UNIVERSITI TEKNOLOGI MARA

NANOSTRUCTURED TITANIUM DIOXIDE THIN FILM FOR DYE-SENSITIZED SOLAR CELL APPLICATIONS

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Abstract

Nanostructured Titanium Dioxide (TiC^) thin film for Dye-Sensitized Solid State Solar Cell (DSSSC) application has been synthesized using sol-gel method and deposited onto silicon and glass substrates using spin coating technique. The optimized annealing temperature and sol-gel concentration were obtained a| 500°C and 0.2M, respectively. Basically, there were four properties studied; surface morphology, structural, electrical and optical properties. Field Emission Scanning Electron Microscopy (FE-SEM) / Scanning Electron microscopy (SEM) were carried out to observe the changes in surface morphology whenever there are changes on the parameters. X-Ray Diffractions (XRD) characterization of the samples was taken to examine the TiC>2 crystalline phases and the intensity of nanocrystalline particles in the thin film. I-V measurement using two-point probe equipment was used to observe the electrical properties which include the measuring of the sheet resistance, the resistivity and the conductivity of the TiC>2 thin film. The optical properties were observed using UV-Vis-NIR spectrophotometer. The thin film transmittance and the band gap energy were also observed using this spectrophotometer. At the end of this research, uniform and homogeneous TiC>2 thin film has successfully prepared. By controlling the sol-gel concentration, a transparent TiC>2 thin film has been developed which has high transmittance property of above 80%. The TiC>2 thin films which were annealed at a temperature of 500°C and prepared at 0.2M of sol-gel precursor concentration gave the optimum results. By adding TiC>2 nanopowder, the surface area and porosity of TiC>2 thin film is improved, thus good candidate to use in DSSSC application.

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LIST OF ABBREVIATIONS

Ti02	Titanium Dioxide
DSC	Dye-Sensitized Solar Cell
Cul	Copper Iodide
TCO	Transparent Conductive Oxide
DSSSC	Dye-Sensitized Solid State Solar Cell
DSESC	Dye-Sensitized Electrolyte Solar Cell
CuSCN	Copper(I)thiocynate
TTIP	Titanium Isopropoxide
TBOT	Titanium Butoxide
EG	Ethylene Glycol
PV	Photovoltaic
AR	Anti-Reflection
MOSFET	Metal Oxide Semiconductor Field Effect Transistor
DC-Sputtering	Direct Current-Sputtering
TEOS	Tetraethoxysilane
CVD	Chemical Vapor Deposition
SEM	Scanning Electron Microscopy
FE-SEM	Field Emission-Scanning Microscopy
XRD	X-ray Diffraction

I-V	Current-Voltage
UV-Vis-NIR	Ultraviolet-Visible-Near InfraRed
HF	Hydrogen Fluoride
CRT	Cathode Ray Tube
JCPDS	Joint Committee on Powder Diffraction • Standards
GA	Glacial Acetic Acid
NA	Nitric Acid
HC1	Hydrochloric Acid
TF-GA	Thin Film using Glacial Acetic Acid
TF-NA	Thin Film using Nitric Acid
TF-TTIP	Thin Film using Titanium Isopropoxide
TF-TBOT	Thin Film using Titanium Butoxide

CHAPTER 1

INTRODUCTION

1.1 Background

The search of new source has started as early as in 1839, where Alexandre Edmond Becquerel [1] a French physicist, first discovered the phenomenon of light in electricity conversion by using the photovoltaic effect. It was extensively studied by many researchers until 1973, where Solarex Corporation was established. At that time, Delaware University was the first institution to develop a photovoltaic system. The system was for domestic application and the price of silicon solar cell was $30 per Watt. Since then, the silicon solar cell has the monopoly in the photovoltaic market until 1991, where O'Regan and Gratzel [2] introduced a very promising alternative inorganic pn-junction solar cell using the concept of nanoporous semiconductor material. Semiconducting material that had been used is called nanocrystalline Titanium Dioxide (Ti02) material. Solar cell that was introduced by O'Regan and Gratzel is called dye-sensitized photoelectrochemical solar cell.

The research of dye-sensitized solar cell has attracted many researchers around the world. Improving dye-sensitized solar cell is the first agenda in this recent year. There are some problems that occurred in solar cell produced by O'Regan and Gratzel, which will be discussed in Chapter 2. Due to the problem in Gratzel cell, Tennakone et. al [3,4] have discovered a dye-sensitized solid state cells (DSSSC) which could solve the previous problem. Due to its simplicity and low cost production of DSSSC, this solar cell may overcome the fossil source problem.

As for a country like Malaysia, it has a lot of benefits if the solar energy that we have all year round can be used to overcome the problem as mentioned earlier. In order to improve DSSSC, we must know the configuration of DSSSC and then the

mechanism of the solar cell. The following section will discuss the configuration of DSSSC and its operation on the solar cell.

1.2 Dye-Sensitized Solid State Solar Cells (DSSSC)

1.2.1 Structure of Dye-Sensitized Solid State Solar Cells (DSSSC)

DSSSC that has been discovered by Tennakone et al. [3, 4] consist of 5 different layers; first layer is a transparent conductive oxide (TCO) being used as the electrode, second layer is n-type semiconductor TiC>2 thin film, third layer is dye-sensitizer, fourth layer is p-type Copper Iodide (Cul) thin film and fifth layer is platinum coated glass as the counter electrode. Figure 1.1 illustrates the diagram of DSSSC. Every layer has its function to perform for the DSSSC.

a. Transparent conductive oxide (TCO) layer

   TCO layer react as conductive electrodes which is use to connect from DSSSC to outer circuit to complete the circuit of DSSSC.

b. N-type semiconductor nanocrytalline Ti02 thin film

   Nanostructured Ti02 thin films which act as photoelectrodes have two functions in the dye-sensitized solar cell which is:

   a) It provides the surface for the dye adsorption

   b) It functions as electron acceptor for the excited dye and it serves as electron conductor.

c. Dye-sensitizer

   Dye is photoactive element of the photovoltaic device, harvesting the incident light for the photon-to-electron conversion. The dye should ideally cover a wide range of the solar spectrum. More than 50 % of the solar energy is emitted in the region from 400 to 800 nm.

d. P-type semiconductor nanocrytalline CuI thin film

Copper Iodide (CuI) is one of p-type semiconductor that can use as hole collector in DSSSC.

e. Platinum coated glass as counter electrode

The counter electrode has ideally a high conductivity and exhibits an Ohmic contact to the hole conductor. It is also used to complete the operation of DSSSC.

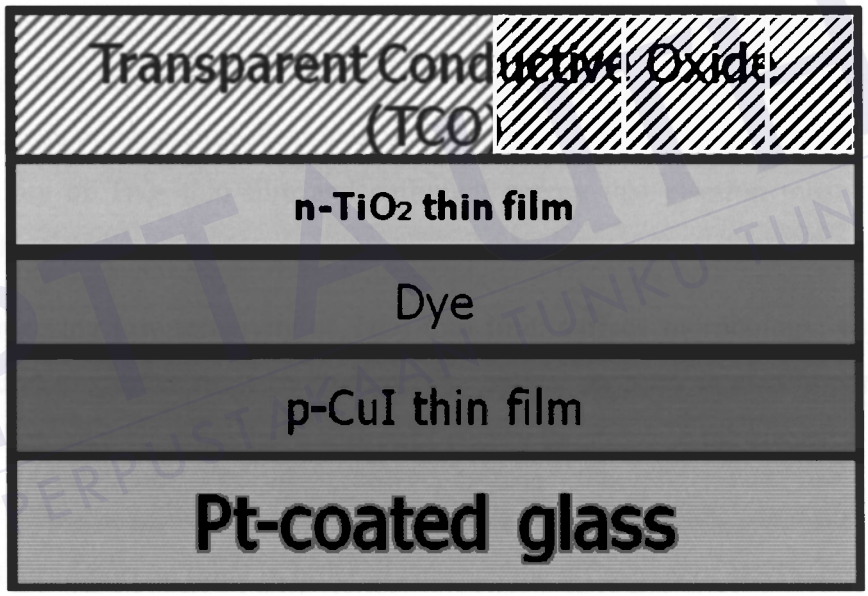


Figure 1.1 Configuration of Dye-sensitized Solid State Solar Cell (DSSSC)

1.2.2 How does DSSSC works?

After knowing the configuration of DSSSC, it is better to understand the operational of DSSSC. Figure 1.2 is the diagram of DSSSC when light is illuminated. We can see that nanocrystalline TiO_2 thin film, dye-sensitizer layer and

Cul thin films are illustrated in nanoparticles images and also the electron transportation route from inside to outside of DSSSC.

The DSSSC works when light is illuminated directly on the top of TCO layer. We understood from previous section, the TCO is transparent. The light will penetrate through the whole cell. When the dye molecules dye in the layer is illuminated, electrons are excited to a higher energy level and injected into the conduction band of n-type semiconductor (Ti02 thin film). After the injection, electrons are transported through the semiconductor to the back contact to perform electrical work in an outer circuit. The electrons subsequently return to the cell via a counter electrode.

The electron movement starts from dye molecule to Ti02 thin film and lastly to the Cul thin film for completing the circuit. The efficiency will improve if as many as electrons can complete the electrical circuit. With this idea, is it important to have low resistivity of Ti02 thin film and sufficient energy that electron must have to complete the circuit.

For preparing low resistivity of Ti02 thin film, surface morphology, electrical and structural properties must be studied. The optical property is also important in order to ensure that electrons have sufficient energy to complete the electrical circuit of DSSSC.

The other important thing in order to enhance the efficiency of DSSSC is to have high surface area and high porosity of nanostructured Ti02 thin film. The nanostructured Ti02 thin film is the film that dye molecule will be adsorb and the electron will injected into conduction band of Ti02 thin film. It is very important to dye molecule to adsorb as many as it can to enhance the efficiency of DSSSC. The nanostructured Ti02 thin film is one of the critical parts in DSSSC application.

In the next section, the problem statements, objectives of the thesis and scope of the thesis will be discussed.

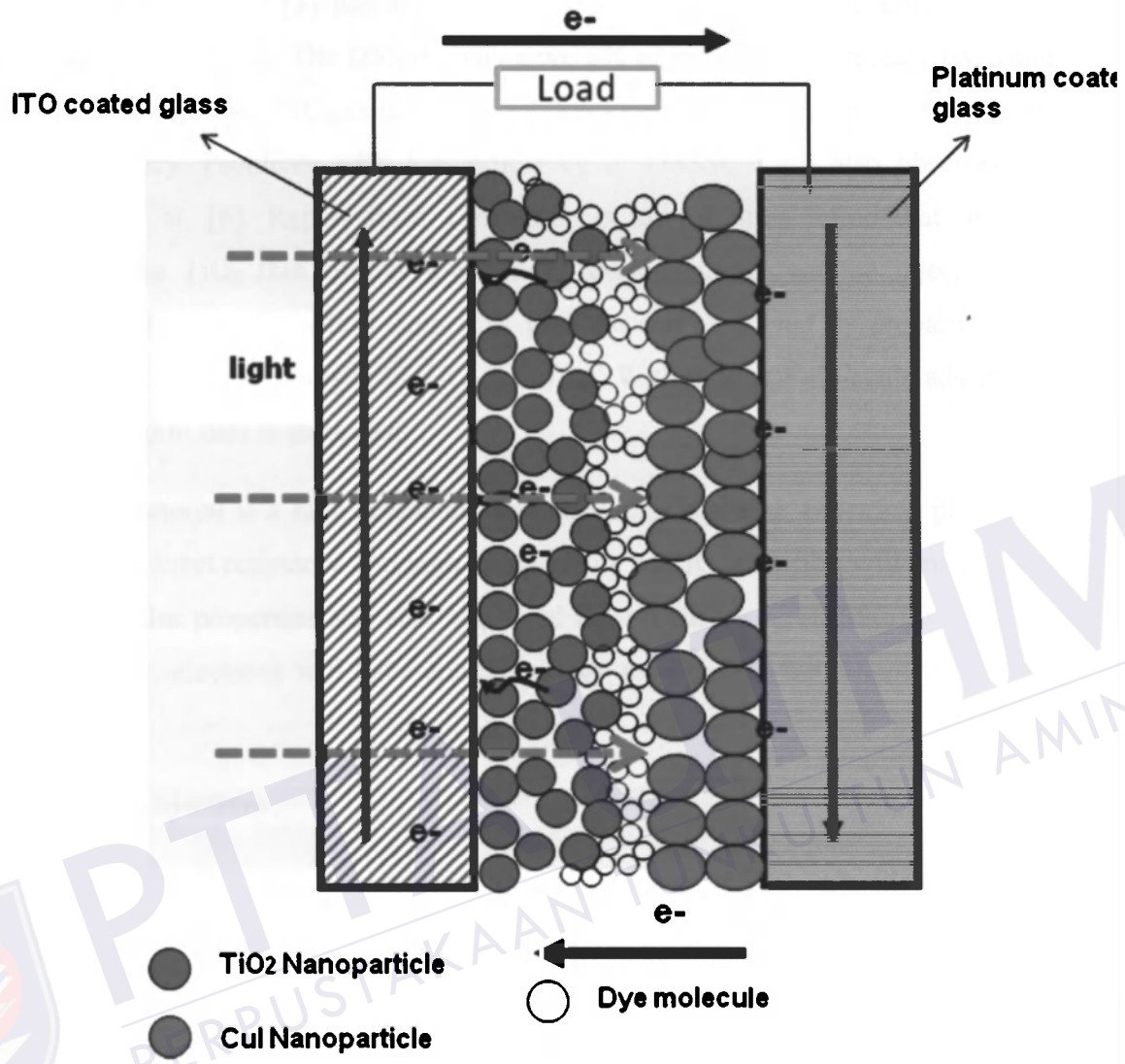


Figure 1.2 Illustration of DSSSC when illuminated with visible light

1.3 Problem statements

The configuration and mechanism of DSSSC have been discussed in the previous section. There are still a lot of works to be done in order to replace fossil source to DSSSC. The biggest challenge is the cell efficiency. Many researchers have provided DSSSC and measured the efficiency but still it is below 10%. It is too low compared to silicon solar cell which has efficiency about 33%.

Tennakone et al. [3] has assembled DSSSC and measured the efficiency for different kinds of dye. The DSSSC only gave 6% of solar cell efficiency. By using different mesoporous TiO_2 thin film, Karthikeyan et al. [5] only got 0.5% of solar cell efficiency. Problems with low efficiency of DSSSC were also observed by O'Regan et al. [6]. Report from Tennakone et al. [3], it is found that the dye adsorption to TiO_2 thin film is low. Thus, fewer electrons can be injected into conduction band of TiO_2 thin film. This problem can be solved by preparing high surface area and high porosity of Ti02 thin film. With this, dye molecule adsorption to the TiO_2 thin film is increased.

TiO_2 material is a high resistance semiconductor material. Electrical properties such as low sheet resistance and high conductivity of TiO_2 thin film will enhance the TiO_2 thin film properties and also improved the efficiency of DSSSC. With better conductivity, electrons will have enough energy to complete the circuit to perform electricity.

1.4 Thesis objectives

The main aim of the research is to prepare transparent TiO_2 thin film which has high surface area and low resistivity of electrical properties. With this thin film, it can be used in DSSSC applications and enhance the efficiency of the solar cell. There are 4 procedures that have been subjected in this research. At the end, it will improve the TiO_2 thin film for DSSSC application. The 4 main procedures of this project are:

i. To prepare nanostructured TiO_2 particles.

ii. To apply the nanotechnology in TiO_2 thin film preparation.

iii. To characterize the electrical, optical and structural properties of TiO_2 thin film.

iv. To obtain optimum parameters of TiO_2 thin film for Dye-Sensitized Solar Cell.

From all of the mentioned procedures, preparation of suitable Ti02 thin films will be achieved. The optimum parameters identified in the experiment for the prepared nanostructured TiO_2 thin film could enhance the efficiency of DSSSC.

There are 8 chapters in this thesis. The introduction to the thesis will be discussed in this chapter, followed by literature review and methodology in Chapter 2 and Chapter 3, respectively. For result and discussion of this thesis, it will be included in Chapter 4 until Chapter 7. Finally, the thesis draws a conclusion and recommendation for future research in Chapter 8.

1.5 Scope and limitation

For the scope and limitations in this research, the focus is only for the preparation of n-type semiconductor nanocrystalline TiO_2 thin film. The method for the preparation of n-type semiconductor nanocrystalline TiO_2 thin film is the sol-gel process and the technique that was used in TiO_2 thin film deposition is the spin coating technique. For the result characterization of TiO_2 thin film, the structural, optical and electrical properties were done to ensure the prepared TiO_2 thin film can be used in the **DSSSC** application and enhance its efficiency.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Dye-Sensitized Solar Cell (DSC)

As mentioned in Chapter 1, the thesis will focus on nanostructured Ti02 thin film that most suitable for DSSSC. In this chapter, we will discuss on nanostructured Ti02 thin film.

In Chapter 1, we understand that DSSSC is one of the photovoltaic effects which are based on a concept of converting solar energy into electricity that has opened wide to alternative energy generation. Today the photovoltaic market is monopolized by silicon solar cell. Although silicon solar cell has efficiency of 33%, but it still have disadvantages and problems to solve. In solid state physics point of view, silicon is not ideal material for photovoltaic conversion as for two reasons:

i. There is mismatch between absorption to the semiconductor and the sunlight spectrum [7].

ii. Silicon is an indirect semiconductor which has valence band maximum and conduction band minimum which are not in same axis to each other in k-space. Light absorption is much weaker in an indirect gap semiconductor than in a direct semiconductor [8].

While look in this problem of silicon solar cell, Gratzel [9] found other solutions to produce photovoltaic device called dye-sensitized photoelectrochemical solar cell.

2.1.1 Dye-Sensitized Electrolyte Solar Cell (DSESC)

Dye-sensitized photoelectrochemical solar cell is also called dye-sensitized solar cell (DSC) and dye-sensitized electrolyte solar cell (DSESC). It is composed of two surfaces of highly transparent conductor material mostly from conducting oxide on glass. On top of the conductor material, there are a few micrometer thick films of wide band gap semiconductor which is formed of a self connected network, highly surface area and porosity which is in nanometer size particles. The energy conversion in the DSC is based on the injection of an electron from a photoexcited state of the sensitizer dye (ruthenium dye) into the conduction band of the nanocrystalline semiconductor, as illustrated in Figure 2.1 [9]. The solar cell employs a liquid electrolyte, usually an iodide or triiodide redox active couple dissolved in an organic solvent which is to reduce the dye cation (regenerate the ground state of the dye).

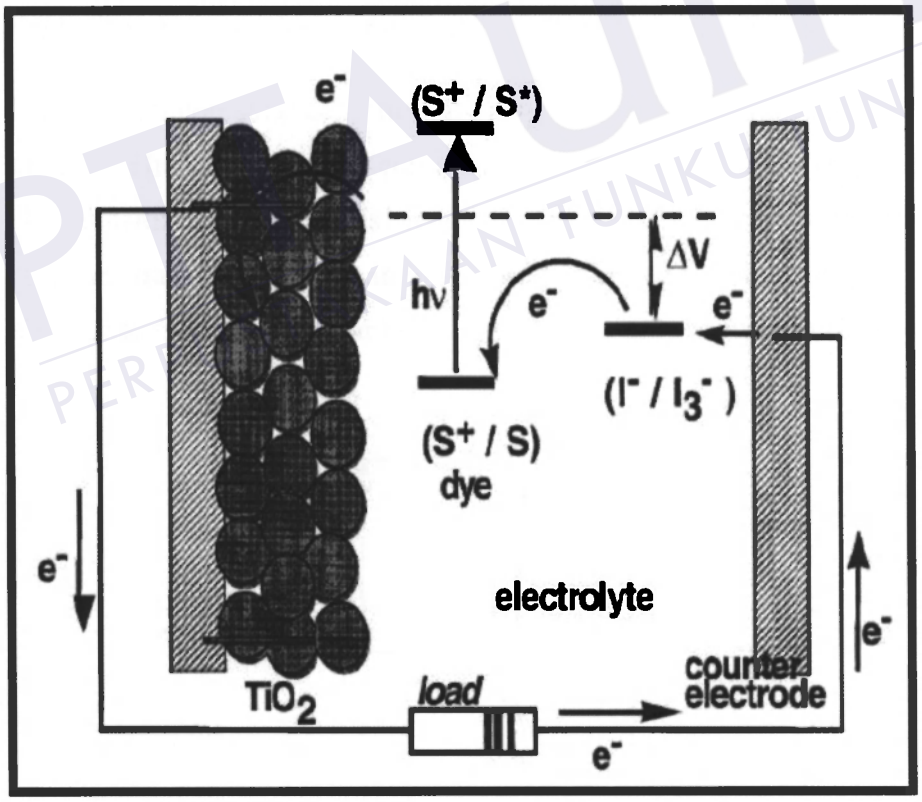


Figure 2.1 Principle operation of Dye-Sensitized Electrolyte Solar Cell (DSESC) [9]

The electricity conversion of DSSSC is differs from the conventional silicon solar cell. Figure 2.2 shows the energy band diagram of a p-n junction after equilibrium of charge carriers. The uncompensated charges caused by the diffusion

of holes to the n region and electron to the p region will formed an electric field at the interface between the n-type and p-type semiconductor which is characterized by the built in potential eV_{bi} . Absorption of photons with an energy higher than the band gap results in the generation of excitons which interact via columbic forces. The excitons recombine after a certain time under emission or photons or heat. The comparison of DSSSC and silicon solar cell as follows:

i. Light absorption and charge carrier transport are separated in DSSSC, where dye layer will acted as light absorber and TiO_2 thin film will be charge carrier transport. For silicon solar cell, both processes are established by the semiconductor in the silicon solar cell.

ii. An electric field is necessary for charge separation in the p-n junction cell. For DSSSC, the sizes of TiO_2 particles are too small to sustain a build-in field. Therefore the charge transport occurs mainly via diffusion.

iii. Inside pn silicon solar cell, minority and majority of carriers coexist in same volume. This will make silicon solar cells sensitive to bulk recombination. Dye-Sensitized solar cell is majority charge carrier devices in which the electron transport occurs in TiO_2 thin film and hole transport in the electrolyte. Therefore, recombination processes only occur at surface.

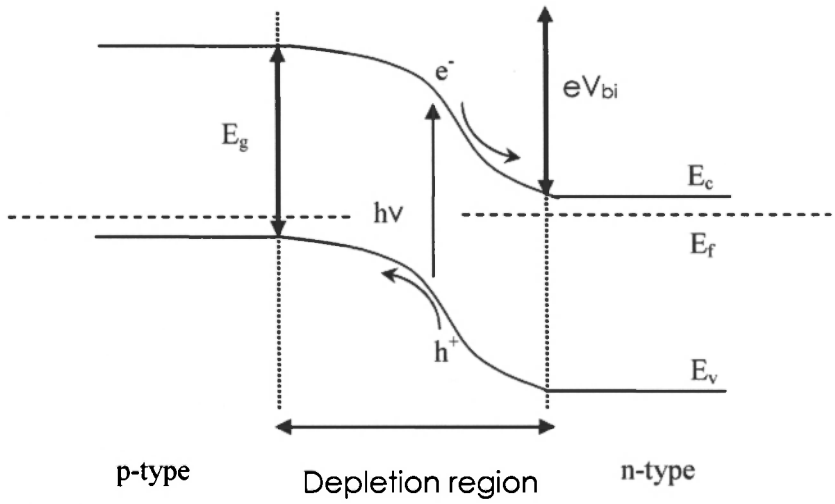


Figure 2.2 Energy band diagram of a conventional pn junction solar cell under short circuit conditions

Even though in this recent years, DSESC gives an efficiency of about 5% to 10% were fabricated [2], [10], these solar cells were affected by several problems and long term degradation of efficiency [11-13]. Technical problems that affected the efficiency are as follows:

i. The volatility of the electrolyte and the corrosive action of the iodide redox couple.

ii. Long term application of DSESC is limited by the electrolyte permeability of the encapsulation and its inertness towards the iodine.

iii. Dye desorption, imperfection of DSESC sealing, reaction of the sealant with the electrolyte and reaction of the redox cycle [14-15].

A lot of effort has therefore been done in finding less volatile electrolyte and solving other technical problems. Approaches to replace the liquid electrolyte include application of ionic conducting polymer gels electrolyte gellated with amino acid derivatives or room temperature molten salts. Complete replacement of the liquid electrolyte system has been established using inorganic p type semiconductors, such as Cul [16] or CuSCN [17] as well as organic hole conductors including low molecular weight charge transport materials and semiconducting polymers.

2.1.2 Dye-Sensitized Solid State Solar Cell (DSSSC)

The replacement of DSESC with a Dye-sensitized solid state solar cell (DSSSC) has important consequences for the electronic processes in solar cell technology. A dye-sensitized solid state solar cell based on sensitized TiC>2 thin film and Cul thin film was first demonstrated by Tennakone et al. [4]. The configuration and the operational system of DSSSC have already been discussed in the Chapter 1. Although DSSSC is low cost production, simple fabrication and non toxic solar cell, it still has several problems to be solved in order to compete with conventional silicon solar cell and DSSSC.

Many studies have being done to improve the performance and stability of DSSSC. One of the options is to enhance the properties of nanostructured Ti02 thin

film. As mentioned in Chapter 1, 4 kinds of study will be discussed in order to enhance nanostructured Ti02 thin film which can increased the performance of DSSSC. In this thesis, the properties of TiCh thin film such as surface morphology, structural, electrical and optical properties will be studied.

a. Structural properties

Tennakone et. al [18] has studied and try different p type semiconductor of DSSSC by selecting appropriate dyes. And also designing a new deposition technique of p type semiconductor by Kumara et. al [19]. There has been a long study of nanocrystalline TiC>2 thin film by Gratzel group, focusing on TiC>2 novel and spectacular physical and chemical properties. These particular properties resulted from nanostructured particle of TiC>2 which is smaller than 50 nm. Using high surface area and mesoporous material, Gratzel group has successfully developed new type of solar cell that is based on a nanocrystalline mesoporous Ti02 thin film electrode coated with dye-sensitizer for light absorption and electron injection into TiC>2 conduction band.

Jinting Jiu et. al [20] has reported that the DSSSC efficiency increased with increasing pore size. They also suggested that only surface area of the film alone is not sufficient, but the pore volume and diameter are also important in determining the overall performance of the DSSSC.

Lee et al. [21] also reported that DSSSC performance depends strongly on the TiC>2 film morphology. Nano particles are essential for increasing the surface area of the film in order to adsorb sufficient dyes. Adjusting pore size distribution is also an important parameter for improving the performance of the devices.

b. Electrical properties

Electrical properties such as low sheet resistance, low resistivity and high conductivity of nanostructured TiC>2 thin film are playing major role to produce high efficiency of DSSCs. Research has been done to produce better performance for electrical properties. Deshmukh et al. [22] has studied electrical properties for TiC>2 thin film using spray deposition method. They have studied the temperature and post

annealing effect to the electrical properties, whereby the thin film resistivity is decreased when the annealing temperature is increased.

Akl et al. [23] have studied the influence of oxygen additives and film thickness on the electrical properties of Ti02 thin film grown by Radio Frequency (RF) magnetron sputtering technique. It is indicated that the films have high resistance and it has n-type semiconductor. It is also indicated that increased of temperature was accompanied by decrement of film resistivity.

Ko et al. [24] has studied the effect doping process to dye-sensitized solar cell, where the performance of doped TiC>2 dye-sensitized solar cell was better than those with undoped Ti02 dye-sensitized solar cell. As the introducing dopant to TiC>2 thin film, it gives two effects; the changes of powder morphology and defect content such as ion Ti^{3+}.

c. Optical properties

In order to optimize higher efficiency of dye-sensitized solar cell, it is important to control the optical absorption of the thin film. Shen and Toyoda [25] reported the study of optical absorption and electron transport properties of four kinds of nanocrystalline Ti02 electrodes. Based on the result, the optical absorption and electron transport properties depend greatly on the compositions of the paste for preparation of the Ti02 films.

Lee et al. [26] has studied the optical properties towards the effects of nanodispersion of the aggregated Ti02 powder on Ti02 thin film. It is found that transmittance property was increased with increasing milling speed. It is due to highly dispersed nature induced by microbead milling. Photocurrent density was increased from 6.89 to 10.94mA/cm^2, corresponding to 59% increment.

Deshmukh et al. [22] has studied optical properties for Ti02 thin film using spray deposition method. The transmittance property of the film is increased with substrate temperature. The increment of transmittance may be attributed to the thickness of the film and nature of microstructure and surface morphology.

2.2 Nanostructured Titanium Dioxide

Titanium Dioxide (TiO_2) exists in nature as the minerals anatase, rutile and brookite. TiO_2 of the rutile phases is a relatively abundant mineral [27], however anatase and brookite are extremely rare in nature [28]. Nanostructured TiO_2 has been investigated extensively in recent years because of its utilization as a low cost material in photo-catalysis [29], in photovoltaic [30], or as gas sensor [31]. Compared to others semiconductors, TiO_2 material are favoured for such applications because of its high photo-activity, biologically and chemically inert, readily available and low cost material [32]. Dye-sensitized solar cell (DSC) is a device for the conversion of visible light into electricity based on the sensitization of wide band gap semiconductor. TiO_2 is transparent semiconductor material which has melting and boiling point of 1870°C and 2972°C, respectively [33]. TiO_2 is material with excellent merits in solar energy transferring and photo-catalysis of poison compounds in environment [34]. As a semiconductor material, TiO_2 has indirect band gap and n-type semiconductor which has band gap energy of 3.2eV at room temperature [35].

Nanostructured TiO_2 synthesized by hydrothermal processing of Titanium alkoxides, such as Titanium Isopropoxide (TTIP) and Titanium Butoxide (TBOT). It has been widely studied and investigated in photocatalyst and Dye-Sensitized Solar Cell (DSC). As titanium alkoxides are used as starting material, the primary particle size of nanostructured TiO_2 ranges from several to dozens of nanometers. The conventional process of sol-gel method for the preparation of anatase TiO_2 nanocrystalline is written as follows:

Hydrolysis process:

$$Ti(OR)_x + {}_xH_2O \longrightarrow Ti(OH)_x + {}_xROH$$

Polycondensation process:

$$nTi(OH)_x \longrightarrow Ti_nO_{2n} + H_2O$$

The hydrolysis process is completed in a very short time and then the polycondensation reactions continue. TiO_2 gives its significant when anatase crystalline phase, which is it has high surface area and porosity [36]. It has also particles size from 5 to 20nm [37].

With this small particles size of TiO_2, it has significant effect on the electronic magnetic and optical properties. Thermodynamically stable rutile TiO_2 nanocrystalline are difficult to synthesize by the sol-gel and hydrothermal methods using titanium alkoxides and organics salts. The rutile phases can be obtained by the high annealing temperatures of the kinetically stable anatase phase. Aruna et al. [38] reported the synthesis of 20nm rutile nanocrystalline from Titanium Isopropoxide in the present of nitric acid (pH 0.5) under vigorous stirring during hydrothermal treatment. The synthesis of brookite TiO_2 free from contamination by other phases is rather difficult. The formation of metastable brookite is usually accompanied by anatase and rutile. Kominami et al. [39] reported that phase pure brookite TiO_2 nanocrystalline with an average particle size of 14 to 67nm are synthesized by the thermal treatment of oxobis(2,4-pentanedionato-0,0') titanium($TiO(acac)_2$) in ethylene glycol (EG) in the present of sodium laurate or sodium acetate and a little water at 300°C. Figure 2.3 shows the structure of an anatase and rutile crystal. Although rutile and anatase are both of tetragonal crystallographic structure, rutile is more densely packed and thus possesses a greater density.

2.2.1 Nanostructured Titanium Dioxide Thin Film

There are several motivations for investigating TiO_2 thin films in this work. TiO_2 thin films are used currently as the Photovoltaic (PV) industry and standard Anti-Reflection (AR) coating on the vast majority of screen-printed solar cells. The important research is for the industry familiar with the technology and is not reluctant to adapt to fabrication processes based around TiO_2 and the necessary deposition equipment is operating today on the factory floor. TiO_2 thin films are generally amorphous for deposition temperatures below 300°C and above 300°C anatase phases will be formed. The most stable crystalline phase, rutile, is formed at temperature above 800°C. The brookite phase is rarely observed in deposited thin films. The functional properties of TiO_2 thin films, powders and ceramics are

strongly dependent on the phase of the material. For many applications, the sizes of crystals that are present also alter the behaviour of the film. Typical properties of TiC>2 included:

- Electrical properties with high electrical resistance, resistivities of 10^{14} Qcm [40] and dielectric constants of up to 180 are possible for rutile crystals [41].
- Mechanical properties with high durability [42] and hardness [43].
- Optical properties with very high refractive index which is up to 2.70 at wavelength of 600nm for rutile thin film [43, 44] and very good transmittance in the visible region.
- Chemical properties with good chemical resistance, non-toxic, inert and high chemical stability [45, 46].

Ti02 powders and thin films are used in an extremely wide range of commercial applications and research areas. Ti02 powder exists in white pigment which is used in plastic, paint, inks and cosmetics. It is also used in washing powder, toothpaste, sunscreen, foodstuffs, pharmaceuticals, photographic plates for creating synthetic gemstones and as a catalyst.

Ti02 thin film is used for ultra thin capacitors and MOSFETs due to its high dielectric constant. It is also used in humidity and oxygen sensors due to the dependence of its electrical conductance on the gases present. Due to its high refractive index, Ti02 was used as protective coatings and corrosion resistant barrier and photoanode in solar cells due to high surface area and high porosity.

2.3 Nanostructured Ti02 thin film preparation method

In this section, we will discuss regarding the preparation of nanostructured Ti02 and the deposition method to prepare the nanostructured Ti02 thin film. There are many methods to produce nanostructured material or particles, such as DC-sputtering, pulse laser deposition (PLD) and spray pyrolysis method. However in this thesis the sol-gel method will be used. The sol-gel process has several advantages due to its simplicity, easy control of the thin film composition, safety, low cost of the

apparatus and raw materials. This section also will discuss the thin film deposition method of spin coating technique.

2.3.1 Sol-gel method

The term sol-gel is a compound of the abbreviation sol for solution and the word gel, describing a dense network of fine particles dispersed in a solvent. The earliest application of sol-gel technology was during the Old Stone Age (the Upper Paleolithic), 17000 years ago in Lascaux (France). These cave paintings of the first modern humans, the Cro-Magnon hunters, showed realistic images of large animals and human handprints.

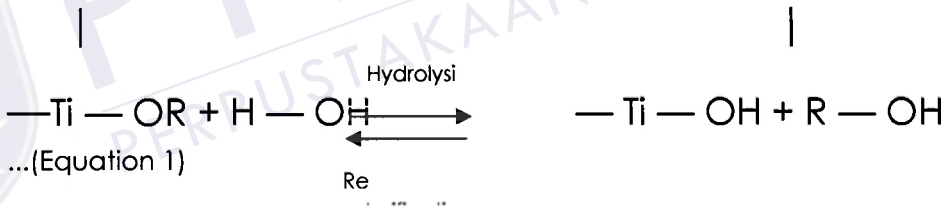
The sol-gel technology was improved and recently, sol-gel process is a novel technique for the preparation of many kinds of thin films including nanocrystalline Ti02. It has been demonstrated that through sol-gel process, the physic-chemical and electrochemical properties of Ti02 can be modified to improve its efficiency. Sol-gel method uses a wet chemical process which is synthesis technique for preparation of oxide gels, glasses and ceramics at low temperatures. It is based on control of hydrolysis and condensation of alkoxide precursors.

As early as the mid 1800s, interest in the sol-gel processing of inorganic ceramics and glass materials has begun with Ebelman and Graham's studies on silica gels [47]. The researcher recognized that the product of hydrolysis of tetraethoxysilane (TEOS) under acidic conditions is Si02. In the 1950s and 1960s Roy and co-workers used sol-gel method to synthesize a variety of novel ceramic oxide compositions with very high levels of chemical homogeneity, involving Aluminium and Zirconium, which could not be made using traditional ceramic powder methods [48-51]. It is possible to fabricate ceramic or glass materials in a variety of forms, such as ultra-fine powders, fibers, thin films, porous aerogel materials or monolithic bulky glasses and ceramics [52].

Since then powders, fibers, thin films and monolithic optical lens have been made from the sol-gel glass. Technical applications are planar devices such as sensors for heat and pressure, structured materials, for example, photonic crystals, chemical sensors and biomedical applications as entrapment of molecules for biosensors. In addition, complex geometry such as multi-core fibers or micro

structured fibers with gradients in the dopant concentration or even mixed or multiple doping conditions can easily be produced. Sol-gel technique offers the flexibility of dopant content, any water or ethanol soluble dopant can be incorporated, homogeneity of the dissolved parts, and adjustable processing temperatures (200°C – 2000°C). The sol-gel route is generally very cost-effective.

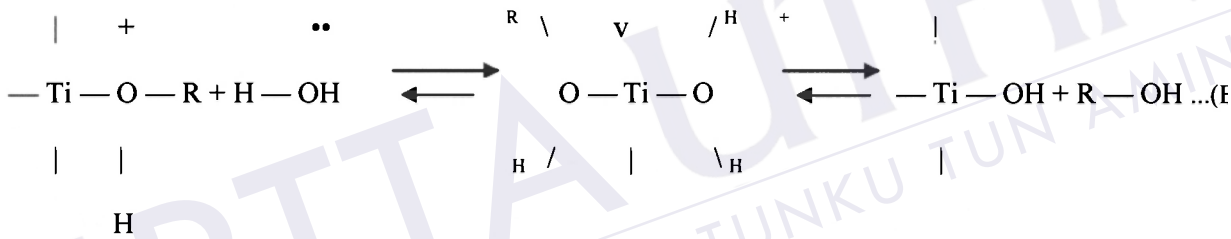
The sol-gel process involves transition from a liquid 'sol' (colloidal solution) into a 'gel' phase [53]. Usually inorganic metal salts or metal organic compounds such as metal alkoxide are used as precursors. A colloidal suspension or a 'sol' is formed after a series of hydrolysis and condensation reaction of the precursors. Then the sol particles condense into a continuous liquid phase (gel). With further drying and heat treatment, the 'gel' is converted into dense ceramic or glass materials. Generally three reactions are used to describe the sol-gel process, which is hydrolysis, alcohol condensation and the use of solvent. Due to the presence of the co-solvent, the sol-gel precursor, alkoxide, mixes well with water to facilitate the hydrolysis. There are five processes to form a thin film starting hydrolysis, condensation, gelation, ageing, drying and densification.



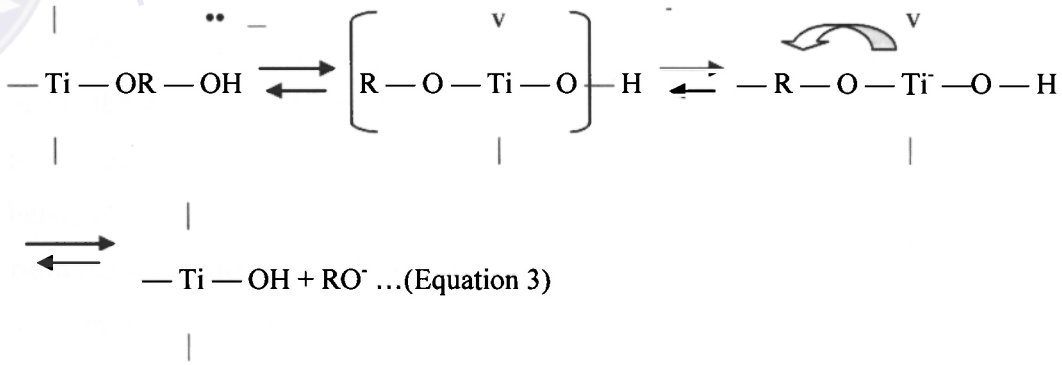
...(Equation 1)

During the hydrolysis reaction, the alkoxide group (OR) are replaced with hydroxyl group (OH) through the addition of water. Subsequent condensation reaction involving titanium hydroxide group (Ti-OH) produces titanium hydroxide bonds (Ti-O-Ti) with by product of water (water condensation) or alcohol (alcohol condensation). As the number of titanium hydroxide group increase, they bridged with each other and a titanium network is formed. Upon drying, the solvents that are trapped in the network are driven off. With further heat treatment at high temperature, the organic residue in the structure is taken out, the interconnected pores collapse and a densified glass or ceramic is formed.

Although hydrolysis can occur without additional catalyst, it has been observed that with the help of acid or base catalyst the speed and extent of the hydrolysis reaction can be enhanced. Under acid conditions, the alkoxide group is protonated rapidly. As a result, electron density is withdrawn from the silicon atom, making it more electrophilic with partial positive charges. Therefore it is more susceptible to be attacked by the nucleophile, water molecule. Subsequently a penta-coordinated transition state is formed with SN2 type characters, where there is simultaneous attack of the nucleophile and displacement of the leaving group. When the nucleophile attacks the centre atom, Ti, it is on the opposite side to the position of the leaving group, R-OH. Finally the transition state decays by breaking of the Ti-OHR bond and ends up with an inversion of silicon configuration as shown in equation. The acid-catalyzed mechanism can be described as following:

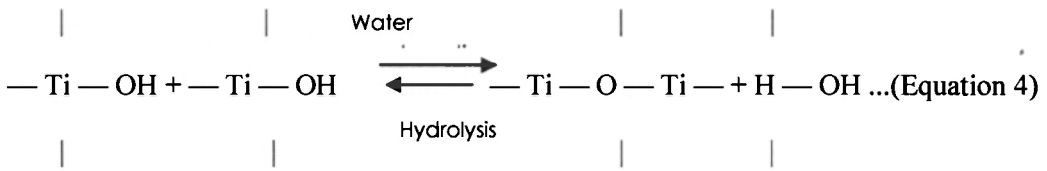


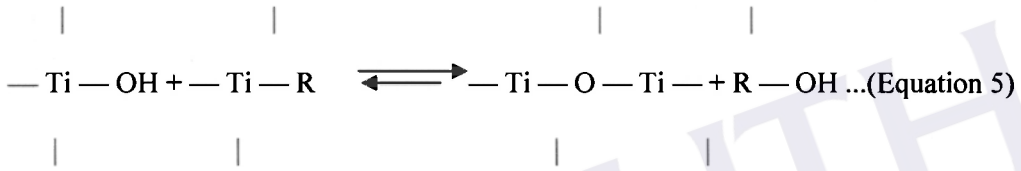
the silicon atom. Again, an SN2 type mechanism has been proposed in which OH displaces OR group. The mechanism of the base-catalyzed mechanism can be described as following:



When into the gelation step, alkoxide gel precursor undergoes polymerization (condensation) reaction with by product of water or alcohol. Similar to hydrolysis, the condensation reaction is also affected by the acid base catalyst. With the existence of acid catalyst, weakly cross-linked polymer is formed and can easily

aggregate after drying yielding low porosity micro porous structure. On the contrary, if base catalyst is used, discrete highly branched clusters are formed and lead to a mesoporous structure after gelation.





The continuing chemical and physical changes during ageing after gelation are very important. During this process, further cross-links continues, the gel shrinks as the covalent links replace non-bonded contacts and the pore sizes and pore wall strengths change with the evolution of the gel's structure.

The gel has a high ratio of water and three dimensional inter-connected pores inside the structure. Before the pore is closed during the densification process, drying is needed to remove the liquid trapped in the interconnected pores. On the other hand, removal of the liquid from the tiny pores causes significant stress resulting from inhomogeneous shrinkage. Therefore the main problem in the drying process is to overcome the cracking problem due to the large stress in the structure. For small cross sections, such as powder, coating, or fiber, the drying stress is small and can be accommodated by the materials, so no special care is needed to avoid cracking for those sol-gel structures. While for monolithic objects greater than 1cm, drying stress developed in ambient atmosphere can introduce catastrophic cracking, as a result

control of the chemistry of each processing step is essential to prevent cracking during drying.

Although there are many applications of sol-gel titanium prepared and dried at or near room temperature (especially those involving trapping functional organic or biological molecules with the gel pores), heat treatment of the porous gel at high temperature is necessary for the production of dense glass or ceramics from the gel silica. After the high temperature annealing, the pores are eliminated and the density of the sol-gel materials ultimately becomes equivalent to that of the fused. The densification temperature depends considerably on the dimension of the pores, the degree of connection of the pores and the surface areas in the structure [54].

Sol-gel method is a very flexible way to fabricate glass/ceramic under mild condition. From the introduction above, the advantages of the sol-gel method become apparent [55-58]:

1. Sol-gel method involves wet chemical synthesis of materials, so the composition of the materials can be tailored at molecular level.
2. Since liquid precursors are used it is possible to cast the glass and ceramics in a range of shapes, such as thin film, fibers and monoliths, without the need of machining or melting.
3. The precursors such as metal alkoxides with very high purity are commercially available which makes it easy to fabricate materials with high quality.
4. It is cost effective because the temperatures required in the process are low, close to room temperature and no delicate vacuum system is needed.
5. The sol-gel method can be performed at lower temperature compared to other methods. For example, Direct Current (DC) sputtering or Chemical Vapour Deposition (CVD).

6. It provides a simple and easy means of synthesizing nanoparticles at ambient temperature under atmospheric pressure and this technique does not require complicated set-up.

Despite all the advantages, sol-gel method still has some limitations. Solvents such as alcohol and water are involved in the process so it is not appropriate for fabrication which is very sensitive to solvents. Very careful attentions are needed to avoid cracking. Despite the disadvantages, sol-gel method is a very mild and flexible method to fabricate materials that posses properties not attainable by other methods. It inspires us to further investigate and modify the method to exploit its maximum value in application.

2.4 Nanostructured TiCh thin film deposition method

2.4.1 Spin Coating technique

Spin coating is one of the deposition techniques used to apply uniform thin films to flat substrates such as glass, quartz and silicon substrates. In short, an excess amount of a solution is placed on the substrate, which is then rotated at high speed in order to spread the fluid by centrifugal force. Spin coating is a convenient method. It delivers layers of high thickness homogeneity and can extend down below a thickness of 200nm [59].

Spin coating technique planarizes structured surfaces better than the other deposition technique such as pulse laser deposition, dip coating technique and sputter coating technique. There is only a residual relief due to the evaporation of the solvent after solidification of the layer. This shrinkage is approximately proportional to the local resist thickness. It is because heating decreases the viscosity of the resist, subsequent tempering steps can reduce the observed relief in the case of densely located structures.

The main problem is topographic failures are higher than the final resist layer because it leads to long ranging inhomogenities in the thickness. For low topographic relief, spin-coating is an interesting deposition technique for nanotechnology. A

precondition for an application of spin coating is the feeding of the layer-building material as a spinable resist. It requires viscous floating of the resist material. The layer material has to be soluble in solvent which exhibits an adequate evaporation rate during the spinning process so that a stabilization of the chosen layer thickness is achieved. It requires the application of mixture of solvents with different evaporation rates. The solvent in sol-gel process, with the lower evaporation rate will facilitates the thin film stabilization, where as that with the higher rate leads to a homogenous, crack-free thin film. The remaining solvent is usually removed in a subsequent drying step.

The equipment used for spin coating technique is called a spin coater, or spinner. Rotation is continued while the fluid spins off to the edges of the substrate, until the desired thickness of the film is achieved. The solvent used is usually volatile, and subsequently evaporates. Therefore, the higher the angular speed of spinning, the thinner is the film that can be produced. The thickness of the film is also depends on the concentration of the solution and the solvent.

There are many applications of spin-coating where relatively flat substrates or objects are coated with thin layers of material. The material to be made into the coating must be dissolved or dispersed into a solvent of some kind and this coating solution is then deposited onto the surface and spun-off to leave a uniform layer for subsequent processing stages and ultimate use. Some technologies that depend heavily on high quality spin coated layers are:

- Photoresist for defining patterns in microcircuit fabrication.
- Dielectric/insulating layers for microcircuit fabrication - polymers, SOG, SiLK, etc.
- Magnetic disk coatings - magnetic particle suspensions, head lubricants, etc.
- Flat screen display coatings. - Antireflection coatings, conductive oxide, etc.
- Compact Disks - DVD, CD ROM, etc.
- Television tube phosphor and antireflection coatings.

CHAPTER 3

METHODOLOGY

3.1 Introduction to sample preparation and substrate cleaning

This chapter discusses the methods used in this research. It included the preparation of the thin film and characterization method in this thesis. Figure 3.1 shows the flow chart for nanostructured TiO_2 thin film preparation and characterization. Nanostructured TiO_2 thin film will be deposited onto glass and silicon substrates for surface morphology study, electrical, structural and optical properties.

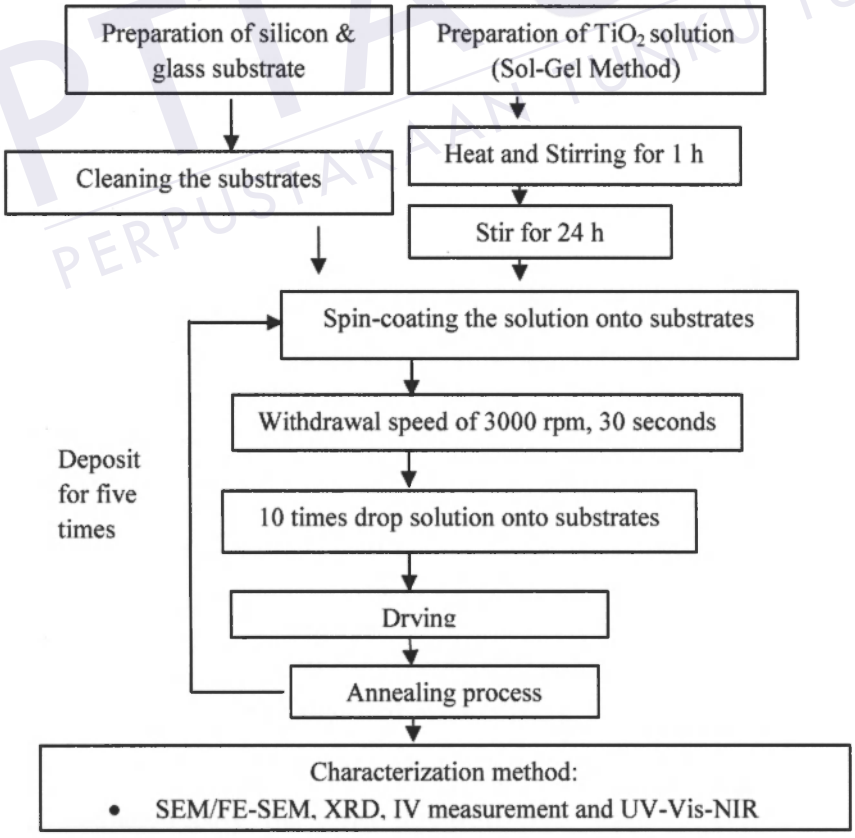


Figure 3.1 Flow chart of nanostructured TiO_2 thin film preparation and characterization method

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