

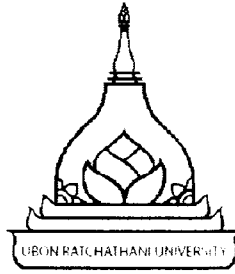


**THE PHASE TRANSFORMATION AND STRUCTURES
OF TITANIA (TiO₂) NANOTUBES ARRAYS PREPARED
BY ANODIZATION METHOD FOR ENERGY
CONVERSION**

NARONGSAK KODTHARIN

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REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE
MAJOR IN PHYSICS
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THESIS APPROVAL
MASTER OF SCIENCE
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บทคัดย่อ

- เรื่อง : การเปลี่ยนเฟสและโครงสร้างท่อนาโนไททาเนีย ที่เตรียมโดยกระบวนการแอโนไดเซชันเพื่อการผันพลังงาน
- ผู้วิจัย : ณรงค์ศักดิ์ โคตราริน
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- คำสำคัญ : ท่อนาโนไททาเนียมไดออกไซด์, เซลล์แสงอาทิตย์สีย้อมไวแสง, แอโนไดเซชัน, การเปลี่ยนเฟส

ท่อนาโนไททาเนียมที่ถูกประดิษฐ์โดยกระบวนการแอโนไดเซชันและถูกใช้เพื่อผลิตเซลล์แสงอาทิตย์สีย้อมไวแสง สารละลายที่ใช้เป็นสารละลายชนิดผสมซึ่งประกอบด้วย แอมโมเนียฟลูออไรด์ น้ำ และ เอทาลีนไกลคอล แรงดันไฟฟ้ากระแสตรง 70 โวลต์ที่ถูกใช้ในกระบวนการแอโนไดเซชัน ตัวอย่างที่ได้ถูกอบด้วยความร้อนที่อุณหภูมิ 300 - 700 องศาเซลเซียส เป็นเวลา 2 ชั่วโมง ท่อนาโนไททาเนียมถูกศึกษาลักษณะโดย กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด เทคนิคการเลี้ยวเบนรังสีเอกซ์ ผลการวิจัยพบว่าจะเกิดการเปลี่ยนรูปร่างจากผลึกอนาเทสเฟสเป็นรูไทล์ หลังจากอบที่ 450 - 500 องศาเซลเซียส หรือ อุณหภูมิที่สูงขึ้น เมื่ออบที่อุณหภูมิที่ 700 องศาเซลเซียส หรือ อุณหภูมิที่สูง เกิดการเปลี่ยนเฟสอย่างสมบูรณ์เป็นรูไทล์ และท่อนาโนไททาเนียมเป็นผลึกนาโน ประสิทธิภาพการผันพลังงานของเซลล์แสงอาทิตย์สีย้อมไวแสงเพิ่มขึ้นเมื่อบำบัดด้วยความร้อน 450 องศาเซลเซียส ประสิทธิภาพเซลล์แสงอาทิตย์สูงสุดคือ ร้อยละ 0.530

ABSTRACT

TITLE : THE PHASE TRANSFORMATION AND STRUCTURES OF
TITANIA (TiO₂) NANOTUBES ARRAYS PREPARED BY
ANODIZATION METHOD FOR ENERGY CONVERSION

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KEYWORDS : TITANIA (TiO₂) NANOTUBES, DYE-SENSITIZED SOLAR
CELLS, ANODIZATION, PHASE TRANSFORMATION

The films of TiO₂ nanotube arrays were fabricated by the anodization of Ti metal sheets for dye-sensitized solar cells (DSSCs). The anodization was carried out under the electrolyte of 0.3 wt% NH₄F and 2 V% ethylene glycol in deionized-water. DC power supply was used at a constant voltage of 70 Volts. The TiO₂ nanotubes were annealed at different temperatures from 300°C to 700 °C. The morphology of the nanotube arrays was characterized by scanning electron microscopy (SEM). The phase and structure of the TiO₂ nanotube array films were determined by X-ray diffraction (XRD). The phase of the nanotubes is transformed from anatase to rutile when annealing temperature is changed from 450 °C to 500 °C or higher. When annealing temperatures at 700 °C or higher, the phase of the nanotubes became completely rutile and the nanotubes changed to nanocrystalline. The efficiency of dye-sensitized solar cells which annealed at 450 °C was 0.530%

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CHAPTER 1

INTRODUCTION

1.1 Introduction and background

The world energy is used largely in everyday and the demand is increased every day, while the world energy is limited. The use of energy results in depleting in fossil fuels such as oil, natural gas and coal. In addition, the consumption of the fossil fuels leads to air pollution and greenhouse effect. This problem is one of the biggest challenges ahead of human. Scientists have developed urgently to replace the existing power source as petroleum, coal; nuclear power which are reduced. We have looked for other alternative energy in the forms of wind energy, hydrogen, biomass and solar cells. Thailand has to answer the problem by developing environmentally friendly energy. So, the sun is source of clean energy, cheap and already used by nature to sustain almost all life on earth.

The sunlight is converted to several forms of energy such as heat and chemical which are converted to electricity later. The conversion of sunlight into electricity directly by photovoltaic materials such as silicon and titania is the most elegant way. Solar cells are devices that can change sunlight into electrical energy. Conventional solar cells are made of p-n junction materials such as Si, GaAs, CdTe, GaInP, and Cu(InGa)Se₂. Non-conventional solar cells are made of semiconductor nanomaterials such as ZnO and TiO₂ for dye-sensitized solar cells (DSSCs). Solar cells are widely studied as renewable energy and as one of the competitive alternatives to fossil fuel - based energy sources [1]. DSSCs are one of the most promising ways to realize solar cell economy for the following reasons: this process is based on solar energy, from sunlight which is a clean.

In recent years, nanostructured Titanium dioxide nanotubes (TiO₂) have attracted more attention due to their excellent electronic, photonic and gas-sensitive properties [2]. They have been widely studied in several scientific and used in various applications such as solar cells [3], photocatalysis [4], gas sensors [5], sol-gel transcription [6], self-cleaning surfaces [7] and biomedical industry [8].

In 1991, O'Regan and Gratzel of the Swiss Federal Institute of Technology at Lausanne introduced dye-sensitized solar cells (hereinafter referred to as DSSCs) as new class of low cost solar cells [9], whose solar energy conversion efficiency was reported to be as high as 7.1% in simulated solar light, and 12% with the TiO₂ nanoparticle [10]. This efficiency is low for commercialization of DSSCs. Recently; TiO₂ nanotubes have received great attention due to their one dimensional structure to provide a direct path for electrons [11]. For application in DSSCs, TiO₂ nanotubes have higher charge collection efficiencies than a nanoparticle structure due to their faster transport and slower recombination of electrons [12].

TiO₂ nanotubes thin films can be fabricated by several methods, e.g., magnetron sputtering, vacuum evaporation, chemical vapor deposition, sol-gel transcriptions [13], hydrothermal techniques [14] liquid-phase deposition and electrochemical anodization, etc. Among these techniques, anodization is relatively cheap and simple. Electrochemical anodization can be more efficient and cost effective method of preparing TiO₂ nanotubes layers on titania substrates [15-18]. In addition, the anodization process, preparation parameters influencing the structure of TiO₂ nanotubes have been reported. The process parameters include electrolyte composition, the anodic voltage, time and pH [19].

In this work, we are interested in fabricating TiO₂ nanotubes by anodization method for dye-sensitized solar cells. The electrolytes of contain ethylene glycol (EG), ammonium fluoride (NH₄F) and deionized water (H₂O). DC power supply will be used at a constant voltage of 50 Volts. We will then fabricate dye sensitized solar cells and finally measure the conversion efficiency of TiO₂ nanotubes solar cells.

1.2 Research objectives

In this work, we plan to synthesize, study the physical properties of TiO₂ nanotubes and use TiO₂ nanotubes to fabricate dye-sensitized solar cells (DSSCs) as well as measure the conversion efficiency of the DSSCs.

1.3 Scope of this work

TiO₂ nanotubes will be grown by anodization method at room temperature. Titanium sheets will be cut in circular shape with diameter of 2 cm. The electrolyte is the mixture of ethylene glycol (EG), ammonium fluoride (0.3 wt% NH₄F) and deionized water. After that, the anodization will be used dc power supply at 50 V for 1 h. Then, the TiO₂ nanotubes will be annealed at 300 to 700 °C for 2 h. The surface morphology and microstructure of TiO₂ nanotubes will be studied by scanning electron microscope (SEM). Crystalline phase and microstructure will be examined by X-ray diffraction (XRD). Finally, DSSCs will be fabricated and measured the light-to-electricity conversion efficiency of TiO₂ nanotubes.

1.4 Thesis Organization

This thesis consists of 5 chapters. Chapter I is introduction. Chapter 2 deals with theory and related research. Chapter 3 provides experimental details. Chapter 4 shows the results and discussion about titania nanotubes and DSSCs based on prepared titania nanotubes. Chapter 5 is conclusion.

CHAPTER 2

LITERATURE REVIEWS

This chapter contains a review of the properties of TiO₂ material, TiO₂ crystal structure photocatalysis process, effect of deposition parameters the microstructural properties of titania nanotubes thin films, and related research about DSSCs. In general preparation of TiO₂ nanotubes thin films can be used many methods such as sol-gel [20], hydrothermal process [21] sputtering process [22] and anodization method [23]. But, anodization is one of simplest and cheapest method [24]. We study work related with TiO₂ nanotubes thin films in optimal parameters by anodization method, dye-sensitized solar cells. The mechanism of TiO₂ nanotubes formation is presented in this Chapter.

2.1 Properties of TiO₂ material

Titanium (Ti) is one of the most abundant elements on Earth. Titanium dioxide (TiO₂) or titania is the naturally occurring oxide of titanium. Titanium dioxide occurs in nature as well-known minerals rutile, anatase and brookite. TiO₂ is a cheap and innocuous inorganic material which is extensively employed in industrial and commercial applications such as pigment in the paint industry and as a binder in medicinal fields. For instance, more than 4 million tons of the white pigments are annually consumed by the paint industry worldwide, being the pigment most widely used because of its brightness, high refractive index and low-cost [25]. TiO₂ is a wide band gap semiconductor with 3.2 eV that presents photoactivity upon near UV or higher irradiation, absorbing photons and transforming them into chemical redox energy. Although TiO₂ is inert and do not occur chemical reactions without irradiation, the handling of very finely divided TiO₂ particles requires taking safety measures. TiO₂ is rapidly growing worldwide due to its unique electronic properties, combined with the possibility of easy nanostructure. TiO₂ can be manipulated by a wide spectrum of techniques and shaped into a broad range of nanoscale structures: particles, wires, rods, tubes and ultrathin films [26]. Titania exists in a number of crystalline forms the most important of which are anatase and rutile.

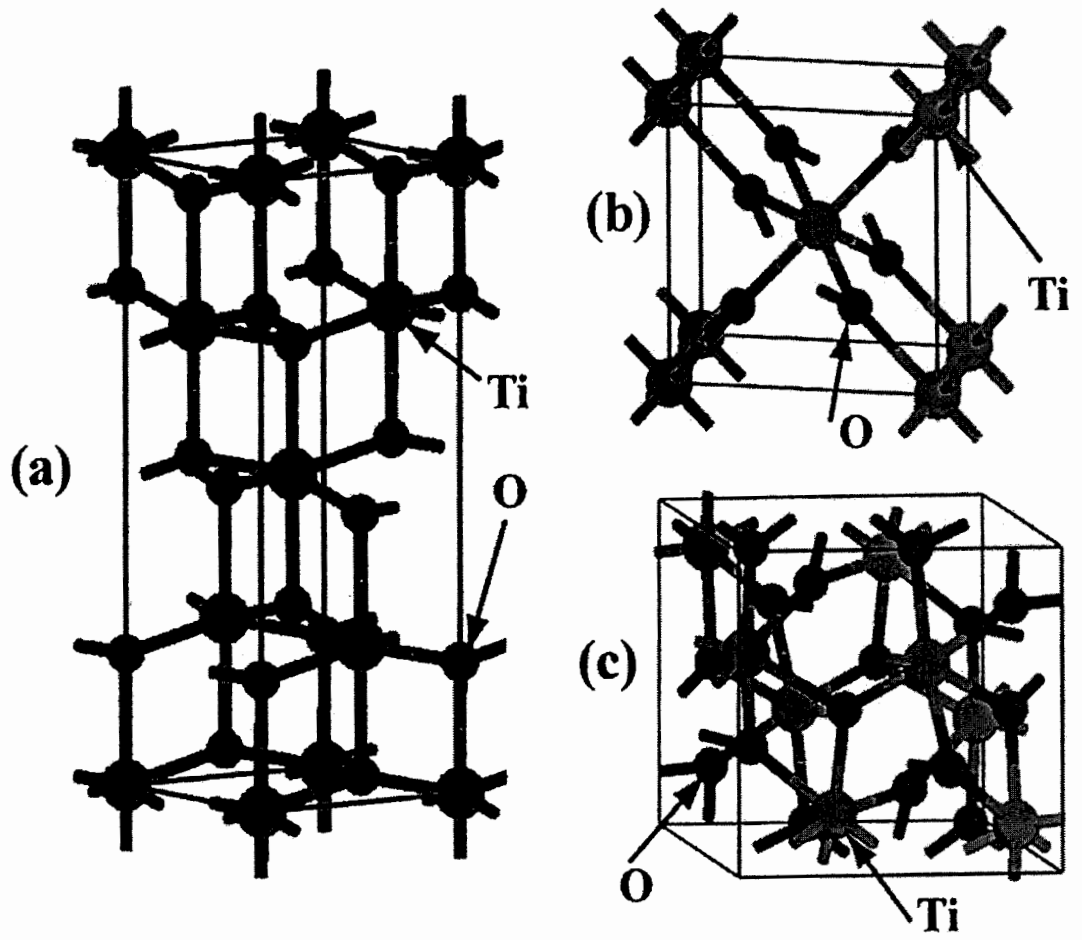


Figure 2.1 A schematic diagram of TiO₂ structure: (a) anatase phase (b) rutile phase and (c) brookite. [27]

Table 2.1 Physical and structural properties of anatase and rutile TiO₂.

Property	Anatase	Rutile
Molecular weight (g/mol)	79.88	79.88
Melting point (°C)	1825	1825
Boiling point (°C)	2500-3000	2500-3000
Light absorption (nm)	< 390	< 415
Mohr's Hardness	5.5	6.5-7.0
Refractive index	2.55	2.75
Dielectric constant	31	114
Crystal structure	Tetragonal	Tetragonal
Lattice constant (Å)	a = 3.78	a = 4.59
	c = 9.52	c = 2.96
Density (g/cm ³)	3.79	4.13
Ti - O bond length (Å)	1.94 (4)	1.95 (4)
	1.97 (4)	1.98 (2)

The crystal structure of anatase and rutile is tetragonal while the brookite has an orthorhombic structure as shown in Figure 2.1. Since brookite is less studied and does not play a considerable role in many of the titania dioxide applications, we will focus only on the anatase and rutile phases. The physical properties of TiO₂ are shown in Table 2.1.

2.2 Crystal structure of TiO₂

Anatase, rutile and brookite phases are three main crystalline TiO₂. In this work, we focus on the first and second of two main crystallites because they have an effect to the optical and electronic properties of films serving as photoanodes. Anatase, rutile and brookite phases are shown in Figure 2.1. In titania polymorphs, the basic building blocks consist of a titanium atom surrounded by six oxygen atoms in a more or less distorted TiO₆ octahedral configuration. Crystal structures differ by the distortion of each octahedral and by the assembly patterns of the octahedral chain.

In rutile, neighboring TiO₆ units share corner, being stacked with their long axis alternating by 90°. Anatase framework consists of strongly distorted edge sharing TiO₆ octahedral. Corner sharing and edge sharing octahedral units give rise to the three-dimensional network of TiO₂-B. Differences in mass density and electronic band structure are explained in terms of the different lattice structures. The anatase and TiO₂-B phases are known to be thermodynamically less stable than the rutile phase so that they are transformed into the other phases at high temperature. It is generally accepted that anatase is the most photoactive form of titania [28]. The bulk structure of titania networks is quite complex with various types of intrinsic defects including oxygen vacancies. Such as oxygen deficiencies implied the presence of some Ti (III) centers that behave electron-donating species, providing an n-type character to the semiconductor.

The phase change from amorphous to the crystal anatase and rutile phase occurs when titania are treated with the increased temperature or heat treatment although the anatase and rutile are stable structures at low and high temperature, respectively. The amorphous can convert to anatase with heat treatment higher than approximately 280 °C and mixed anatase and rutile at higher temperature than 430 °C. Figure 2.2 is indicated that TiO₂ nanotubes being nanocrystallines after annealing or heat treatment. The exhibition of Glancing angle X-ray diffraction patterns of the nanotube array samples were annealed at temperatures ranging from 230 °C to 880 °C in dry oxygen ambient for three hours.

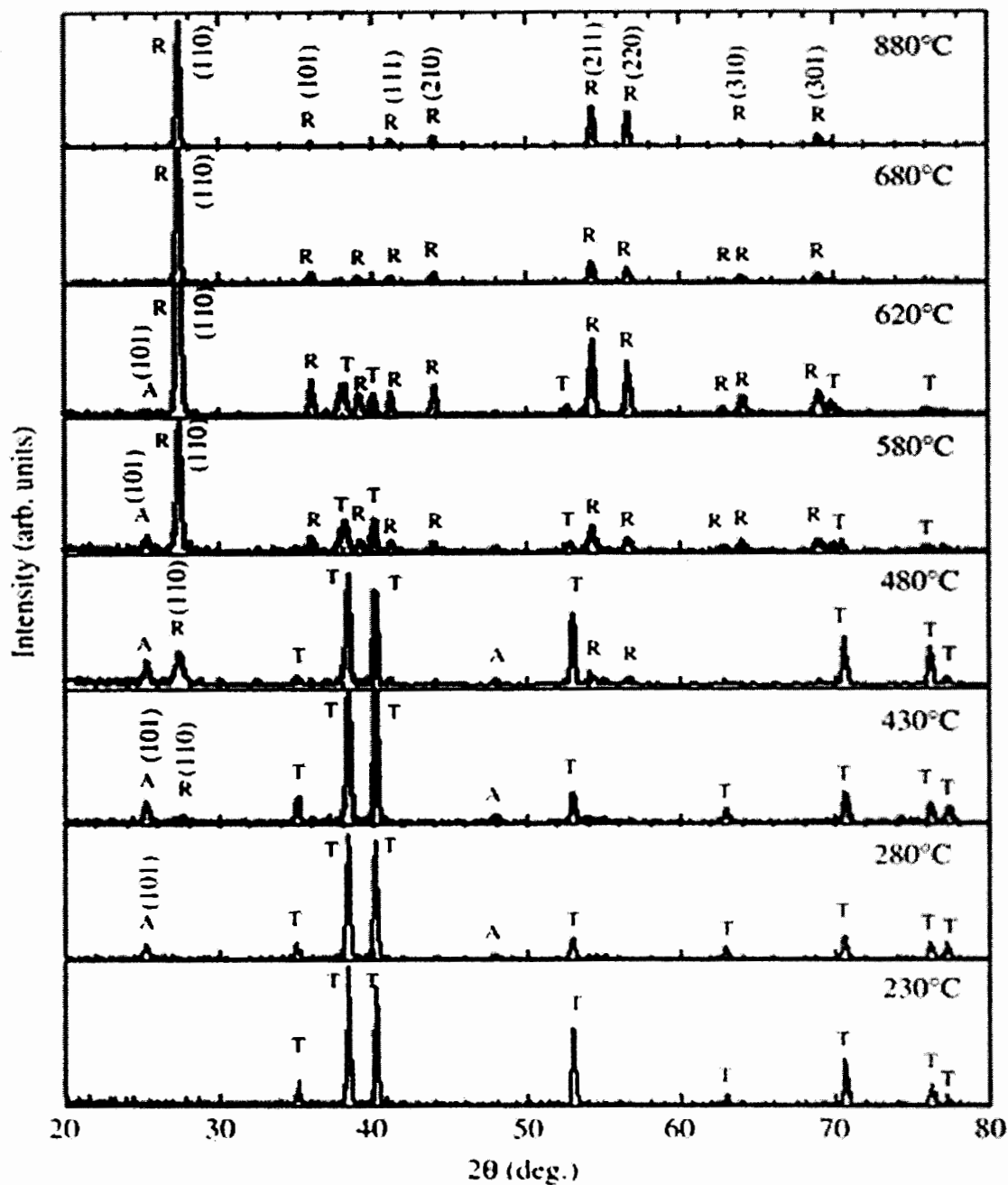


Figure 2.2 Glancing angle X-ray diffraction patterns of the nanotube arrays annealed at temperatures ranging from 230 to 880 °C dry oxygen ambient for three hours A, R and T represent anatase, rutile and titania respectively. [29]

2.3 Semiconducting properties of TiO₂

We can understand the properties of semiconductors by chemical interpretation of the band theory to show Figure 2.3. On this theory, at 0 K, a perfect crystal of a semiconductor material possesses a group of very close filled electronic states (valence band, VB) and another group of close empty electronic states at higher energies (conduction band, CB). A region where no electronic states are available (band gap) exists between the VB and the CB.

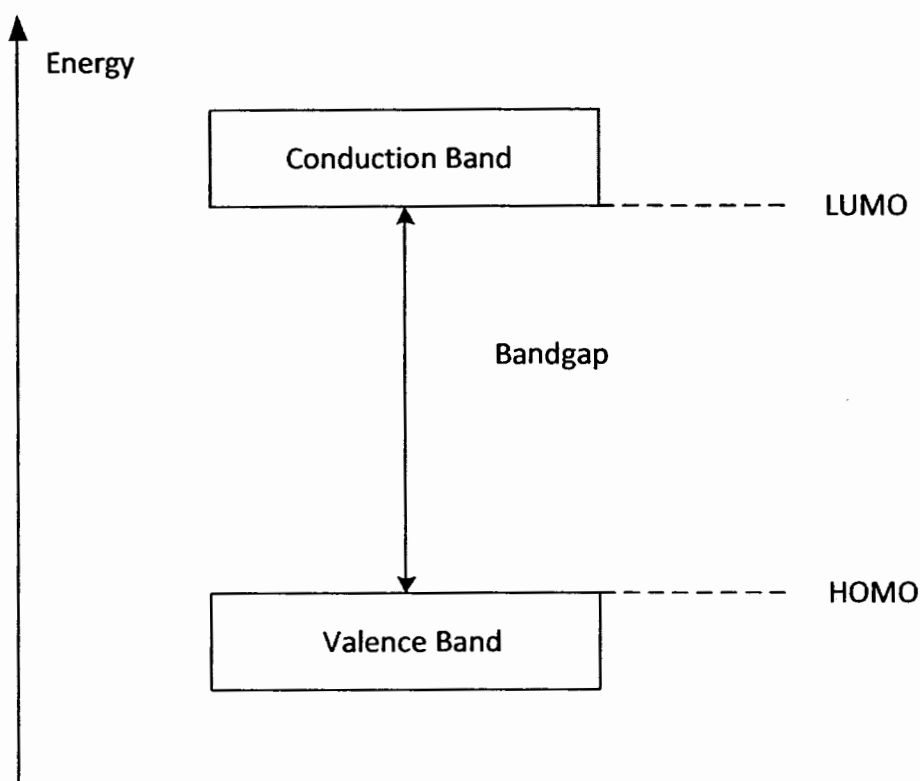


Figure 2.3 A schematic diagram shows the band gap of semiconductor.

Titania is a wide band gap semiconductor material around 3.0 - 3.2 eV depending on the crystalline phase [30], capable of converting energy from the sunlight into chemical redox energy. When a photon with an energy equal higher than the band gap of the semiconductor incidents an electron, the electron from the VB is promoted into the CB leaving a hole behind. The number of photogenerated electron-hole pairs depends on the semiconductor band structure as well as the photon energy and the effective intensity of the incident light.

For redox potentials associated to the conduction and valence bands of titania define thermodynamic requirements for interfacial electron transfer reaction in figure 2.4. While titania electron conduction band is a moderate reducing agent, hole valence band possesses strong oxidizing power. In order to generate an electron acceptor, titania can be spontaneously photoreduced. The CB reduction potential of the A/A^- pair occurs. Following a similar reasoning, photo energy is supplied to assist the oxidation of an electron donor D. The potential of semiconductor VB must be more positive than the reduction potential of D^+/D pair. Therefore, assuming no kinetic limitations, light-induced semiconductor-assisted interfacial redox reactions will take place with acceptors and electron donors whose respective reduction potentials are comprised between CB and VB band positions. TiO_2 are inert, low-cost and low-soluble. TiO_2 are situated in the position of applications based on semiconductors.

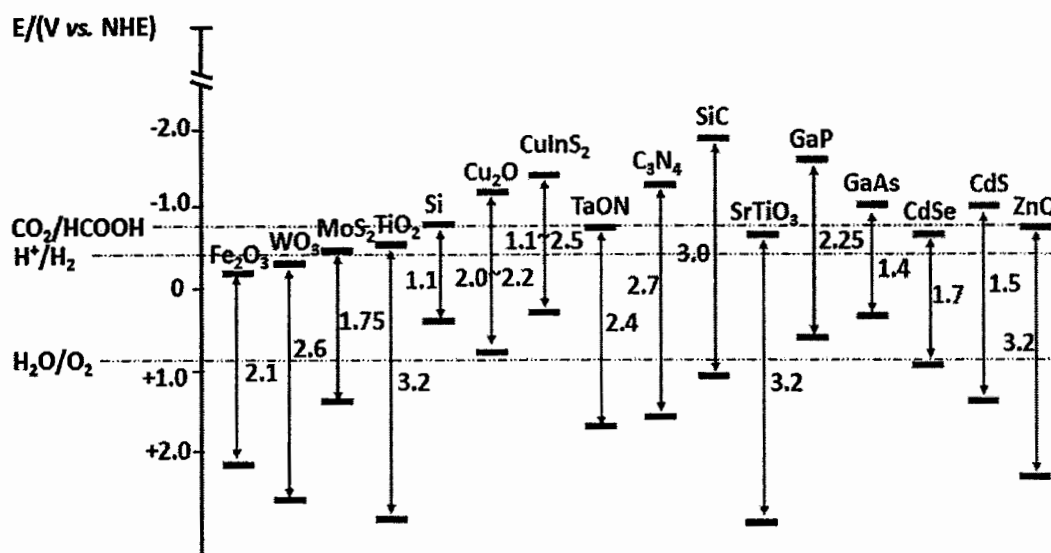


Figure 2.4 A schematic shows energy gap values of some Semiconductor materials. [31]

2.4 The photocatalytic of Titania dioxide

Titania dioxide (TiO_2) also known as titania, is an important commercial product that has been used in many commercial application that range from industrial to cosmetic. On a research level it is interested for water splitting solar photovoltaic cell and water or air remediation. Many studies used TiO_2 as photocatalysts for water to produce hydrogen. Even though the crystal lattices of rutile and anatase are similar but

there are a few significant differences. Band gaps of rutile and anatase are 3.02 eV and 3.2 eV, respectively. Rutile and anatase also have different numbers of active site. A common observation is that for anatase good photocatalytic activity is observed while rutile shows good photocatalytic activity in some and almost zero activity in other studies. The small difference of band gap between rutile and anatase cannot explain their different activities. A main difference is their recombination rate of photoinduced electrons and holes that anatase is higher than rutile. Often heat treatment at high temperatures is used to obtain the rutile phase resulting in the irreversible loss of surface hydroxylation and increased crystal growth of which decrease the photocatalytic activity of TiO_2 . On the other hand a combination of the two crystal phases can lead to an enhancement of the photocatalytic activity. The recombination of anatase and rutile is the P25 powder from Degussa (commercial name) which has become a reference powder photocatalyst. Photoinduced processes on TiO_2 are characterized by the presence of photoinduced phenomena. All these photoinduced processes originate from the semiconductor band gap as show in Figure 2.5.

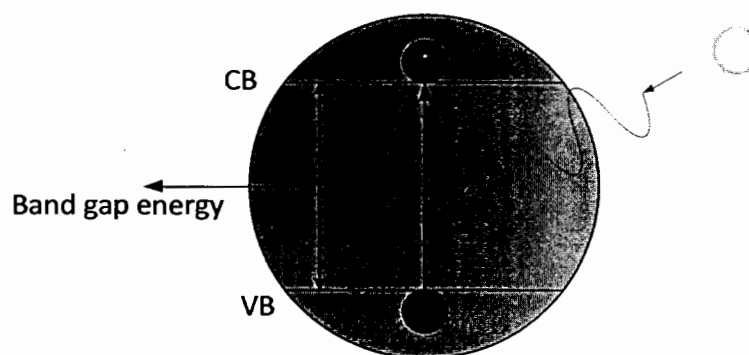


Figure 2.5 Photocatalyst processes on TiO_2 . [32]

When photons have a higher energy than this band gap they can be absorbed and an electron is promoted to the conduction band leaving a hole in the valence band. This excited electron can either be used directly to create electricity in photovoltaic solar cells or drive a reaction which is called photocatalysis. A special phenomenon was recently discovered trapping of holes at the TiO_2 surface causes a high wettability and is termed photoinduced superhydrophilicity (PSH). All photoinduced phenomena involve surface bound redox reaction. TiO_2 mediated photocatalytic reactions are

gaining nowadays more and more importance and this is reflected in the increasing number of publication that deals with theoretical aspects and practical application of these reactions as illustrated in Figure 2.5. By far the most active field of TiO_2 photocatalysis is the photodegradation of organic compounds.

2.5 Formation of TiO_2 nanotube arrays

Electrochemical anodization is a process of oxidizing a bare metallic surface. This oxidation process is done by the effect of applied electric field between this metallic surface and another chemically inert metal when both are immersed in a given electrolyte. The anodization process acts to uniformly oxidize the surface of the required metal. The oxide layer is controlled by many factors; in most cases, the main factors that control the oxide layer properties are the applied voltage, the electrolyte, and the duration time of the anodization process. The anodization can be done through two different setups, two-electrode anodization cell or three-electrode anodization cell as shown in Figures 2.6 (a) and (b).

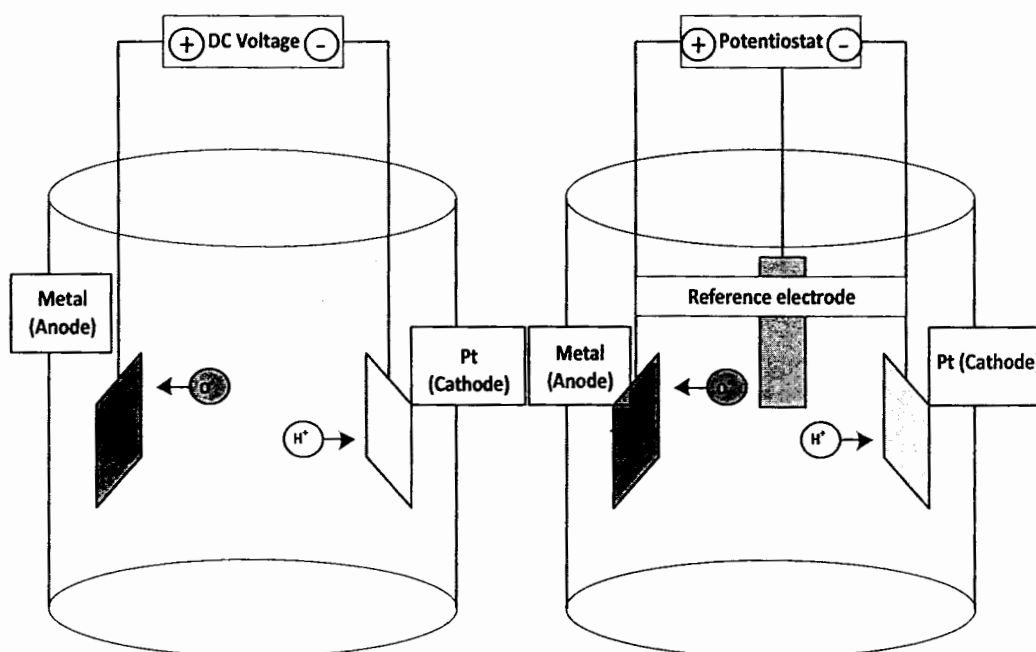


Figure 2.6 Scheme for (A) two electrodes and (B) three electrodes anodization.

In the two-electrode cell, the positive terminal of a DC power supply is connected to the given metal which acts as the anode and the negative terminal is connected to

platinum rod which acts at the cathode. Both anode and cathode are immersed in a specific electrolyte. Under appropriate voltage when the DC power supply is switched on, an electric field is generated in the electrolyte which pulls the positive ions (hydrogen ions) towards the cathode and the negative ions (oxygen ions) towards the anode. At the metal surface, the oxygen ion loses its electrons to the metal atoms and bond with these atoms to form a metal oxide. After the first wave of oxygen ions reach the metallic surface, a metal oxide layer forms and covers the metallic surface. The successive waves of oxygen ions have to diffuse through the recently formed oxide layer to reach the metallic surface underneath and react with those atoms to create another oxide layer under the older one. In time, the oxide layer grows and becomes thick so the diffusion rate is slower and weaker. If this process continues, only the oxide layer will reach a critical thickness where it is impossible for oxygen ions to penetrate to reach the metallic surface. Another process which keeps the anodization reaction going is the dissolution of the oxide layer in the electrolyte. Most electrolytes dissolve metal oxide; in this case, the first layer of the oxide to dissolve is the oldest layer or the first layer formed.

As a result of these two combating reactions, oxidation at the metallic surface and dissolution at the oxide surface, the thickness of the oxide layer is controlled. On the other hand the position hydrogen ions are pulled toward the cathode where it receives electrons and hydrogen gas is formed in the form of gas bubbles. At equilibrium, ionic current is continuously flowing in the electrolyte while electrical current is flowing in the external circuit. The thickness of the oxide layer can be increased by choosing conditions that will make the oxidation rate higher than the dissolution rate, which will slowly increase the oxide layer thickness. This can be observed by noticing the current drop in the external circuit as the oxide thickness increases [33].

2.6 Fabrication of titania dioxide nanotubes by electrochemical anodization

In 1999, Zwillling et al reported for the first time the possibility of fabricating self-organized porous titanium dioxide by electrochemical anodization of Ti-based alloy in an acidic fluoride-based electrolyte [34, 35]. The actual start of this method was in 2001, when Gong et al [36] fabricated self-organized, highly uniform titanium dioxide nanotube arrays by anodizing titania in an aqueous dilute HF electrolyte

[36, 37]. Their discovery opened a huge field of research in mastering the electrochemical anodization method; this was driven by the belief of many research groups that the huge success of electrochemical anodization method in porous aluminum oxide can be achieved in the case of titanium dioxide nanotubes. In less than 10 years researchers were able to refine the methods and enhance the techniques. The methods evolved through four generations, each of which represents an important leap in the fabrication ability namely the nanotube length. In the following sections, we present four generation. Electrochemical anodization method has many advantages over all other fabrication techniques these advantages includes, but not limited to

(1) Simplicity, it is a one step process that starts from a titanium foil and end up with array of titania dioxide arrays.

(2) Scalability, it is applicable for micro scale anodization for research, also extendable to meters in scale for industrial applications without losing control over the nanotube parameters.

(3) Economical favorable, the cost of titanium dioxide nanotubes fabrication through this method is considered the cheapest amongst all other fabrication methods. The cost is just for the price of the titanium foil and the acids, and they can be reused many times until completely consumed.

(4) Control, No other method offers better control over the nanotube parameters than the electrochemical anodization. It has a very narrow distribution of nanotube parameter (nanotube length nanotube diameter and nanotube wall thickness) for each fabrication recipe, and though slightly variation of the fabrication recipe, a very wide range of nanotube parameters can be achieved. It has the ability to precisely tune the nanotube parameters from a wide range of selections.

(5) Structure, One of the fascinating results of this method its ability to order the structure of the nanotubes in precise arrays. This makes it a self-engineered method ready for usage in many anticipating applications.



2.7 Introduction to Dye-sensitized solar cells (DSSCs)

Photoelectrochemical solar cells (PSCs), consisting of a photoelectrode a redox electrolyte and a counter electrode, have been studied extensively. Several semiconductor materials including single-crystal and polycrystal forms of n- and p-Si, n- and p-GaAs, n- and p-InP and n-CdS have been used as photoelectrodes. These materials, when used with a suitable redox electrolyte can produce solar light-to-electricity conversion efficiency of approximately 10%. However under irradiation, photocorrosion of the electrode in the electrolyte solution frequently occurs resulting in poor stability of the cell, so efforts have been made worldwide to develop more stable PSCs [38].

Dye-sensitized solar cell (DSSCs) is a real revolution in solar energy after 40 years of the invention of silicon solar cells. The working mechanism is based on photoelectrochemical mechanism resembling the photosynthesis in plant leaves. The efficiencies of the DSSCs in high as those obtained from amorphous silicon solar cells 10-11% [39]. Thus, to improve light-harvesting efficiencies and cell performance, researchers used two approaches: developing photoelectrodes with larger surface areas that could adsorb large amount of dye and synthesizing dyes with broader absorption ranges. Significant improvements in the performance of dye-sensitized solar cells have been mainly due to the development of high-performance nanoporous TiO_2 thin-film electrodes that have a large surface area capable of adsorbing a large amount of photosensitizers.

Table 2.2 Efficiencies of DSSCs using different dye sensitizer [40].

Dye	Efficiency of DSSCs
N3	11.03%
N719	11.18%
Black dye	11.10%
Z910	10.20%
K77	9.00%
D205	7.20%
C217	10.30%

2.8 The efficiency of dye-sensitized solar cells (DSSCs)

The current-voltage (IV) characteristics of a solar cell under illumination are used to determine the power conversion efficiency. The photovoltaic tests of quasi-solid-state dye-sensitized solar cell are carried out by the ratio of the maximum electrical power output P_{\max} to the solar energy input P . The maximum electrical power output P_{\max} is calculated by the current at the maximum power J_{mp} and the voltage at the maximum voltage power V_{mp}

$$P_{\max} = (J_{\text{mp}} \times V_{\text{mp}}) \quad (2.1)$$

The solar power input is taken as the product of the irradiance of the incident light that is measured in W/m^2 .

$$\eta = \frac{P_{\max}}{P_{\text{light}}}$$

$$\eta = \frac{J_{\text{mp}} \times V_{\text{mp}}}{P_{\text{light}}} \quad (2.2)$$

The fill factor ff is a measure of the quality of the solar cell, and it can be calculated by comparing the maximum short-circuit J_{sc} current and maximum open-circuit voltage V_{oc} to the maximum current J_{mp} and maximum voltage V_{mp}

$$ff = \frac{(J_{\text{mp}} \times V_{\text{mp}})}{J_{\text{sc}} \times V_{\text{oc}}}$$

$$\eta = \frac{(J_{\text{sc}} \times V_{\text{oc}} \times ff)}{P_{\text{light}}} \times 100\% \quad (2.3)$$

When

ff is the fill factor

V_{oc} is the open-circuit voltage

V_{mp} is the maximum voltage

J_{sc} is the short circuit current

J_{mp} is the current at the maximum power

P_{max} is the maximum power

P_{ligh} is the incident light power

η is the energy conversion efficiency

P_{ligh} (100 mW/cm^2) is the solar cell testing standard under terrestrial conditions with air mass 1.5 [41].

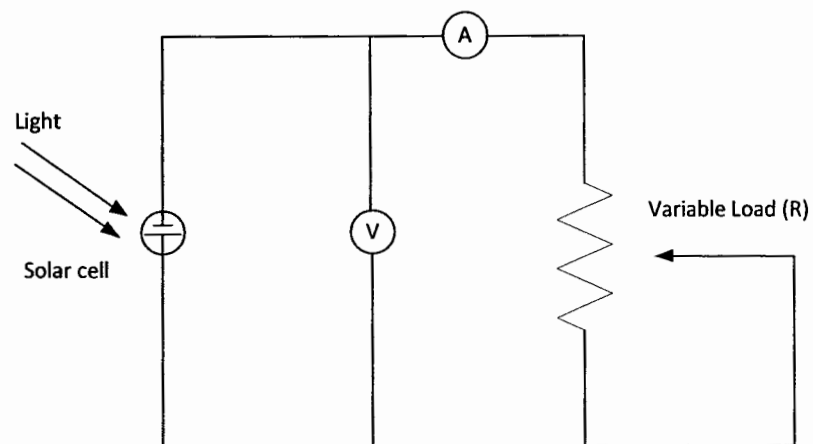


Figure 2.7 Light or solar cell I-V characteristic measurement set up.

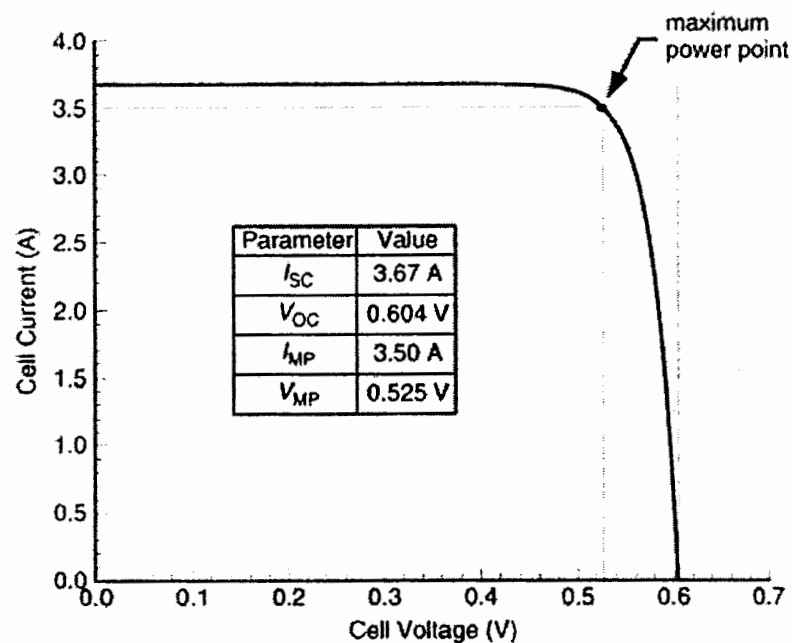


Figure 2.8 I-V characteristic curve of dye solar cell [42].

2.9 Literature Review

The first practical solar cell was developed at bell laboratories in 1954. With the advent of the space program photovoltaic cell made from semiconductor-grade silicon. In the early 1970s, the disruption of oil supplies to the industrialized world led to serious consideration of photovoltaic as a terrestrial power source. The application focused research attention on improving performance, lowering costs and increasing reliability [43]. In 1972 Fujishima and Honda began the application of titanium dioxide (TiO_2) in photocatalytic splitting of water [44]. This discovery was a driving force and motivation to thin films creation and development of other materials. TiO_2 nanotubes can be prepared by anodization method in application dye-sensitized solar cells (DSSCs). The anodization was carried out under the electrolyte of NH_4F and deionized-water in ethylene glycol. DC power supply was used at a constant voltage of 60 Volts at 4 h efficiency is 2.44 %. In addition the anodization at 30 Volts was used in anodization for 16 h efficiency is 1.98% [45]. The different voltage of 20 Volts is longer than 10 volts [46].

Titania (TiO_2) nanotubes were prepared by anodization Titania (Ti) sheet in electrochemical. In the first case a 0.5% (m/m) HF aqueous solution was used and the

anodization at 20 Volts for 30 min. In the second case, a 0.5% (m/m) NH_4F solution in ethylene glycol with 0.9% (m/m) deionized H_2O added was used and the anodization was at 50V for 60 min. The thermal treatments were carried out using a commercial 2.45 GHz/800W microwave oven. The investigated thermal treatment times were 1, 2, 3, and 4 min. Titania (TiO_2) nanotubes obtained on a Ti substrate by anodization in aqueous or organic medium, were successfully crystallized into the anatase phase by microwave-assisted thermal treatment for very short times [47].

Nanoporous TiO_2 layer were prepared in 1% HF solution at 20, 30, 40, and 50 Volts in 30 min. Microporous TiO_2 layer were formed in 1 M H_2SO_4 (98%) electrolyte at 100, 150, 200 and 250 Volts in 10 min. The electrochemical anodization of all samples was carried out by using at DC power supply and at room temperature. TiO_2 layers with nanoporous structures were annealed at 480 °C for 2 h. the samples anodized at 250 Volts and 20 Volts respectively. For the microporous samples it can be concluded that increasing anodization voltage yields better photocatalytic characteristics. On the other hand increasing voltage has a negative impact on the photocatalytic properties of nanoporous samples since the best result was obtained at the lowest anodization voltage [48].

The TiO_2 NTs were fabricated by a two-step anodization process. The first prepared electrolytes consisted of 0.3wt% NH_4F in EG solution with 2 vol% water. In the first-step anodization at 60 Volts for 30 min. The second anodization at 20 to 50 Volts for 1 h. After the two-step anodization the prepared TiO_2 NTs was annealed in air at 450 °C for 1 h with a heating rate of 5°C min⁻¹. Which the honeycombed TiO_2 NTs have been successfully prepared by a two-step anodization adjusting voltages in the second step anodization, the structure parameter of the honeycombed TiO_2 NTs can be tuned. The 1-step honeycombed photocatalytic degradation efficiency TiO_2 NTs [49].

Recent Zhang et al. reported a high power conversion efficiency of 11.5–12.8% with cyclopentadithiophene-benzothiadiazole derivatives [50]. This research group cografted the dyes having poor light absorption abilities, by which they successfully removed the penetration channels for Co (III) redox ions and thereby restricted the charge recombination at the titania surface. The dyes they used contain triphenylamine and benzoic acid moieties on each end of the cyclopentadithiophene-

benzothiadiazole group, where different orders of the moieties generate two different dyes. The high PCE of 12.8% is even comparable to the Ru-based dyes, which proves that metal-free organic DSSCs can be as efficient as conventional DSSCs and sets a new standard for organic DSSCs for peer researchers [51].

CHAPTER 3

EXPERIMENTAL

3.1 Materials and Thin films preparation

We prepared titania (TiO_2) nanotubes by anodization method. The materials used in the experiments consist of Titanium metal sheet (Ti) with 0.25 mm thick 99.7% purity purchased from Sigma Aldrich, ethylene glycol (EG), ammonium fluoride (0.3 wt% NH_4F) and deionized water (2 Vol % H_2O). The materials for growing Titania dioxide (TiO_2) nanotubes were analytical grads. First, Ti metal sheets were cut in circular shape with diameter of 2 cm. The Ti metal substrates were degreased ultrasonically in the solution containing Isopropanol, deionized water and ethanol with duration time 10 – 15 min respectively. Then, the substrates were dried in air and used immediately in the O-ring set the electrolyte and electrodes container. Finally, they connected with a homemade power supply for anodization method. Before the anodization, Ti substrates were mounted in a home-made housing. Only one face of the substrates was contacted with the electrolyte and was anodized. The system consisted of a two-electrode configuration with a piece of highly pure platinum (Pt) counter electrode. The anode electrode was put at the Ti sheet. For, the cathode electrode was put at the platinum counter electrode used in the process.

3.2 Anodization method

Titanium Dioxide nanotubes were preparation by anodization method. The materials used in the experiments consist of Titanium sheet (Ti) with TiO_2 nanotubes were grown by anodization method at room temperature. First, Titanium sheet (0.25 mm thick, 99.7% purity purchased from Sigma Aldrich) were cut in circular shape with diameter of 2 cm and served as substrates. The Ti substrates were degreased ultrasonically in the mixture solution containing isopropanol, deionized water and ethanol. The electrolytes were the mixtures of ethylene glycol (EG), ammonium fluoride (0.3 wt% NH_4F) and deionized water (2 Vol% H_2O) (kept for 5 h before anodization). A constant dc power supply at 50 V was used in anodization for

1 h. Ti substrates were mounted in a home-made housing. Only the face of the substrate in contact with the electrolyte was anodized. The system consisted of a two-electrode configuration with a piece of highly pure platinum counter electrode. The anodized Ti substrates were washed with ethanol and ultrasonically to remove occluded ions from the surface of the TiO_2 nanotubes. The samples were annealed at different temperatures from 300 to 700 °C for 2 h. Samples were studied by X-ray diffraction (XRD) to investigate crystalline phase. Scanning Electron Microscopy (SEM) was used to study the surface morphology of TiO_2 nanotube arrays.

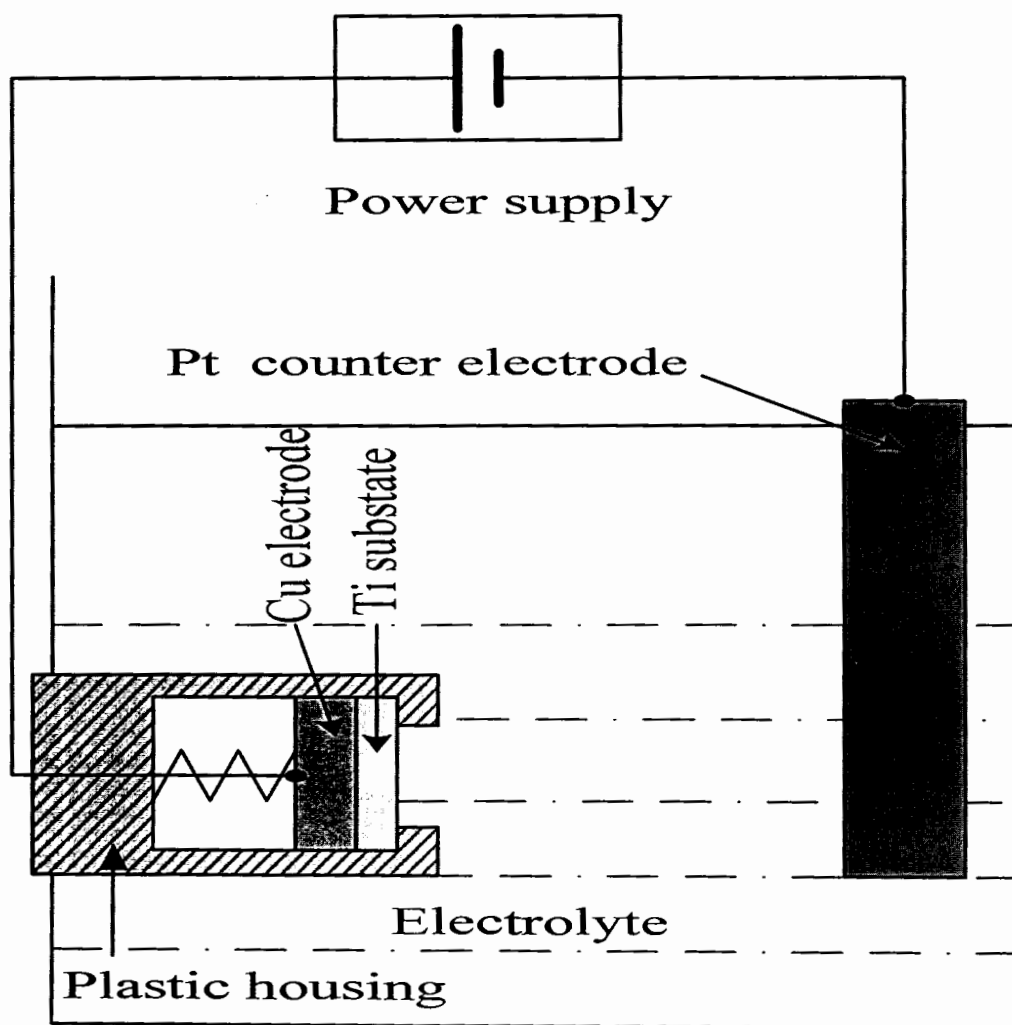


Figure 3.1 The schematic diagram of one-face anodization process.

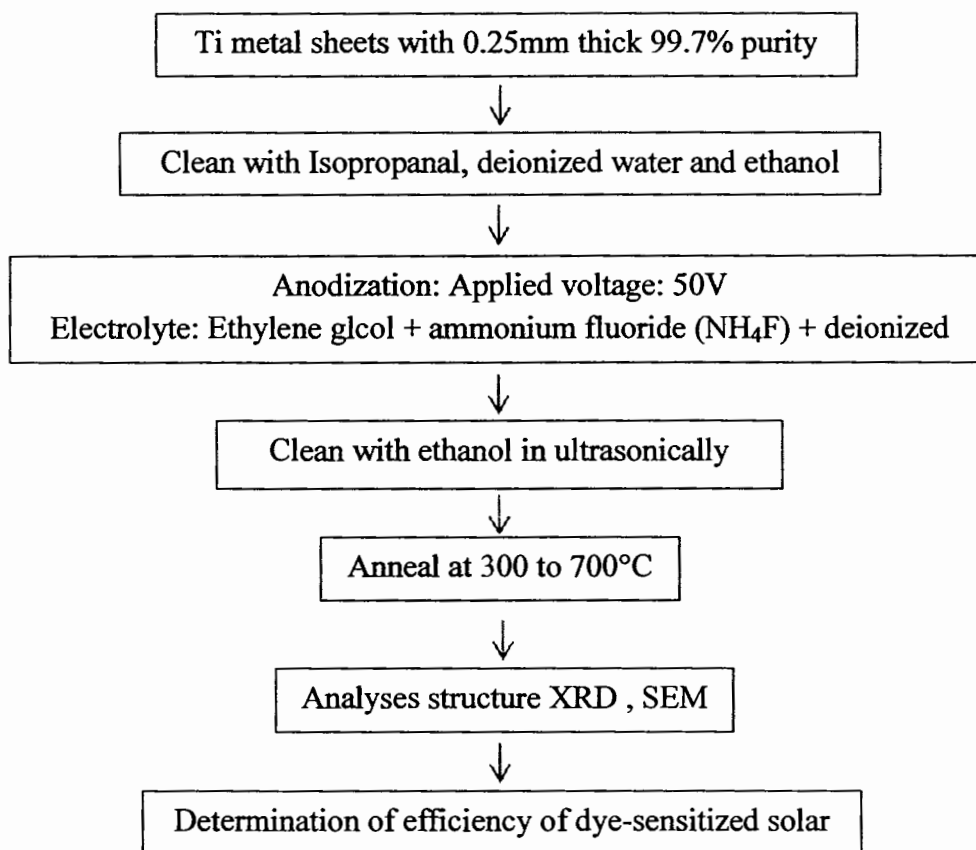


Figure 3.2 Flowchart of preparation of TiO₂ nanotubes by Anodization method for dye sensitized solar cells.

3.3 The characterization of TiO₂ nanotubes

In this work, we used X-ray diffraction (XRD) to investigate crystalline phase TiO₂ nanotube arrays, Scanning Electron Microscopy (SEM) to study the surface morphology of the TiO₂ nanotube arrays.

The crystalline morphology TiO₂ nanotubes were studied crystalline phase, by Scanning Electron Microscopy (SEM) Figure 3.3 shows JEOL JSM-5410 Scanning Electron Microscopy. The morphology of nanostructures was initially characterized with SEM. Figure 4.2. The samples were mounted to samples holder without coating because the samples were conductive materials. The SEM was operated at 30 KV.

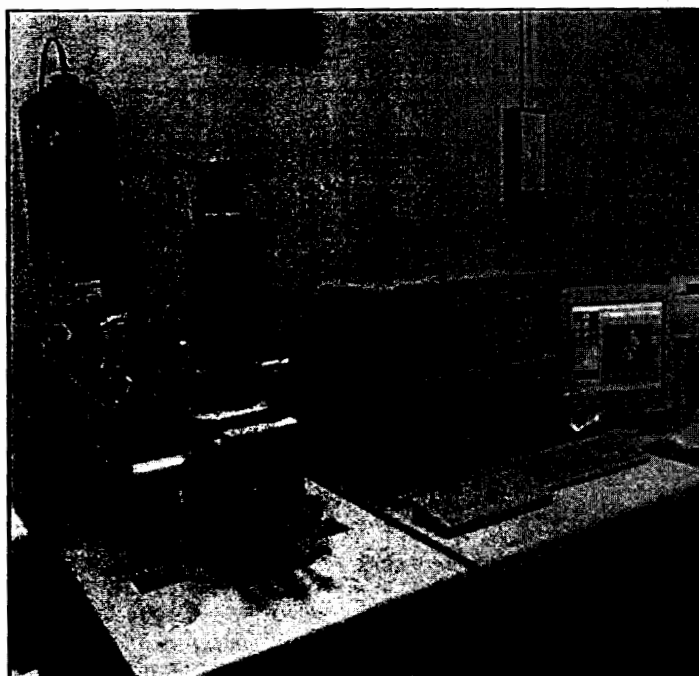


Figure 3.3 A JEOL JSM-5410 Scanning Electron Microscopy (SEM).

X-ray Diffraction analysis (XRD)

X-ray diffraction (XRD) patterns of TiO₂ nanotubes were collected by Philips X'Pert MPD Diffractometer (PHILIPS X'Pert MPD 2000). The PHILIPS X'Pert MPD was operated with scanning angle from 20-80° and condition are 40 kV and 30 mA with Cu K α radiation 1.54 Å. We used program X'Pert High Score to analyze XRD patterns. The data were presented in Chapter 4. The picture of our XRD was shown in Figure 3.4.



Figure 3.4 A Philips X'Pert MPD Diffractometer using $\text{CuK}\alpha$ radiation of a wavelength of 0.154 nm.

3.4 The preparation of dye-sensitized solar cells

When samples were processed through the annealing at different temperatures of 300-700 °C for 2 h, the phases and microstructures of the sample were different.

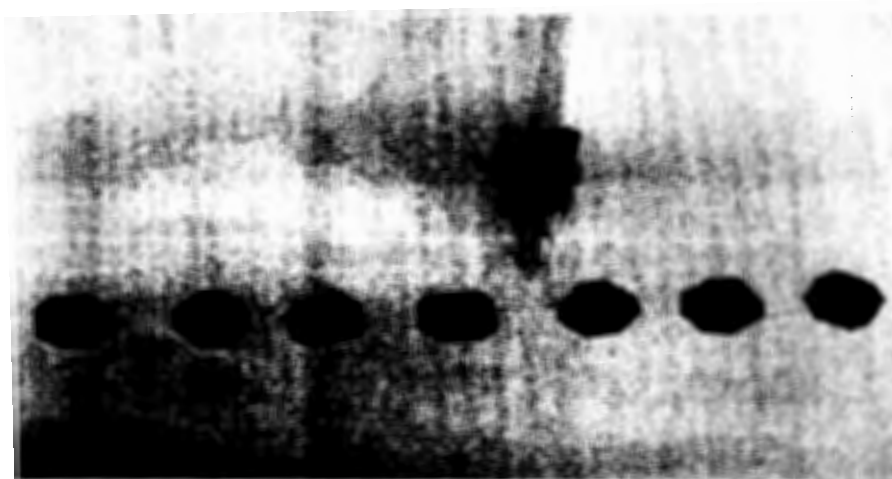


Figure 3.5 annealed at different temperatures of 300-700 °C for 2 h.

TiO₂ nanotube films were immersed in a standard dye solution (N719) for 24 h to absorb the dye adequately then the dye sensitized TiO₂ films were washed up with anhydrous ethanol and dried in moisture-free air.

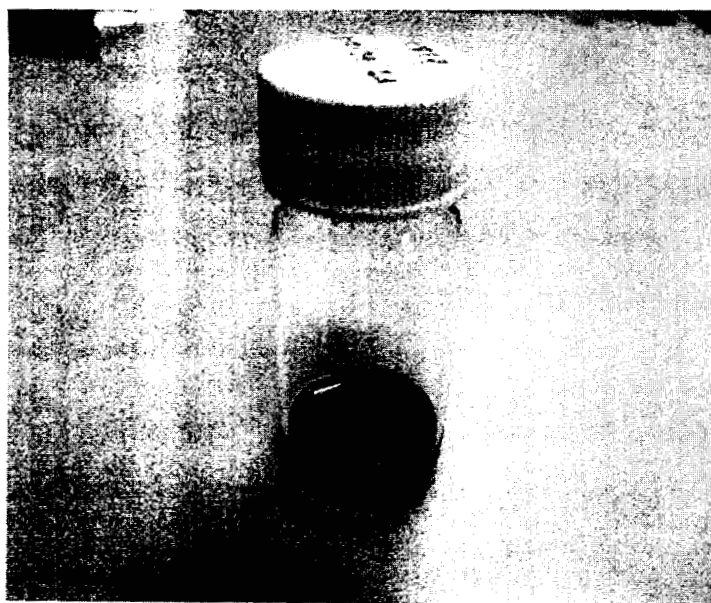


Figure 3.6 TiO₂ nanotube films were immersed in a dye (N 719).

The preparation electrolyte polymer

Firstly the liquid electrolyte polymer was prepared by mixing the amount of ethylene carbonate (EC), propylene carbonate (PC) and γ -butyrolactone (γ -BL) ratio 3:2:1, m/m/m which dissolved by mixture Potassium iodide 0.5 M (KI) with iodine 0.05 M (I_2) then dissolved in electrolyte polymer as described in paper [52]. We dissolved Poly (acrylonitrile-co-styrene) 17 wt% in acetone 50 ml then mixed in electrolyte. Finally mixing 4-tert-butylpyridine (TBP) was homogeneously stirred at temperature of 75-80 °C. We obtained the polymer gel electrolyte polymer. The prepared polymer gel was shown in Figure 3.8.



Figure 3.7 preparation of polymer gel electrolyte.

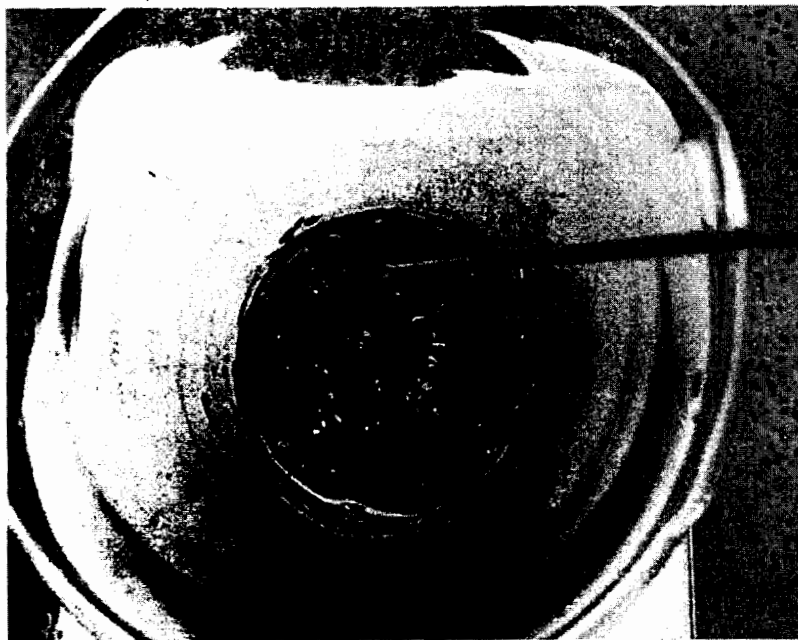


Figure 3.8 Polymer gel electrolyte.

3.5 DSSCs Fabrication

The TiO_2 film electrodes were prepared by anodization method the TiO_2 film electrode was sensitized by immersion into solution of N719 dye in anhydrous ethanol at room temperature for 24 h. The Pt counter electrode was prepared on TCO glass with coating and annealing at $120\text{ }^\circ\text{C}$ for 30 min. A single hole was drilled in the TiO_2 electrode to allow for electrolyte filling. The polymer electrolyte was filled between working electrode (titania nanotubes) and Pt-coated TCO electrode, and clipped together. The DSSCs were obtained by the assembly of the working electrode and counter electrode [53].

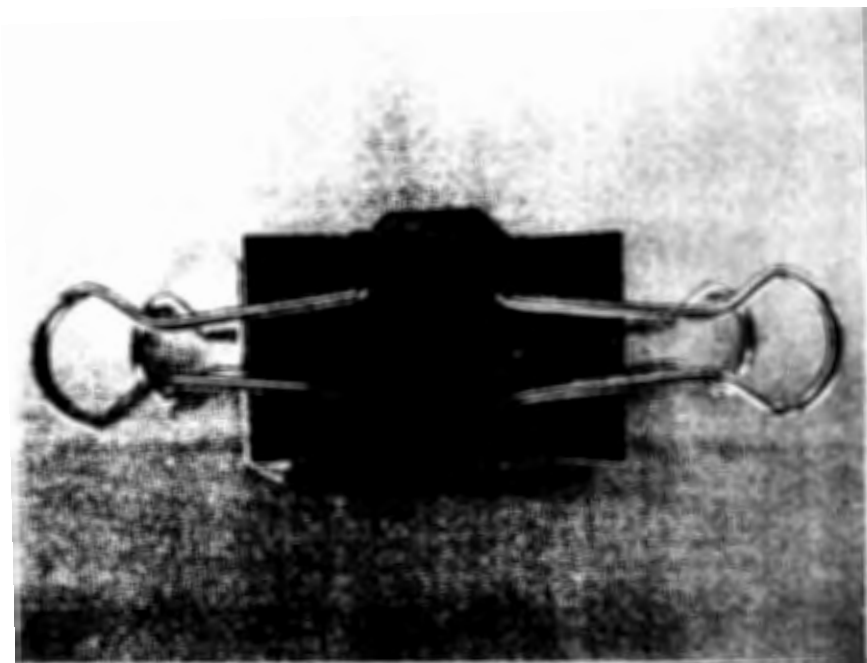


Figure 3.9 Dye-sensitized solar cell (DSSCs).

3.6 Measurement

After IV curves for dye-sensitized solar cells were measured as shown in figure 3.10, we calculated the light-to-electricity conversion efficiency of the dye-sensitized solar cells.

The photovoltaic measurement of the dye-sensitized solar cells were carried out by measure the J-V character curves under sun light of 40 mW/cm^2 and overall areas were 0.25 cm^2 . The data and analysis were presented in Chapter 4. The photoelectronic performances [fill factor (ff) and overall energy conversion efficiency (η)] were calculated by the follow equations,

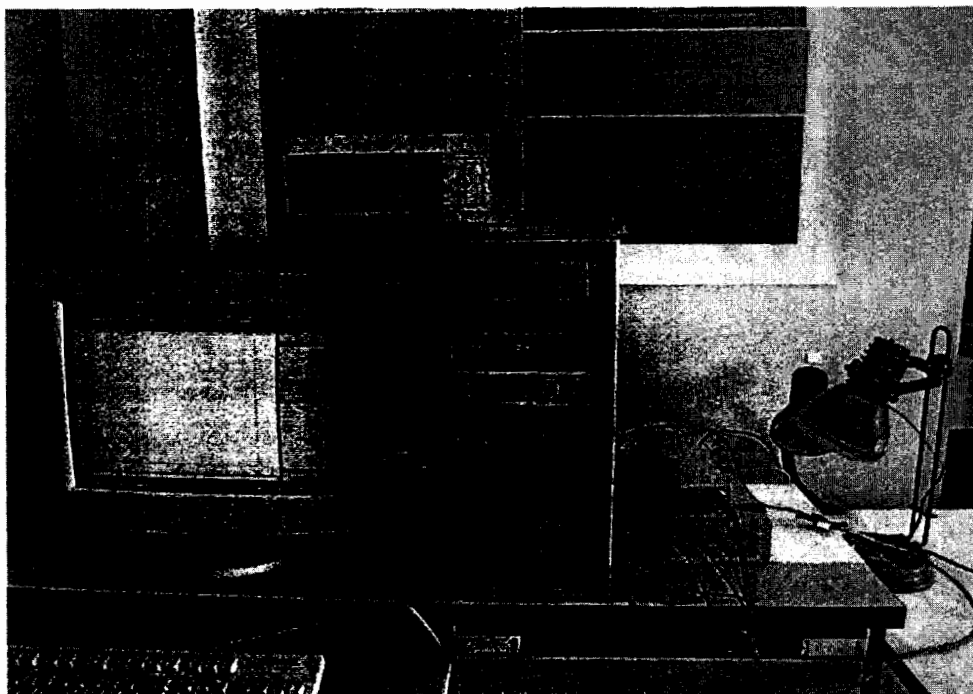


Figure 3.10 measurement efficiency of dye-sensitized solar cells.

CHAPTER 4

RESULT AND DISCUSSION

In this chapter, we present the characterization of TiO₂ nanotubes by X-ray diffraction (XRD) patterns and scanning electron microscopy (SEM) images of TiO₂ nanotubes. Measurements of the conversion efficiency of the dye-sensitized solar cells will be presented and discussed.

4.1 XRD patterns of TiO₂ nanotubes

XRD patterns of TiO₂ nanotubes prepared by anodization without annealing and annealed at different temperatures from 300-700 °C are show in Figure 4.

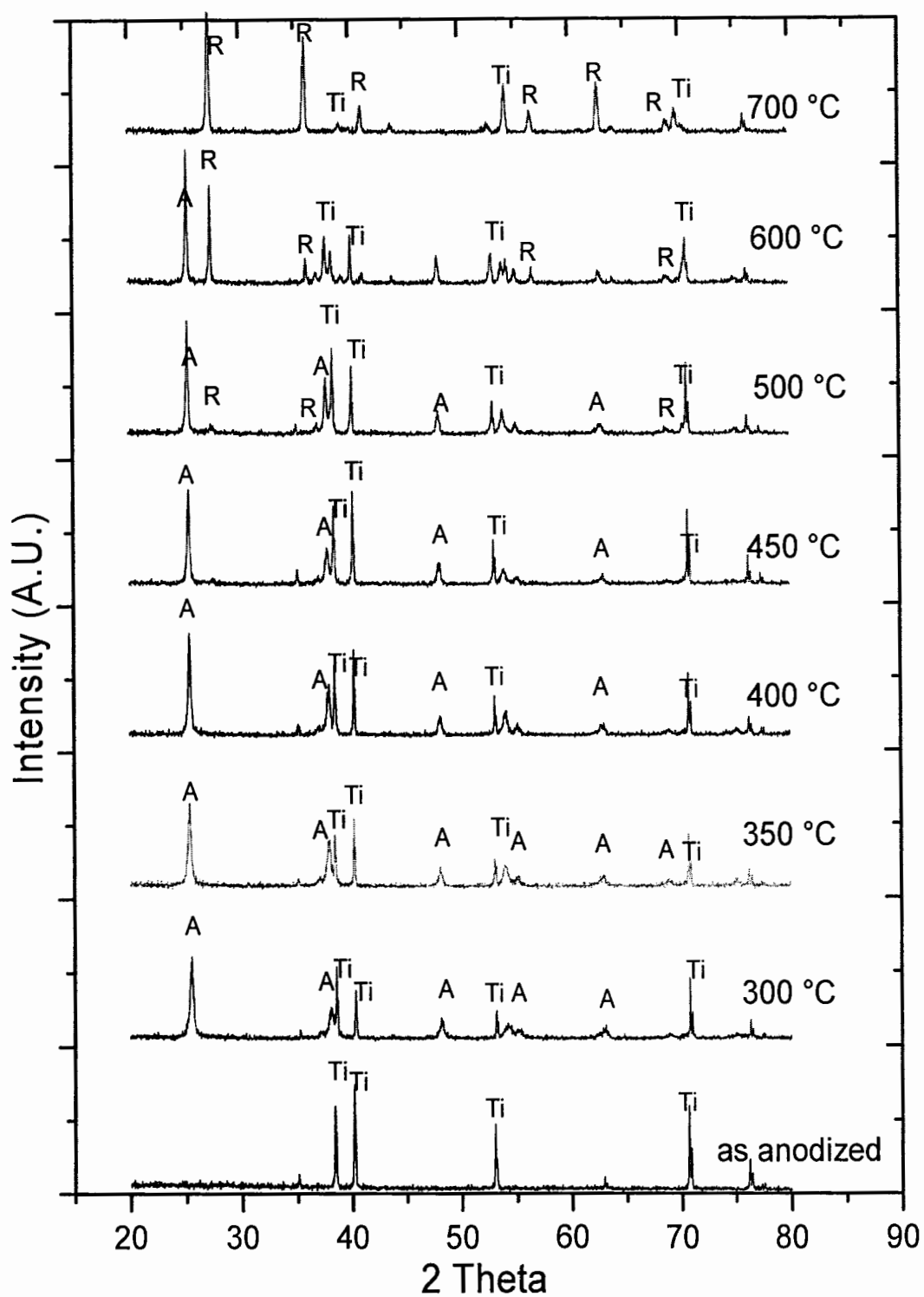


Figure 4.1 XRD patterns of TiO_2 nanotubes grown on a Ti substrate by electrochemical anodization: Ti, (A) anatase TiO_2 , (R) rutile TiO_2 .

Figure 4.1 shows XRD patterns of the TiO_2 nanotubes. Electrochemically synthesized by anodization process before and after annealing sample the absolute-intensity X-ray diffractograms can be seen in Fig 4.1. The phase of the nanotubes is transformed from anatase to rutile when annealing temperature is changed from 450 °C to 500 °C or higher. When the annealing temperatures were 700 °C or higher, the phase of the nanotubes became completely rutile and the nanotubes changed to nanocrystalline.

4.2 SEM images

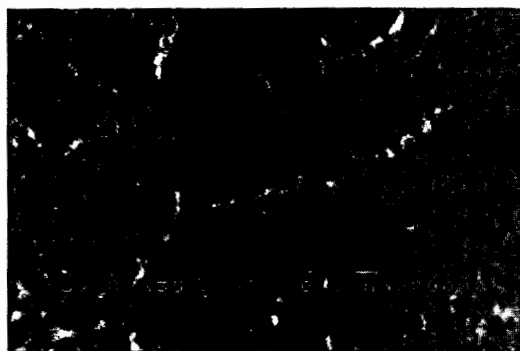


Figure 4.2 SEM image annealed TiO_2 nanotube arrays at 300°C.

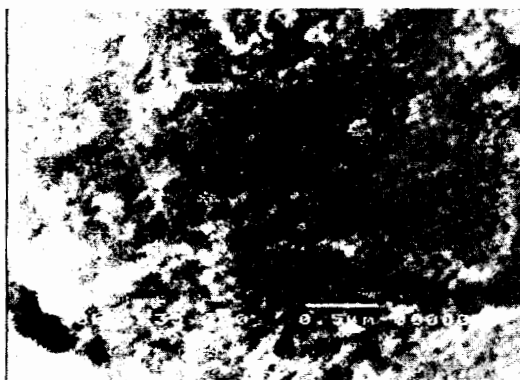


Figure 4.3 SEM image annealed TiO_2 nanotube arrays at 350°C.

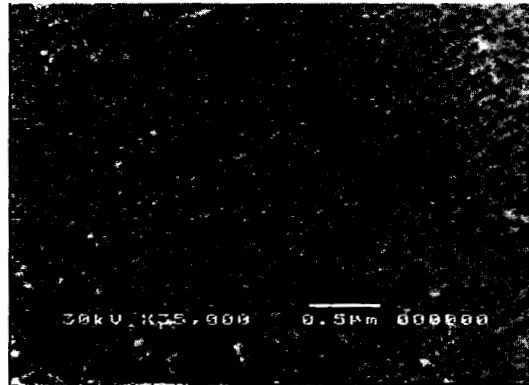


Figure 4.3 SEM image annealed TiO₂ nanotube arrays at 400°C.

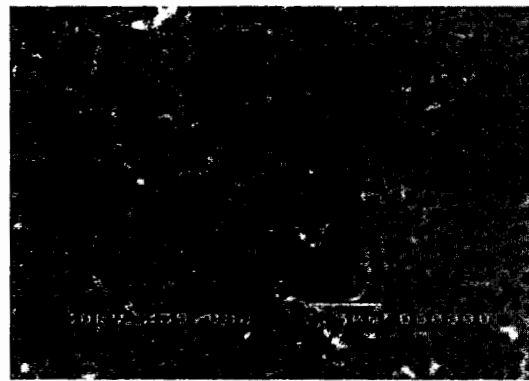


Figure 4.4 SEM image annealed TiO₂ nanotube arrays at 450°C.

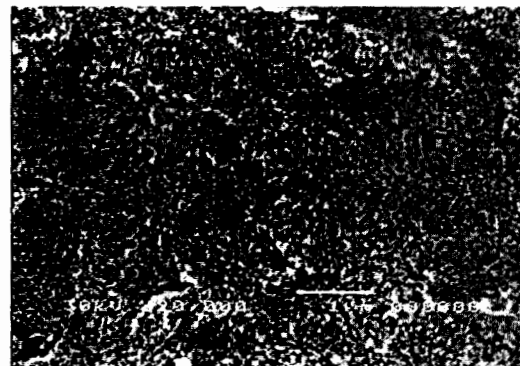


Figure 4.5 SEM image annealed TiO₂ nanotube arrays at 500°C.



Figure 4.6 SEM image annealed TiO₂ nanotube arrays at 600°C.



Figure 4.7 SEM image annealed TiO₂ nanotube arrays at 600°C.

Figures 4.2-4.7 show typical SEM images of TiO₂ nanotube arrays. The well-aligned and uniform TiO₂ nanotubes were observed for all anodization times. It was evident that the TiO₂ nanotubes were small with diameter of about 100 nm. The diameter and the density of the nanotubes are likely to be constant when the annealing temperature increased. The titania nanotubes were transformed to nanocrystalline at 700 °C, as shown in Fig 4.7.

4.3 The efficiencies of the dye-sensitized solar cells

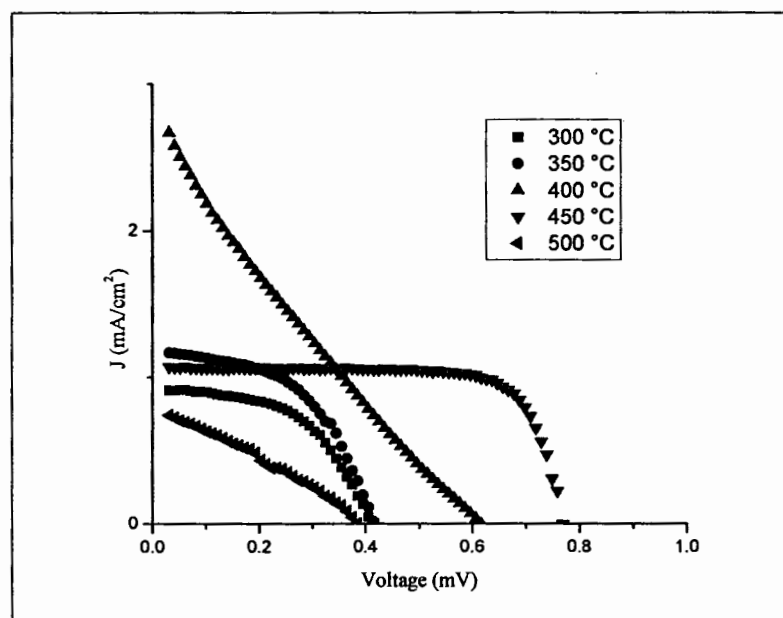


Figure 4.8 I-V characteristic curves of the dye-sensitized solar cells on the TiO_2 nanotubes arrays with different annealing temperatures from $300\text{ }^\circ\text{C}$ to $700\text{ }^\circ\text{C}$.

The conversion efficiencies of dye-sensitized solar cells were measured by current-voltage curves. The I-V curves were showed in figure 4.8. The efficiency was calculated was on current density (current per unit area) based on the area of 0.25 cm^2 . By using the equations (2.2) and (2.3) we obtained the parameters and efficiencies as shown in Table 4.1. The efficiencies of dye-sensitized solar cells increase with increasing anodization time. Increase in anodization time will result in increasing length tubes [54]. Electron transfer will be fast for longer tubes than for shorter tubes. The electron were excited by the incident light and then injected into the conduction band of the TiO_2 . The electrons diffuse rather than the electrons drift that dominates the transport of the electron from the TiO_2 to the transparent electron in dye-sensitized solar cells [55]. As a result the efficiencies of dye-sensitized cells increase with increasing the anodization time.

Table 4.1 The efficiencies of the dye-sensitized solar cells.

Annealing at temperature (°C)	Power (mW/cm²)	Voltage (V)	Maximum current density (mA/cm²)	Fill factor (<i>FF</i>)	Efficiency (%)
300 °C	40	0.27	0.73	0.53	0.20
350 °C	40	0.42	0.92	0.50	0.25
400 °C	40	0.52	1.10	0.23	0.26
450 °C	40	0.54	1.00	0.74	0.53
500 °C	40	0.15	0.35	0.30	0.05
550 °C	40	-	-	-	-
600 °C	40	-	-	-	-
700 °C	40	-	-	-	-

When the annealing different temperatures increase from 300 °C , 350 °C, 400°C, 450 °C, 500 °C, 600 °C, 700 °C the measured conversion efficiencies of the dye-sensitized solar cells are 0.200 %, 0.251 %, 0.260 %, and 0.530 %, respectively. The efficiencies of the dye-sensitized solar cells of annealing with 450 °C the best efficiencies are 0.530 %.

CHAPTER 5

CONCLUSIONS

5.1 Conclusion

In this work, we have prepared TiO₂ nanotube films by anodization method. The as anodized samples were amorphous. The samples were annealed at different temperatures from 300°C, 350°C, 400°C, 450°C, 500°C, 550°C, 600°C, and 700°C. The amorphous TiO₂ nanotubes were recrystallized and transformed to an anatase phase by annealing at certain temperature. The SEM was used to study the morphology and XRD was used to investigate microstructure and phase of TiO₂. The best phase transformation occurs at temperature about 450°C. Pure anatase phase of the nanotubes was achieved when annealed at 450°C. The nanotubes changed to a rutile phase when the annealing temperatures were increased and became pure rutile when annealing at 700°C or higher. Besides the crystalline phases changed, the morphology structure also changed from nanotubes to nanocrystalline at 700°C or higher.

We have achieved the fabrication of dye-sensitized solar cells of TiO₂ nanostructures. The working anodes of the DSSCs were made of titania nanotube arrays while counter electrodes were made from Pt-coated TCO. We also prepared polymer electrolyte and used as electro suppliers for DSSCs. The energy conversion efficiency was carried out under illumination of 40 mW/cm². The conversion efficiencies of the dye-sensitized solar cells were annealed at different temperatures from 300°C, 350°C, 400°C, 450°C, 500°C, 550°C, 600°C, and 700°C were 0.200%, 0.25%, 0.26%, 0.530%, 0.05%, 0%, 0%, and 0%, respectively. These results indicated that the highest efficiency of 0.530% for the dye-sensitized solar cells is obtained when the samples were annealed at 450 °C.

5.2 Suggestion

The efficiencies were low because of several problems. First, we observed that the samples with highest current density behaves similar to a battery and has high internal

resistance and voltage drops suddenly. This problem may be the effect of cell assembly and the resistance of the polymer electrolyte. Further study should focus on the conduction of the polymer electrolyte and awareness of the cells assembly. Second, some of the prepared samples were cracked and ununiformed. These may cause the increase the internal cell resistance that results in decreasing of photocurrent. Further study should improve the homogeneity of the nanotubes film arrays.

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APPENDIX

PUBLICATION/PROCEEDING

PUBLICATION

1. **N. Kodtharin**, R. Vongwatthaporni, and U. Tipparach, "Preparation and " The Phase Transformation and Structures of Titania (TiO₂) Nanotubes Arrays Prepared by Anodization Method", The 4th UBRU International Research Conference An Integration of ASEAN Local Wisdom to International.
2. R. Vongwatthaporni, **N. Kodtharin**, and U. Tipparach. "The Synthesis and Structure of Anodized Titania Nanotubes for Energy conversion Materials", Advance Materials Research, Volume 1105, 2014, Pages 220-224.
3. E.Nyambod Timah, **N. Kodtharin**, and U. Tipparach. "Photocatalytic Performance of Fe-doped TiO₂ Nanotubes in DSSCs", The 3rd Southeast Asia Conference on Thermoelectrics.

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