, hardness and be easy to manufacture</td>
</tr>
<tr>
<td><strong>High Corrosion Resistance</strong></td>
<td>Avoid toxic ions</td>
</tr>
<tr>
<td><strong>High Wear Resistance</strong></td>
<td>Avoid implant loosening.</td>
</tr>
</tbody>
</table>
2.3 Metallic Implant Materials

2.3.1 Overview of Metallic Implant Materials

Metals had been used as implant materials for more than 100 years when Lane used metal plate to fix the bone fracture. However, metal implants suffer from corrosion and strength problems (Lane, 1895). In the 1920s, stainless steel was used for these applications (Hermawan et al., 2011). In 1932, cobalt-based alloys such as Vitallium were introduced for biomedical applications (Elías et al., 2008a). Titanium and its alloys were introduced in 1950s and a number of modification methods were applied to alter the alloy composition and surface properties in order to improve the functionality and implant duration in the human body (Geetha et al., 2009). Apart from that, biodegradable metals have been developed to meet the requirements of biomedical applications. Biodegradable metals permit the implants to degrade in biological environments. In term of mechanical properties, biodegradable metals are more suitable for internal bone fixation compared to the biodegradable polymers (Hermawan & Mantovani, 2009). Table 2.4 shows the examples of metallic biomaterials used for implants and their mechanical properties.

Table 2.4: Comparison of mechanical properties of commonly used metals and its alloys for biomedical applications (Hermawan et al., 2011; Nag & Banerjee, 2012)

<table>
<thead>
<tr>
<th>Metallic Biomaterial</th>
<th>Young’s Modulus (GPa)</th>
<th>Yield Strength (MPa)</th>
<th>Ultimate Tensile Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless Steel</td>
<td>200</td>
<td>170-750</td>
<td>465-950</td>
</tr>
<tr>
<td>Co-Cr-Mo</td>
<td>200-230</td>
<td>275-1585</td>
<td>600-1795</td>
</tr>
<tr>
<td>Commercially pure Ti</td>
<td>105</td>
<td>692</td>
<td>785</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>110</td>
<td>850-900</td>
<td>960-970</td>
</tr>
<tr>
<td>Iron – annealed plate</td>
<td>200</td>
<td>150</td>
<td>210</td>
</tr>
<tr>
<td>Fe35Mn alloy, powder</td>
<td>N/A</td>
<td>235</td>
<td>550</td>
</tr>
<tr>
<td>Magnesium, annealed sheet</td>
<td>45</td>
<td>90</td>
<td>160</td>
</tr>
<tr>
<td>WE43 magnesium alloy, temper T6</td>
<td>44</td>
<td>170</td>
<td>220</td>
</tr>
</tbody>
</table>
2.3.2 Titanium and its Alloys

Titanium and its alloys were widely used as implant materials due to its high biocompatibility and high corrosion resistance. The Young’s modulus of titanium and its alloys is only half of that of stainless steel or Co-Cr alloys. However, the properties of titanium are closer to cortical bones (Hanawa, 2008.). The applications of titanium and its alloys as implants includes cochlear replacements, bone and joint replacements, dental implants for tooth fixation, screw parts for orthodontic surgery, bone fixation like nails, screws and plates, artificial heart valves and surgical instruments (Patel & Gohil, 2012). Table 2.5 shows the mechanical properties of the titanium and its alloys for implants.

Table 2.5: Comparison of mechanical properties among titanium and its alloys (Long & Rack, 1998)

<table>
<thead>
<tr>
<th>Alloy Designation</th>
<th>Microstructure</th>
<th>Young’s Modulus (GPa)</th>
<th>Yield Strength (MPa)</th>
<th>Ultimate Tensile Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercially pure Ti</td>
<td>α</td>
<td>105</td>
<td>692</td>
<td>785</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>α/β</td>
<td>110</td>
<td>850-900</td>
<td>960-970</td>
</tr>
<tr>
<td>Ti-6Al-7Nb</td>
<td>α/β</td>
<td>105</td>
<td>921</td>
<td>1024</td>
</tr>
<tr>
<td>Ti-5Al-2.5Fe</td>
<td>α/β</td>
<td>110</td>
<td>914</td>
<td>1033</td>
</tr>
<tr>
<td>Ti-5Al-5Fe</td>
<td>Metastable β</td>
<td>74-85</td>
<td>1000-1060</td>
<td>1060-1100</td>
</tr>
<tr>
<td>Ti-15Mo-5Zr-3Al</td>
<td>Metastable β</td>
<td>75</td>
<td>870-968</td>
<td>882-975</td>
</tr>
<tr>
<td>Aged β + α</td>
<td>88-113</td>
<td>1087-1284</td>
<td>1099-1312</td>
<td></td>
</tr>
<tr>
<td>Ti-15Mo-2.8Nb-3Al</td>
<td>Metastable β</td>
<td>82</td>
<td>771</td>
<td>812</td>
</tr>
<tr>
<td>Aged β + α</td>
<td>100</td>
<td>1215</td>
<td>1310</td>
<td></td>
</tr>
<tr>
<td>Ti-13Nb-13Zr</td>
<td>α/β</td>
<td>79</td>
<td>900</td>
<td>1030</td>
</tr>
<tr>
<td>Ti-15Mo-3Nb-0.3O (21SRx)</td>
<td>Metastable β + silicides</td>
<td>82</td>
<td>1020</td>
<td>1020</td>
</tr>
<tr>
<td>Ti-55Nb-7Zr-5Ta</td>
<td>Metastable β</td>
<td>55</td>
<td>530</td>
<td>590</td>
</tr>
<tr>
<td>Ti-55Nb-7Zr-5Ta-0.4O</td>
<td>Metastable β</td>
<td>66</td>
<td>976</td>
<td>1010</td>
</tr>
</tbody>
</table>

Among all the titanium and its alloys, commercially pure Ti and Ti-6Al-4V are the most commonly used materials for biomedical and implant applications. Although Ti-6Al-4V has high reputation for biocompatibility and corrosion
resistance, it can release ions such as aluminium (Al) and vanadium (V) which are toxic and can cause long term health problems such as Alzheimers disease, neuropathy, and osteomalacia. These problems affect the long-term use of Ti-6Al-4V for implant applications (Geetha et al., 2009).

On the other hand, commercially pure titanium (Cp Ti) can be considered as the best biomaterial among titanium and its alloys owing to Cp Ti exhibiting the best biocompatible metallic surface. This is due to the build-up of a stable and inert oxide layer. Apart from that, Cp Ti also demonstrates good physical properties such as low level of electronic conductivity, high corrosion resistance, thermodynamic state at physiological pH value, low ion formation tendency in aqueous environments, and isoelectric point of the oxide of 5-6 (Elias et al., 2008a). Generally, Cp Ti can be classified into four types which are Cp Ti Grade 1, Cp Ti Grade 2, Cp Ti Grade 3 and Cp Ti Grade 4. Among all types of Cp Ti, Cp Ti Grade 4 has highest ultimate tensile strength and yield strength at 1.0% offset but lowest elongation. The mechanical properties for different types of Cp Ti are presented in Table 2.6.

Table 2.6: Mechanical properties of different grade of Cp Ti (ZAPP Materials Engineering, 2012)

<table>
<thead>
<tr>
<th>Types of Cp Ti</th>
<th>Ultimate Tensile Strength (MPa)</th>
<th>Yield Strength at 1.0% Offset (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp Ti Grade 1</td>
<td>290-410</td>
<td>≥ 200</td>
<td>30</td>
</tr>
<tr>
<td>Cp Ti Grade 2</td>
<td>390-540</td>
<td>≥ 270</td>
<td>22</td>
</tr>
<tr>
<td>Cp Ti Grade 3</td>
<td>460-590</td>
<td>≥ 350</td>
<td>18</td>
</tr>
<tr>
<td>Cp Ti Grade 4</td>
<td>540-740</td>
<td>≥ 410</td>
<td>16</td>
</tr>
</tbody>
</table>

2.3.3 Properties of Titanium Implants

It is well known that titanium and its alloys are one of the popular biomaterials for implants application due to its properties such as biocompatibility, osseointegration, good mechanical properties, low modulus of elasticity, and high corrosion resistance. Nowadays, there is an increasing trend in using titanium implants especially for dental implants and prostheses (Özcan & Hämerle, 2012). The important
properties of titanium and its alloy for biomedical application are presented in Table 2.7.

Table 2.7: Important properties of titanium in biomedical applications (Mohammed et al., 2012; Oldani & Dominguez, 2012; Ogawa & Nishimura, 2003; Sumner & Galante, 1992; Lilley et al., 1992)

<table>
<thead>
<tr>
<th>Properties of titanium and its alloys</th>
<th>Description</th>
</tr>
</thead>
</table>
| Biocompatibility                      | • Cp TI, α + β and β type  
• Non-toxic  
• Hydrated titanium oxide enhanced the growth of calcium phosphorous compounds and accelerated the osseointegration |
| Osseointegration                      | • Able to integrate well with adjacent bone  
• Success rate ≈ 65 % |
| Mechanical Properties                 | • Able to withstand a variety of loads during physical activities  
• High strength, high ductility, high fracture toughness, crack resistance, high bending strength, high fatigue resistance, and admission strain (the ratio of yield strength to modulus of elasticity).  
• Suitable for load bearing or non-load bearing applications. |
| Low Modulus of Elasticity             | • Not very high of compared to human bone  
• Adequate mechanical stress on the adjacent bone can be avoided due to the low modulus of elasticity.  
• Reduce the probability of bone cells damage |
| Corrosion Resistance                  | • Protective TiO$_2$ surface layer |

2.3.4 Application of Titanium and its Alloy in Biomedical Industry

Titanium and titanium alloys are widely used in biomedical devices and components, especially as hard tissue replacements and for cardiac and cardiovascular applications. Figures 2.2 to Figure 2.5 show the applications of titanium and its alloys in biomedical applications.
Figure 2.2: Artificial heart value (Liu et al., 2014).

Figure 2.3: Artificial vascular stents (Liu et al., 2014).
Figure 2.4: Bone screw and bone plate (Liu et al., 2014).

Figure 2.5: Commercial dental implant (Elias et al., 2008a).
2.4 Titanium Dioxide

2.4.1 Overview of Titanium Dioxide

Titanium is an oxide of titanium and is also known as titanium (IV) oxide, titania, titanium white, E171 in food colouring and pigment white 6 in building paints. The photocatalytic property of TiO₂ was first discovered when used as a white pigment in buildings since the pigment bleached under solar irradiation. Since then TiO₂ has been widely used in many industrial applications (Lan et al., 2013).

2.4.2 Polymorphs of Titanium Dioxide

The oxide layer on titanium is a passive film and normally made up of two forms: amorphous or low crystalline stoichiometric TiO₂. Titanium dioxide has three naturally occurring crystallographic forms which are anatase, brookite and rutile. Rutile is the most common and stable form and only anatase and rutile are manufactured on a large scale.

Rutile structure consists of a slightly distorted hexagonal close packing of oxygen atoms with the titanium atoms occupying half of the octahedral interstices. On the other hand, anatase and brookite are both based on cubic packing of the oxygen atoms with octahedral coordination (Rouquerol et al., 2013). It is reported that anatase is the most active, rutile is less active, and brookite is not active at all for photocatalytic applications (Liu, 2012). Anatase TiO₂ is generally accepted to be a better photocatalyst than rutile and brookite. However, rutile TiO₂ is the most thermodynamically stable phase among all the titanium dioxide forms (Mantz, 2010). Figures 2.6 to 2.8 demonstrate the crystal lattice structures of rutile, anatase, and brookite TiO₂. Table 2.8 compares the properties between rutile, anatase, and brookite forms of TiO₂.
Figure 2.6: Structure of rutile TiO$_2$ (Winkler, 2003).

Figure 2.7: Structure of anatase TiO$_2$ (Winkler, 2003).

Figure 2.8: Structure of brookite TiO$_2$ (Winkler, 2003).
Table 2.8: Properties of rutile, anatase, and brookite TiO$_2$ (Winkler, 2003)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Rutile TiO$_2$</th>
<th>Anatase TiO$_2$</th>
<th>Brookite TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm$^3$)</td>
<td>4.2 – 4.3</td>
<td>3.8 – 3.9</td>
<td>3.9 – 4.1</td>
</tr>
<tr>
<td>Point group according to Schonflies</td>
<td>D$_{4h}$</td>
<td>D$_{4h}$</td>
<td>D$_{2h}$</td>
</tr>
<tr>
<td>a (nm)</td>
<td>0.4594</td>
<td>0.3785</td>
<td>0.9184</td>
</tr>
<tr>
<td>b (nm)</td>
<td>0.4594</td>
<td>0.3785</td>
<td>0.5447</td>
</tr>
<tr>
<td>c (nm)</td>
<td>0.2958</td>
<td>0.9514</td>
<td>0.5245</td>
</tr>
<tr>
<td>Volume of the elementary cell (nm$^3$)</td>
<td>62.07</td>
<td>136.25</td>
<td>257.38</td>
</tr>
<tr>
<td>Molar volume (cm$^3$/mol)</td>
<td>18.693</td>
<td>20.156</td>
<td>19.377</td>
</tr>
<tr>
<td>Moh’s hardness</td>
<td>6.5 – 7</td>
<td>5.5 – 6.0</td>
<td>5.5 – 6.0</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1830 – 1850</td>
<td>Transforms to</td>
<td>Transforms to</td>
</tr>
<tr>
<td></td>
<td></td>
<td>rutile</td>
<td>rutile</td>
</tr>
</tbody>
</table>

2.4.3 **Photocatalytic Properties of Titanium Dioxide**

The Singh (2008) defined photocatalysis as a process in which light is used to activate a substance, the photocatalyst, which modifies the rate of a chemical reaction without being involved itself in the chemical transformation. Photocatalysis can be classified as an advanced oxidation process. Photocatalysis in the presence of an irradiated semiconductor has proven to be effective in the field of environmental remediation. Semiconductors are superior photocatalyst due to it favourable combination of electronic structure, light absorption properties, charge transport characteristics, and long lifetimes. In fact, the irradiation of a semiconductor oxide with light will produce hydroxyl radicals on the catalyst surface (Augugliaro et al., 2010).

Photocatalysts are widely used in common industrial applications such as photocatalytic water splitting, purification of pollutants, photocatalytic self-cleaning, photocatalytic antibacterial, photo-induced super hydrophilicity, and photosynthesis (Lan et al., 2013). To date, researchers in the photocatalysis field have clarified the following advantages of photocatalysis (Kaneko & Okura, 2002).

(a) Multiple process such as reduction and oxidation, proceed successively in a one pot reaction
(b) Catalysts can be separated and reused easily
(c) The reactions proceed at ambient temperature under atmospheric pressure
(d) Unlike ordinary organic synthetic procedures, water can be used as a solvent and this enables the use of water-soluble organic substrates
(e) Sustainable and environmentally friendly chemical processes
(f) Inexpensive
(g) Minimal infrastructural requirements

Semiconductors such as titanium oxide (TiO$_2$), zinc sulphide (ZnS), strontium titanate (SrTiO$_3$), zinc oxide (ZnO), zirconium dioxide (ZrO$_2$), cadmium sulphide (CdS), molybdenum disulfide (MoS$_2$), iron (III) oxide (Fe$_2$O$_3$), tungsten trioxide (WO$_3$), has been widely used as photocatalysts. In fact, the photocatalytic properties of the photocatalyst is strongly dependent on the band gap, energy level locations, mean life time, and mobility of electron and holes, light absorption coefficient, nature of the interface, as well as the method of preparation. Figure 2.9 shows the band gaps of different semiconductors (Augugliaro et al., 2010).

An ideal photocatalyst should present the following characteristics (Augugliaro et al., 2010):
(a) High reaction rate with wider band bad
(b) Photostability
(c) Chemical and biological inactivity
(d) Low cost
(e) Non-toxic and harmless
The photocatalyst will produce pairs of electrons and holes after it absorbs the UV irradiation from the sunlight or illuminated light source. The electrons in the valance band of the photocatalyst become energetic after irradiation by UV. The electron will be excited to the conduction band and thus creating negative electron (e\textsuperscript{-}) and positive hole (h\textsuperscript{+}) pairs. The electrons and holes can recombine and can release the absorbed heat without any chemical effects. The valance band hole is strongly oxidising. However, the conduction band electron is strongly reducing. The band gap is the energy difference between the valance band and conduction band. The positive hole of the photocatalyst can react with water molecules to form hydrogen gas and hydroxyl radicals (•OH). The •OH radicals are able to rapidly attack the pollutants at the solution surface. On the other hand, the negative electrons will react with the oxygen molecule and form superoxide anions (O\textsuperscript{2-}). The process will continue as long as there is irradiation (Augugliaro \textit{et al.}, 2010 & Al-Rasheed, 2005). Figure 2.10 shows the simplified mechanism for the photocatalytic process of a semiconductor catalyst.
The equations 2.1 to 2.10 show chemical reactions that occur during the photocatalytic process at the TiO$_2$-water interface. Generally, •OH, •O$_2^-$ and H$_2$O$_2$ are the key reactive oxygen species (ROS) are formed during the photocatalytic process (Augugliaro et al., 2010 & Cai, 2013).

- TiO$_2$ reacts with UV light and produces pairs of free electrons (e$^-_{(CB)}$) and positively charged holes (h$^+_{(VB)}$) as shown in Equation 2.1.

$$\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2 (e^-_{(CB)} + h^+_{(VB)}) \quad (2.1)$$

- Equation 2.2 and Equation 2.3 show the water molecular or hydroxide ions trapped in the positively charged hole and form the hydroxyl radicals (•OH)

$$\text{H}_2\text{O} + h^+_{(VB)} \rightarrow \cdot\text{OH} + \text{H}^+ \quad (2.2)$$

$$\text{OH}^- + h^+_{(VB)} \rightarrow \cdot\text{OH} \quad (2.3)$$

- The Ti$^{4+}$ reacts with the conduction band electron and is reduced to Ti$^{3+}$ as shown in equation 2.4.

$$\text{Ti}^{4+} + e^-_{(CB)} \rightarrow \text{Ti}^{3+} \quad (2.4)$$
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