

FABRICATION AND CHARACTERIZATION OF  
NANOSTRUCTURED FLUORINE DOPED TIN  
OXIDE THIN FILM FOR DSSC BY  
HYDROTHERMAL METHOD

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*To my beloved parents*

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- 1 **M. L. M. Napi**, N. Nayan, M. K. Ahmad, F. I. M. Fazlee, N. K. A. Hamed, & N. S. Khalid, "Fabrication of Fluorine Doped Tin Oxide With Different Volume Of Solvents On FTO Seed Layer by Hydrothermal Method", *Sains Malaysiana*, vol. 45, no. 8, pp. 1207-1211 (2016).
- 2 F. I. M. Fazli, N. Nayan, M. K. Ahmad, **M. L. M. Napi**, N. K. A. Hamed & N. S. Khalid, "Effect of Annealing Temperature on TiO<sub>2</sub> Thin Films prepared by Spray Pyrolysis Deposition Method", *Sains Malaysiana*, vol. 45, no. 8, pp.1197-1200 (2016).
- 3 N. K. A. Hamed, N. Nayan, M. K. Ahmad, N. S. Khalid, F. I. M. Fazli, & **M. L. M. Napi**, "Influence of Hydrochloric Acid Volume on the growth of Titanium Dioxide (TiO<sub>2</sub>) Nanostructures by Hydrothermal Method", *Sains Malaysiana*. (in review)
- 4 N. S. Khalid, N. Nayan, M. K. Ahmad. C. F. Soon, **M. L. M. Napi**, N. K. A. Hamed, & F. I. M. Fazli, "Biocompatibility of TiO<sub>2</sub> Nanorods and Nanoparticles on HeLa cells", *Sains Malaysiana*. (in review)
- 5 M. K. Ahmad, **M. L. M. Napi**, N. F. Izyani, C. F. Soon, N. Nafarizal, A. B. Suriani, A. Mohamed, M. H. Mamat, M. F. Malek, M. Shimomura, & K. Murakami, "A Facile Method for Synthesis of Nanorice Fluorine Doped Tin Oxide for use in Dye-Sensitized Solar Cells", *Materials Letters*. (in review)
- 6 **M. L. M. Napi**, M. F. Maarof, C. F. Soon, N. Nayan, F. I. M. Fazli, N. K. A. Hamed, S. M. Mokhtar, N, K, Seng, M. K. Ahmad, A. B. Suriani, & A. Mohamed, "Fabrication of Fluorine Doped Tin Oxide (FTO) Thin Films Using Spray Pyrolysis Deposition Method For Transparent Conducting Oxide", *ARPJ Journal of Engineering and Applied Sciences (JEAS)*, Vol. 11, no. 14, pp. 8800-8804 (2016).

- 7 F. I. M. Fazli, A. N. Suhaimi, N. S. Khalid, N. K. A. Hamed, **M. L. M. Luqman**, S. M. Mokhtar, N. K. Seng, N. Zainal, N. Nayan, S. C. Fhong, A. B. Suriani & M. K. Ahamd, “The Effects Of Annealing Temperature On Properties Of Aluminium-Doped Tin Oxide (Al/SnO<sub>2</sub>) Thin Films Deposited By Spray Pyrolysis Deposition (SPD) Method”, *ARPJ Journal of Engineering and Applied Sciences (JEAS)*, vol. 11, no. 14, pp. 8840-8845 (2016).
- 8 S. M. Mokhtar, M. K. Ahmad, N. M. A. N. Ismail, M. S. Mamat, F. I. M. Fazli, N. K. A. Hamed, **M. L. M. Napi**, N. S. Khalid, N. K. Seng, N. Zainal, S. C. Fhong, N. Nayan, & A. B. Suriani, “Fabrication Of Co/SnO<sub>2</sub> On Glass Substrate Using Spray Pyrolysis Deposition Technique With Variation Of Annealing Temperature”, *ARPJ Journal of Engineering and Applied Sciences (JEAS)*, vol. 11, no. 14, pp. 8873-8877 (2016).
- 9 **M. L. M. Napi**, N. K. Seng, & M. K. Ahmad, “Surface Morphology and Electrical Properties of FTO (Fluorine Doped Tin Oxide) with Different Precursor Solution for Transparent Conducting Oxide”, *Applied Mechanics and Materials*, vols. 773-774, pp. 682-685, (2015).

## ABSTRACT

Nanostructured Fluorine Doped Tin Oxide (FTO) thin film has been successfully synthesized on top of bare FTO layer substrates using hydrothermal method. The performance of FTO thin film including conductivity and transparency depend on the surface morphology and the properties of the material. Hydrothermal method has proven to be a very good method for the fabrication of novel metal oxides. Thus, a new nanostructured FTO thin film like nanorice has been fabricated using one step hydrothermal method. FTO nanorice thin films were obtained from the reaction of tin (iv) chloride ( $\text{SnCl}_4$ ), ammonium fluoride ( $\text{NH}_4\text{F}$ ), acetone, deionized water and hydrochloric acid (HCl). The compound was prepared in an autoclave at  $150^\circ\text{C}$  hydrothermal temperature for different reaction times of 5 hours, 10 hours, 15 hours, and 20 hours. FESEM studies on the surface morphologies of all the samples showed that nanorice structure had formed to fully cover the bare FTO substrate. Then, to further the optimization of FTO nanorice thin film, this research focused on studying the effect of hydrothermal temperature on FTO nanorice thin films. The experiments were conducted at  $130^\circ\text{C}$ ,  $140^\circ\text{C}$ ,  $150^\circ\text{C}$ ,  $160^\circ\text{C}$ , and  $170^\circ\text{C}$  of hydrothermal temperature in constant reaction time of 10 hours. Basically, there were six properties studied; surface morphology, structural, element composition, thickness measurement, electrical and optical properties. At the end of this research, homogeneous FTO thin film has been successfully prepared. By controlling the reaction time and hydrothermal temperature, a transparent FTO film with beyond 85% percentage of transmittance was developed. The FTO thin film produced at 10 hour reaction time and  $150^\circ\text{C}$  of hydrothermal temperature time gave the low sheet resistance of 0.012 Ohm/sq with high transparency. The DSSC fabricated using the optimized FTO film gave higher efficiency of 2.77% compared to commercial FTO of 1.93%.

## ABSTRAK

Nanostruktur Fluorin Dop Stanum Oksida (FTO) tipisan nipis telah berjaya disintesis di atas lapisan FTO substrat yang kosong menggunakan kaedah hidroterma. Bagi prestasi FTO tipisan nipis yang meliputi kekonduksian dan kelutsinaran bergantung pada morfologi permukaan dan juga sifat-sifat bahan tersebut. Kaedah hidroterma telah terbukti menjadi satu kaedah yang sesuai untuk pemfabrikasi logam oksida yang baharu. Demikian itu, satu jenis nanostruktur FTO tipisan nipis seperti nanonasi telah berjaya difabrikasi menggunakan satu peringkat kaedah hidroterma. FTO nanonasi tipisan nipis diperolehi daripada reaksi antara timah (iv) klorida, ammonium fluoride, aseton, air ternyahion, dan asid hidroklorik. Sebatian itu disediakan di dalam autoklaf di suhu hidroterma iaitu 150°C pada tempoh masa tindak balas yang berbeza-beza iaitu 5 jam, 10 jam, 15 jam dan 20 jam. Penelitian FESEM menunjukkan bahawa ada perubahan atas permukaan morfologi iaitu struktur nanonasi telah menutupi FTO substrat kosong. Seterusnya, untuk mengoptimalkan lagi FTO nanonasi tipisan nipis, kajian ini telah memfokuskan kepada kesan suhu hidroterma terhadap FTO nanonasi tipisan nipis. Eksperimen-eksperimen telah dijalankan pada pelbagai suhu hidroterma iaitu 130°C, 140°C, 150°C, 160°C dan 170°C pada satu tempoh masa tindak balas yang tetap iaitu 10 jam. Secara asasnya, terdapat enam ciri yang diteliti; morfologi permukaan, struktur, komposisi elemen, pengukuran ketebalan, sifat elektrik dan optik. Dipenghujung kajian ini, FTO tipisan nipis yang homogen berjaya disediakan. Dengan mengawal masa reaksi dan suhu hidroterma, FTO yang lutsinar telah dijayakan dengan melebihi 85% transmisinya. FTO tipisan nipis yang menggunakan 10 jam masa reaksi pada 150°C suhu hidroterma mempunyai rintangan keping yang rendah iaitu sebanyak 0.012 Ohm/sq dengan kelutsinaran yang tinggi. DSSC telah difabrikasi menggunakan FTO nanonasi yang optimum ini dan memberikan kecekapan yang tinggi iaitu 2.77% dibandingkan dengan komersial FTO iaitu 1.93%.

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**LIST OF ABBREVIATION**

$A$	-	Cross sectional area
$\eta$	-	Efficiency
$I$	-	Current
$k$	-	Kilo
$L$	-	Length
$\rho$	-	Resistivity
$R$	-	Resistance
$R_s$	-	Sheet resistance
$t$	-	Thickness
$V$	-	Voltage
DSSC	-	Dye sensitized solar cells
FTO	-	Flourine doped tin oxide
HCl	-	hydrochloric acid
$\text{SnCl}_4$	-	Tin (iv) chloride
TCO	-	Transpaerent conducting oxide
$\text{TiO}_2$	-	Titanium dioxide
UTHM-	-	Universiti Tun Hussein Onn Malaysia
ZnO	-	Zinc Oxide

## CHAPTER 1

### INTRODUCTION

#### 1.1 Introduction

The electrical energy generated from fossil fuels has become the major factor in the development of civilization from day to day. The generated energy produced by every country would affect the level of industrial and agricultural growth. Thus, sustainable economy in one country depends on the energy that has been conserved constantly. The high supplied of fossil fuels would contribute to the economic wealth and the materials standards of a nation. However, the widely usage of fossil fuels also would lead to the environmental and ecology changes [1]. As the increasing energy demand, the environmental friendly alternatives, renewable and non-conventional sources are being searched by many countries [2].

One of the potential sources of renewable energy is solar energy. Solar energy is an effective energy and become an important source of energy because this is the one of the energies that could be used after depletion of another source such as fossil fuels. As solar cells have high commercialization, the variety of technologies which used solar cells have been improved in the research of solar energy.

Solar cell is a photovoltaic device which is basically used to convert solar radiation to electricity based on photosynthesis concept of sunlight. The solar cell is very useful because of its ability to generate the electricity which have been thoroughly discussed in several recent reports [3, 4]. One of the solar cell types is Dye-Sensitized Solar Cell (DSSC) which comprises of five components. They are transparent conducting oxide, semiconductor film, sensitizer adsorber onto the surface of semiconductor, electrolyte and counter electrode [5].

Basically, there are three categories of solar cell. First and foremost is the silicon based solar cell. This type of solar cell is the most popular but expensive due to the high manufacturing cost and limited availability of silicon make to find

alternative material of solar cell. The second generation of solar cell is called thin film solar cells, which is cheaper than the first generation. However the power conversion efficiency of second solar cell is still low. The DSSC is the third generation of solar technology. It provides effective charge separation that allows electricity to be generated even though in low light condition. The first DSSC was invented at 1991 based on artificial photosynthesis system to generate electricity [6]. Currently, DSSC is still in research phase to enhance its efficiency. The average efficiency of this new type of solar cell is 15% [5, 7]. Overall DSSC is considered as a low cost, simple and a promising technique to provide high performance of electrical generation. Furthermore, the cost of manufacturing of this DSSC is much lower compared to the first and second generations solar cell.

## 1.2 Research Background

Tin oxide ( $\text{SnO}_2$ ) is a n-type semiconductor with band-gap energy of 3.6eV. A thin films of  $\text{SnO}_2$  is transparent in the visible region and reflecting in the high infrared region [8]. The conductivity of the material is mainly attributed due to the oxygen vacancies in the lattice whose structure is tetragonal and similar to the rutile structure [9]. Conductivity of  $\text{SnO}_2$  can further be increased by doping it with element group III, V, VI and VII of the periodic table; some of which are Ti, Sb, Te and F. Among these elements, the most widely used dopant is fluorine because of the fact that the resultant fluorine doped tin oxide (FTO) film is highly stable chemically and thermally [10, 11]. FTO thin film has been used mainly for electronics devices. The performance of FTO films can be increased with highly crystalline and larger surface area [5]. According to above concept, FTO film with one-dimensional nanoparticle size could give high surface areas for better electron mobility and less electron recombination. It is known in the realm of nanoscience and nanotechnology that nanorods, nanowires and nanotubes have special roles because of their dimensionality. When the diameter of the nanorods, nanowires and nanotubes become small, the physical and chemical properties of the one-dimensional nanostructure are clearly different from those of crystalline solids or even two-dimensional system.

FTO thin films is widely used in various fields of device making technologies such as window layers in solar cells [12], gas sensor devices [13], substrates for electrodeposition [14] and transparent contact in optoelectronics. One of the solar cell type that used FTO thin films as TCO is the Dye-Sensitized Solar Cell (DSSC). FTO film has been used to collect electrons from the sensitized dye. Enhancement in surface area of FTO film will improve the electron collection of DSSC and the efficiency of DSSC is also improved [5].

The application of FTO in various field of the technology is due to its chemical and thermal stability along with the high optical transparency in the visible range and high electrical conductivity [5]. FTO has been prepared by various methods including chemical vapor deposition (CVD) [15], hydrothermal method [16], pulsed laser deposition [17], rf sputtering, sol-gel and spray pyrolysis deposition (SPD) [18]. Spray pyrolysis is widely used to prepare FTO films, owing to its simplicity, low cost experimental apparatus set up, ready incorporatability of various dopants, high growth rate and high mass production capability for large area coatings [19]. Spray pyrolysis is a process in which a thin film of a required material is deposited on to a hot surface by spraying a precursor solution on to it. However the hydrothermal method possesses the great advantages for nanomaterials fabricating such as the production of particles that are monodispersed that affect over their morphology and grain size in addition to their chemical homogeneity with the highest dispersibility [16]. The hydrothermal technique not only helps in processing monodispersed and highly homogeneous nanoparticles, but also act as one of the most attractive techniques for processing nano-hybrid and nanocomposite materials.

Several tin compounds such as tin (II) chloride dihydrate [20], tin (IV) chloride pentahydrate [15], tetra(n-butyl)tin and di(n-butyl)tin(IV)diacetate (DBTDA) [15] have been used as a tin element in the precursor solution for preparing FTO films. Their preferred crystal growth orientation and crystal size differ with the nature of the compounds used which in turn affect the optical and electrical properties of the resulting thin films of FTO. Kaneko et al. [21] has used DBTDA as tin compound for preparing the SnO<sub>2</sub> film and they have studied the initial growth mechanism of SnO<sub>2</sub> formed and the thermal decomposition of DBTDA [21, 22]. SnCl<sub>2</sub> as tin precursor also has been used in fabrication of SnO<sub>2</sub> layer via hydrothermal method as been reported by Wang et al. [23]. The aligned TiO<sub>2</sub> nanorods and nanoflower on FTO substrate using hydrothermal method at low

temperature as low as 150°C were grown [24, 25]. It was believed that nanostructure FTO could be grown using this method with additional processes. In this study, one step process of hydrothermal method has been applied to grow nanostructured FTO thin film on the bare FTO substrates. In the one step process, precursors were used to provide enough energy for the nanostructured FTO thin film growth

### 1.3 Problem Statements

There are still a lot of efforts needed to be done in enhancing the efficiency of DSSC. Many researchers focused on the particular components of DSSC to enhance the performance of the solar cell. One of the crucial DSSC components is transparent conducting oxide (TCO) which is the first layer exposed to the sunlight. Since TCO is a current collector, the fabrication of this material requires a substrate as a base material for depositing a semiconductor and catalyst onto it.

TCO layer should be in high transparency and good conductivity to achieve high efficiency of DSSC. Thus, Fluorine-doped Tin Oxide (FTO) is found as one of the attractive materials that is compatible to be applied as TCO layer which contributes in enhancing the DSSC efficiency. The performance of FTO depends on the nanostructure and properties of the material. There are a lot of type of nanostructures such as nanoparticle [26], nanorod [27], nanoflower [23], nanowire [28] and nanocactus [29]. The fabrication of those nanostructures are dependent on the precursor material and thermodynamics of synthesis method [30]. The hydrothermal method is one of the promising low cost methods to fabricate various nanostructures. This method leads to the production of highly monodispersed nanoparticles with controllable size and morphology. It also has high potential to produce a new nanostructure of thin film [16].

Recently, the fabrication of SnO<sub>2</sub> films was performed by Ming et al. [31] by using SnO<sub>2</sub> as seed layer on FTO substrate. In this report the double layer of novel nanostructures had been successfully fabricated by using hydrothermal method in which the first layer was SnO<sub>2</sub> nanosheet films with 1 μm of thickness and second layer was SnO<sub>2</sub> hierarchical microspheres attached on nanosheets. The first synthesis of double layer SnO<sub>2</sub> film without SnO<sub>2</sub> seed layer was performed by Wang et al. [23] using direct growth from FTO substrates. This work was able to produce double

layer of SnO<sub>2</sub> nanoflower on SnO<sub>2</sub> nanosheets films. This formation was synthesized by using SnCl<sub>2</sub>, NaF, and water as precursor solutions which applied as TCO in solar cell. Overall of the problem related are:

- a) The low efficiency of DSSC is caused by the low performance of FTO thin films.
- b) Nanostructures commercial FTO thin films have low light scattering effect. The high scattering effect could enhance the possibility of light to interact with dye.
- c) The commercial FTO thin films have low electrical conductivity. Therefore, the effectiveness of FTO thin films can be ensured by producing good electrical conductivity with high transparency.

Thus, this work is focused on producing a new nanostructure of FTO films by using hydrothermal method without the seed layer. This fabrication leads to the performance of FTO films which comprise of two proposed nanostructures. First, the new nanostructures with high surface area and a high transparency material above 85% that allows more sunlight absorption and good in conductivity. Second, the deposited spherical nanostructures of thin films on the large surface area of nanostructures. The bilayered thin film consists of FTO films with high surface area as bottom layer is able to increase the dye loading capacity and boost the current collector [31]. Another spherical FTO nanostructure film as top layer to enhance the light scattering ability [32].

#### **1.4 Objectives**

The aim of the research is to prepare the nanostructured FTO films which have high surface area and low sheet resistance by using hydrothermal process. To achieve this goal, the following specific objectives are to be obtained

- (a) To optimize the reaction times and temperatures of the hydrothermal method for the growth of FTO films.

- (b) To investigate the surface morphology, structural, optical and electrical properties of the growth of FTO films.
- (c) To apply FTO nanostructures in DSSC and measure the power conversion efficiency of DSSC using nanostructured FTO films.

## 1.5 Scopes

The scope of the research focuses on the preparation of nanostructured fluorine doped tin oxide thin film using hydrothermal process. The preparation of the FTO thin film is optimized by performing three-time repetitive procedures for different parameters of the deposition methods which are reaction time and hydrothermal temperature. The surface area and the electrical properties of the thin films are examined based on the morphology, structural, optical, and electrical properties. Various properties of the thin films are characterized by using Field Emission Scanning Electron Microscopy (FESEM) for studying the surface morphology, X-ray diffraction (XRD) for examining the structural analysis, Energy-Dispersive X-Ray Spectroscopy (EDX) for recording the element composition, UV-VIS Spectrophotometer for measuring the transmittance percentage of thin film, surface profiler for thickness measurement of thin film and two-point probe methods for identifying the resistance, resistivity and sheet resistance of thin films. The best fabricated FTO films using optimized parameters are assembled in DSSC compared with commercial FTO in term of efficiency. The efficiency of DSSC is examined by the solar simulator.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Transparent Conducting Oxide

TCO is an important component in the DSSC that is exposed to the sunlight radiation for energy absorbance processes. It comprised of current collecting properties that were used to maximize the flow of current and reduced the resistivity of DSSC [33]. In DSSC, the TCO was used as the current collector component which required high transparency as more than 80% for allowing the maximum sunlight radiated on active area of the cell. The high electrical conductivity of the substrates also contributed to increase efficiency of the charge transfer and reducing energy loss [34]. Thus, the effectiveness of TCO could be ensured by producing high electrical conductivity with high transparency.

The growth of the thin film could occur via three stages which were formation of nuclei, crystal growth with preferred orientations, and further normal crystal growth to the surface of the substrate [35]. There are several processes that had been used in fabricating the transparent conducting oxide and also their disadvantages. Firstly is spray pyrolysis deposition which is the easily to handle but it is only possible to fabricate the one type of morphology which is nanoparticle [36], meanwhile RF sputtering also only can fabricated small grain size that leads to increase the resistivity [37]. Another method is chemical vapour deposition (CVD) which has low deposition rate and the sample is easy to prone to the radiation damage and vacuum chamber impurities [38, 39]. Next is sol gel method. This method is very sensitive towards solvents and need to serve carefully to avoid from sample cracking [40]. For inkjet printing, this technique is only able to produce inhomogeneous films [41]. All the deposition techniques were summarized in Table 2.1.

Table 2.1: History of processes for making transparent conductors [42]

<b>Materials and Process</b>	<b>Reference</b>
Ag by <b>chemical-bath deposition</b>	Unknown Venetian
SnO <sub>2</sub> :Sb by <b>spray pyrolysis</b>	J.M. Mochel , 1947
SnO <sub>2</sub> :Cl by <b>spray pyrolysis</b>	H.A. McMaster 1947
SnO <sub>2</sub> :F by <b>spray pyrolysis</b>	W.O.Lytle and A.E. Junge 1951
In <sub>2</sub> O <sub>3</sub> :Sn by <b>spray pyrolysis</b>	J.M. Mochel , 1951
In <sub>2</sub> O <sub>3</sub> :Sn by <b>sputtering</b>	L.Holland and G.Siddall, 1955
SnO <sub>2</sub> :Sb by <b>CVD</b>	H.F. Dates and J.K. Davis, 1967
Cd <sub>2</sub> SnO <sub>4</sub> by <b>sputtering</b>	A.J. Nozik , 1974
Cd <sub>2</sub> SnO <sub>4</sub> by <b>spray pyrolysis</b>	A.J. Nozik and g Haacke 1976
SnO <sub>2</sub> :F by <b>CVD</b>	R.G. Gordon , 1979
Tin by <b>CVD</b>	S.R. Kurtz and R.G. Gordon, 1986
ZnO:In by <b>spray pyrolysis</b>	S.Major , 1984
ZnO:Al by <b>sputtering</b>	T.Minami, 1984
ZnO: In by <b>sputtering</b>	S.N. Qui , 1987
ZnO:B by <b>CVD</b>	P.S. Vijayakumar, 1988
ZnO:Ga by <b>sputtering</b>	B.H. Choi, 1990
ZnO:F by <b>CVD</b>	J.Hu and R.G. Gordon, 1991
ZnO:Al by <b>CVD</b>	J.Hu and R.G. Gordon, 1992
ZnO:Ga by <b>CVD</b>	J.Hu and R.G. Gordon , 1992
ZnO:In by <b>CVD</b>	J.Hu and R.G. Gordon, 1993
Zn <sub>2</sub> SnO <sub>4</sub> by <b>sputtering</b>	H.Enoki , 1992
ZnSnO <sub>3</sub> by <b>sputtering</b>	T.Minami, 1994
Cd <sub>2</sub> SnO <sub>4</sub> by <b>pulsed laser deposition</b>	J.M. McGraw , 1995

Polymer and metals are two types of materials that also could be applied as TCO. The metal used for fabrication of TCO such as stainless steel, tungsten and titanium. Polymer has flexibility and low cost of fabrication [23]. But polymer and metals also have their own disadvantages on the TCO application which were the low efficiency and incompatibility of implementation respectively. The

incompatibility of using metal material includes high cost of fabrication and corrosion due to physical contact with the electrolyte [32].

Based on TCO properties, it also has potential to be applied in various application such as cold heat windows [43], antistatic coatings, polymer light emitting diodes [44], organic light emitting diode [45], electromagnetic materials in rear-view mirrors of automobile [46], solar cells [47], front electrodes in flat panel displays [48], low emissivity window [42], electromagnetic shielding [48], and invisible security circuits [42]. These applications have been summarized in Figure 2.1.

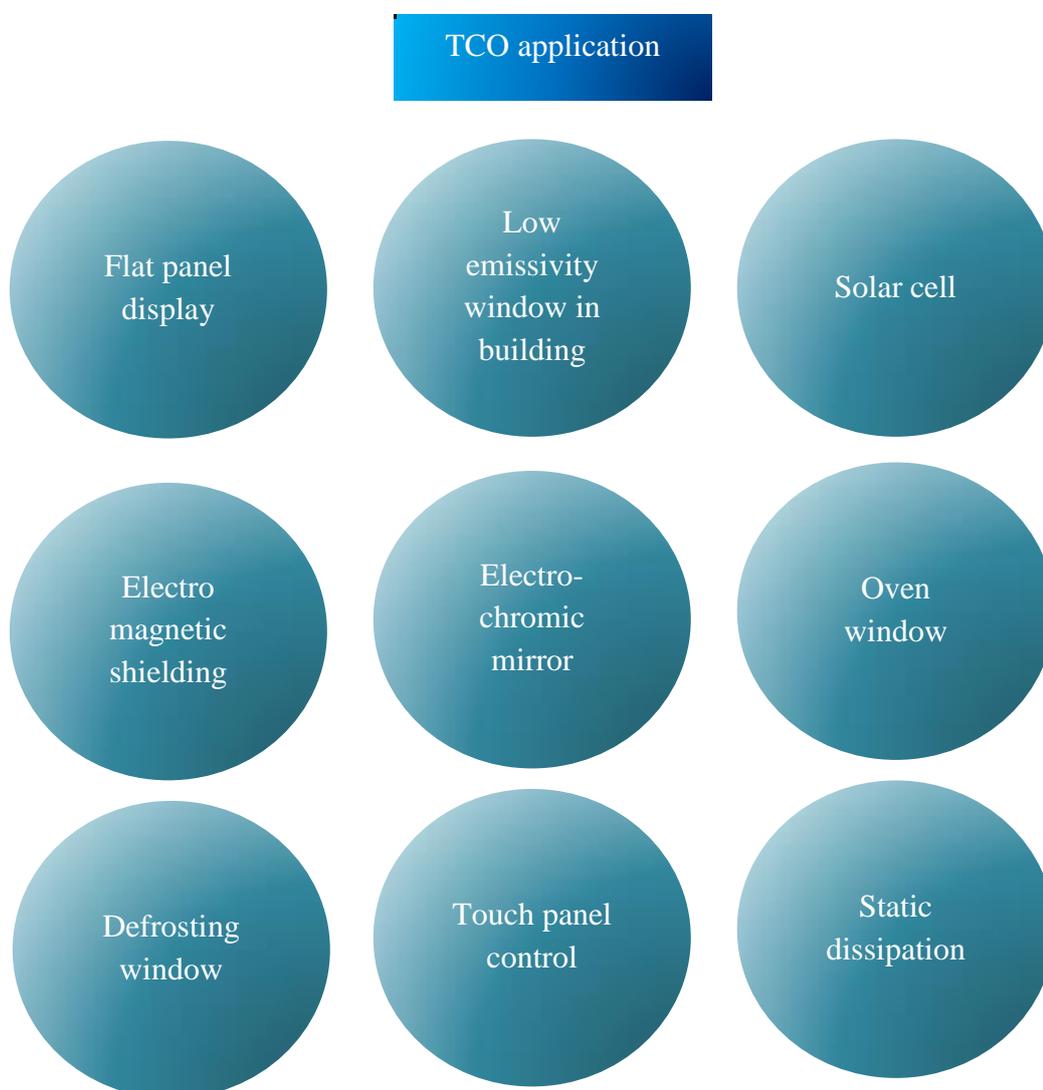


Figure 2.1: The applications of TCO

## 2.2 Fluorine Doped Tin Oxide (FTO)

Tin oxide or stannic oxide ( $\text{SnO}_2$ ) is the one of main oxide of tin instead of stannous oxide ( $\text{SnO}$ ).  $\text{SnO}_2$  is an n-type semiconductor material which suitable to be applied in photovoltaic device as it comprises of a wide band gap, large mobility and higher donor concentration [49]. Compared with  $\text{SnO}$  which has smaller band gap also known as less well characterized. The structure of  $\text{SnO}_2$  was tetragonal rutile with lattice parameters of  $a=b=4.737 \text{ \AA}$  and  $c=3.186 \text{ \AA}$  [50] as shown in Figure 2.2. Generally,  $\text{SnO}_2$  transparent conducting thin films has a direct optical band gap of about 3.87 - 4.3 eV [51].

The properties of this material are dependent on the microstructure, composition, amount of impurities and the deviation of the film composition from the stoichiometry [52]. As reported by Bertil et al. [53] the stoichiometry and oxygen that cause by intrinsic defect would affect the electrical properties of  $\text{SnO}_2$  films. The improvement in conductivity of  $\text{SnO}_2$  also can be enhanced by using annealing process. This process for instance, tends to improve the lattice mismatch and create longer mean path for the free electron [54]. However Saturi [55] reported that annealing process increased, then the energy gap of  $\text{SnO}_2$  was decreased. To sum up, all of these aspects were essential in their applications.

There were several methods in fabricating the  $\text{SnO}_2$  film such as chemical vapour deposition (CVD), hydrothermal method, spray pyrolysis method and RF sputtering.

Using spray pyrolysis method Murakami [56] had observed the initial growth of the  $\text{SnO}_2$  films on the glass substrate. The results suggested, at the very early stage each isolated grains grew at almost the same rate and only its density increased with constant of surface roughness as shown in Figure 2.3. Then, it would spread relatively with an increase of roughness. However, this method was possible to fabricate only the nanoparticles morphology of thin films.

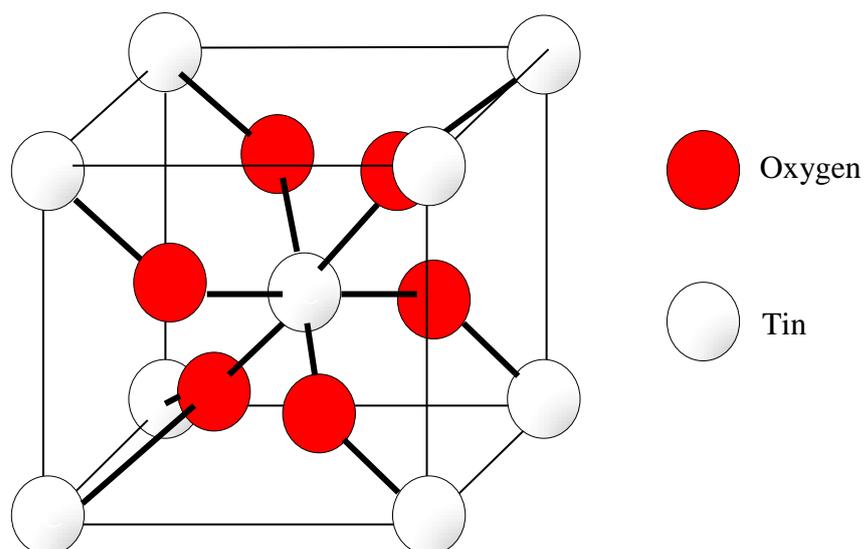


Figure 2.2: Ball and stick of the structure of  $\text{SnO}_2$

However, Liyanage et al. [57] had already improved the spray pyrolysis deposition method (SPD) and it was able to get the FTO nanorod films with low sheet resistance. The improved SPD was using horizontal technique of spray to keep the low pressure during deposition process and maintaining a good percentage of transmittance of FTO films.

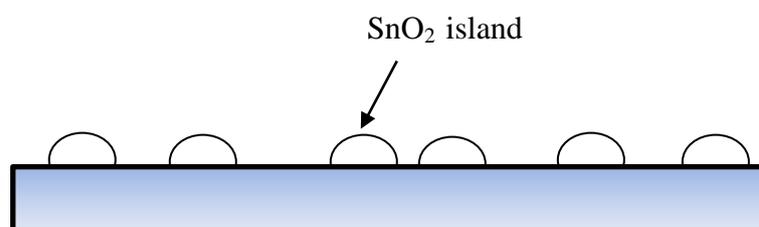


Figure 2.3: The schematic drawing of the  $\text{SnO}_2$  film at early stage formed by the SPD process [56]

The challenge for  $\text{SnO}_2$  films was having high resistivity due to the low intrinsic carrier density and mobility. Thus, Mohalkar et al. [58] reported, for enhancing the conductivity of  $\text{SnO}_2$ , fluorine element which was from group 17 has been introduced to be doped on host of  $\text{SnO}_2$ . These non-stoichiometric films would improve the conductivity which caused by double ionized vacancies serving as donor. The fluorine was compatible with  $\text{SnO}_2$  as it has close ionic size as  $\text{F}^-:1.33\text{\AA}$ ,

$O^{2-}$ :1.32Å, comparable bond energy with tin element (Sn) (Sn-O bond 31.05D°/kJmol<sup>-1</sup>, Sn-F bond 26.75D°/kJ mol<sup>-1</sup>), and low lattice coulomb forces. Since the F<sup>-</sup> charge was half of the O<sup>2-</sup> charge, the fluorine ions were able to occupy the oxygen ions [59].

The grain size of FTO films was dependent on the deposition temperature, time reaction, type of precursor and solvent that were been used [9]. Mohalkar et al. [9] also investigated the effect of various solvents used for FTO films fabrication. From various type of solvents used in FTO films fabrication it would able to get a new morphology of FTO films without affecting the lattice parameter values. However, Agness et al. [60] suggested different type of FTO film morphologies were depend on the precursor and solvents pairs. From this pairing of precursor and solvent, the obtained films layers have been classified into three categories which were smooth, slightly faceted and faceted surfaces.

Another way of promoting the low resistivity was by adjusting the Sn/O ratio. The increasing Sn/O ratio leads to create extra oxygen vacancies [61]. Then, at certain concentration of Sn would able to get high surface area with low sheet resistance. This concentration of precursor has important role to control the grain size of FTO films.

On the other hand, preferred orientation of FTO film growth also influence the electrical conductivity of FTO films as reported by Jian et al. [30]. Resistivity increased with strengthening (110) preferred orientation and weakening (200) preferred orientation. Then, by using hall effect measurement revealed the resistivity was increased due to the decreasing of carrier mobility with the development of (110) preferred orientation.

Studies on effect of annealing temperature and different type of tin precursors were widely performed by many researchers to improve the performance of optical properties of the thin films [55, 62]. The analyzed optical properties of FTO films could be focused on four parameters which are refractive index, extinction coefficient, absorption coefficient and energy gap value. As the annealing temperature rise, the samples were demonstrated with high transmittance beyond 70% but decreased in energy gap value [55].

The FTO performance was related to their nanostructure. There were a lot of nanostructures that could be grown such as nanoparticle [26], nanorod [27], nanoflower [23], nanowire [28], and nanocactus [29]. There were several ways to

fabricate the FTO film such as spray pyrolysis [63], chemical vapour deposition [15], rf sputtering [37] and hydrothermal method [64]. All of these nanostructures can be classified in 0D, core-shell, 1D and 3D structures. The famous structure, used in conventional FTO films was nanoparticle. Which offer high surface area and maximum load of dye adsorption [65]. However, the existence of a lot of boundaries in the FTO films layer increased the tendency of interfacial charge recombination happened between photogenerated electrons and the positive elements in electrolyte. Thus, an attempt from Law et al. [65] by employed 1D nanostructure could provide direct pathway for electron transport. 1D nanostructure such as nanowire, nanorod and nanobelt gave much faster for electron transport compared with conventional nanoparticle films.

The recent research about nanostructure FTO films is focusing on 3D nanostructures. 3D nanostructure provide high surface area and also has excellent capability in achieving high light harvesting and charge transport [66]. 3D nanostructures include of nanotetrapods, branched nanostructured from 1D structure (nanoflower as shown in Figure 2.4, branched nanowire and dendritic nanowire), mesh based 3D photoelectrode and spherical oxide aggregate [67].

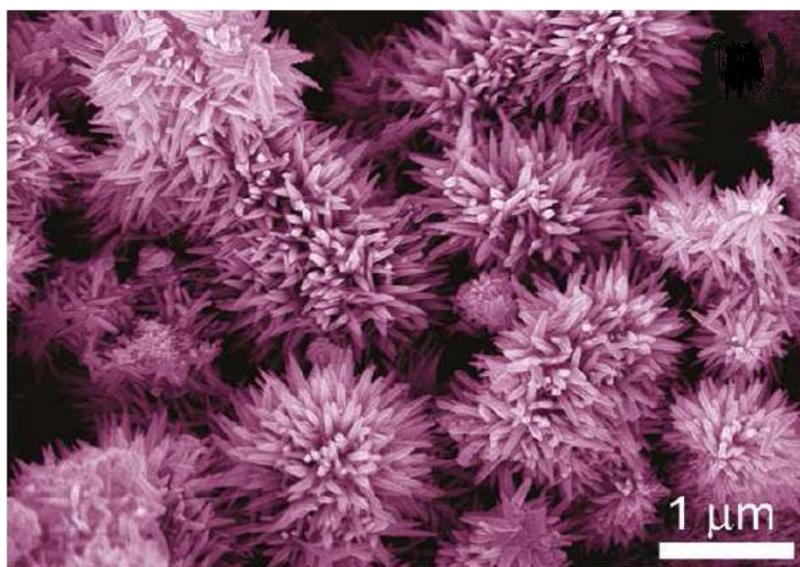


Figure 2.4: FESEM image of SnO<sub>2</sub> nanoflower films [68]

Instead of FTO, the antimony doped tin oxide (ATO) and indium doped tin oxide (ITO) also have been applied as TCO materials for DSSC. As compared to ITO and ATO, fluorine doped SnO<sub>2</sub> has higher transparency in visible range and

possesses extraordinary high temperature resistance. In addition, FTO has strong adhesion to glass and excellent chemical stability. FTO is more preferred for DSSC due to it has low sheet resistance and high temperature stable [27, 34].

### 2.2.1 Precursors for FTO films preparation

Mineral salts or organometallic are made into tin precursors that which contributes in manufacturing the DSSC. For group mineral salts, tin tetrachloride ( $\text{SnCl}_4$ ) was commonly used. One of the major drawbacks in using the salt is it should be stored in large quantities which will form HCl vapour when the  $\text{SnCl}_4$  is in contact with ambient humidity [69].

DBTDA is a chemical material from organometallic tin compounds that has been used successfully to prepare high oriented  $\text{SnO}_2$  thin films on glass substrates [70]. Organometallic compounds have been used as precursors of oxide thin films because they are readily to decompose at or near the surface of the hot glass ribbon [71]. The film obtained from DBTDA were polycrystalline and developed crystallites without sharp edges provide large surface area [72]. The film crystallites do not have sharp edges which were become an advantage for DSSC application as a transparent and conducting electrode in a device [72].

DBTDA precursor were used in preparing thin films due to it compatible in handling [72]. The thermal analysis for DBTDA solution shows the temperature compatible between  $320^\circ\text{C}$  and  $600^\circ\text{C}$ , with 2.5% of the initial mass was condensed [72]. Instead of DBTDA, there were other chemical compounds that could be used as precursor that include tetra-*n*-butyltin (IV) (TBT), tri-*n*-butyltin acetate (TBTA), monobutyltintrichloride (MBTC), phenyltintrichloride (PTTC), tetravinyltin (TVT), Tin (II) Chloride ( $\text{SnCl}_2$ ), and Tin (IV) Chloride ( $\text{SnCl}_4$ ) [15, 70, 71, 73, 74]

Ammonium Fluoride ( $\text{NH}_4\text{F}$ ) was used to prepare fluorine element as it is doped to  $\text{SnO}_2$ . There were different molar ratio of precursor that have been used to prepare F/Sn in stock solution and the most preferable were 1:2 and 1:3 [75, 76]. Several solvents were chosen to dissolve the chemical precursors which are 2 propanol, ethanol, methanol and water. These solvents should be suitable with the type of tin precursor used, for example; DBTDA with 2-propanol [75] and  $\text{SnCl}_4$  with acetone [57].

### 2.3 Hydrothermal method

One of the promising and cost effective methods to prepare a homogeneous thin film is the hydrothermal method. The hydrothermal method is a liquid deposition process which involves soft chemistry (bottom-up approach) and giving homogeneous thin film assisted with stable temperature and pressure [25]. It also can be described as a heterogeneous chemical reaction in a solvent above room temperature and at pressures greater than 1 atm in a closed system [16].

In hydrothermal method, water is the reaction medium. Water is one of the most important solvents in nature and has remarkable properties. It is a reaction medium that operates under hydrothermal conditions which is totally different compared to standard conditions. One of the biggest advantages of using water are the environmental benefit, known as most cost effective solvent and acting as a catalyst for the formation of desired materials. It is nontoxic, nonflammable, noncarcinogenic, nonmutagenic and thermodynamically stable. Water is very volatile as it is easier to be removed from the product.

The dispersity of particles can be improved by the hydrothermal method without any calcination process. Besides, the hydrothermal process requires great level of hydrothermal temperature in range of 120°C to 170°C and consume time around 10 hours [64]. Hydrothermal method usually have been performed under certain temperature and reaction time as 150°C for 10 hours [25], 120-170°C for 10 hours [64] and 180°C for 72 hours [77].

The fabrication of TiO<sub>2</sub> with high homogeneous crystalline product was conducted using hydrothermal method by using low reaction temperature as less than 150°C. The low reaction temperature contributes on reducing in agglomeration between particles, narrow particles size distribution, phase homogeneity, and controlled particle morphology. It also provides a uniform composition, purity of the product, monodispersed particles, control over the shape and size of the particles [16].

One of the significant advantages is it has capability on hybridizing with other process for instance [78-82]. Microwave, electrochemistry, ultrasound, mechanochemistry, optical radiation and hot-pressing are the alternative techniques that concordant with hydrothermal method in enhancing reaction kinetics and increasing ability to fabricate new materials. The hydrothermal synthesis has numerous benefits

over conventional and non-conventional techniques. The crucial assistance of hydrothermal technology for nanomaterial processing is the production of particles that are monodispersed with total control over their shape and size with highest dispersibility of chemical homogeneity. Besides, various advanced nanomaterials whether nanoparticles or nanocomposites comprised of metals, metal oxides, silicates, sulphides, hydroxides, tungstates, titanates, carbon, zeolites, ceramics and composite have been processed using hydrothermal technology [16].

The time variation of hydrothermal method was performed for the nanoparticle ZnO growth based on increasing the reaction time from 5 to 50 hours [16]. Byrapa & Adschiri [16] studied the effect of the formation of pure ZnO phase. It was found that the formation of pure ZnO phase under such low temperature condition required a minimum duration of 40 hours.

## 2.4 Dye-Sensitized Solar Cell

Dye-Sensitized Solar Cells (DSSC) is the third generation of photovoltaics. It was introduced as a promising candidate to replace other type of solar cells due to cost effectiveness and simplicity. This encouraged the academic and industrial researchers for performing the investigations to enhance the efficiency of DSSC. As a result, overall efficiency is as high as 15% as reported by Julian et al. [83]. These investigations shown enhancement of the performance of each component of DSSC.

DSSC comprised of five basic components which were transparent conducting oxide (TCO) [84], semiconductor oxide [85], dye adsorber [86], electrolyte [87] and counter electrode [88]. The operation principles of DSSC are divided in three stages such as absorption, separation and collection [89]. Absorption is the process of light absorption by sensitizing dye molecule and proceeds to excited sensitized state. Meanwhile, separation process is a process of injection of excited electron into the conduction band of semiconductors oxide and the dye molecule being oxidized. Third, the electron from the electrolyte is utilized to reduce the dye molecule and make it stable again.

Figure 2.5 shows the schematic working of DSSC which is function because of the interaction that happened between the working electrode (TCO) and counter electrode. First, the light was transmitted through TCO into the inner part (titanium

oxide).  $\text{TiO}_2$  as the highway for the electron (electricity) flowing through the cell. The nanostructures of titanium oxide films were coated by dye that was used to convert photon into electron. Beside, between both electrodes, it has been filling with an electrolyte to transfer electron from the counter electrode to the dye molecule. The unstable dye after release excited electron would receive extra electron from electrolyte to make it stable and function again. The counter electrode is generally made of platinum receives the electron from the anode after powering whatever type of cell then transfer to the electrolyte.

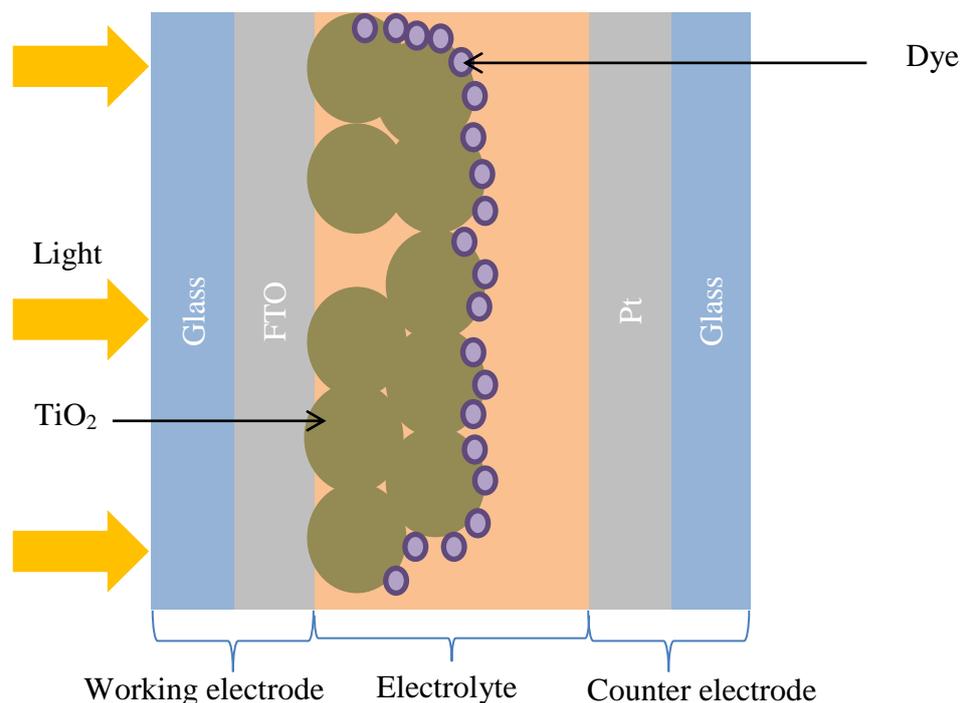


Figure 2.5: The DSSC working components

#### 2.4.1 Titanium Dioxide

The central part of a DSSC device consists a thick nanoparticle film that provides a large surface area for light-harvesting absorption molecules to attract the electron from the excited dye. Metal oxides like titanium oxide ( $\text{TiO}_2$ ), zinc oxide ( $\text{ZnO}$ ), tin oxide ( $\text{SnO}_2$ ), niobium pentoxide ( $\text{Nb}_2\text{O}_5$ ), tungsten trioxide ( $\text{WO}_3$ ), tantalum pentoxide ( $\text{Ta}_2\text{O}_5$ ), cadmium selenide ( $\text{CdSe}$ ), cadmium tellurite ( $\text{CdTe}$ ) and cadmium sulfide ( $\text{CdS}$ ) have been used as the semiconductor material in DSSC device [90]. However,  $\text{TiO}_2$  is the most attractive semiconductor oxide in research

field which has been used at this part of DSSC due to its stability under extreme condition. In DSSC, one of the  $\text{TiO}_2$  properties which lead to efficient injection of electron is it consist of the conduction band edge that slightly lies below the excited state energy level of many dye and it has better morphology compared to other [91]. High refractive index and dielectric constant of  $\text{TiO}_2$  also give advantage in light absorption and preventing electron recombination in photovoltaic application [92, 93].

$\text{TiO}_2$  consist of three crystalline phases which were rutile, anatase and brookite. Anatase phase of  $\text{TiO}_2$  was from tetragonal structure type as shown in Figure 2.6.

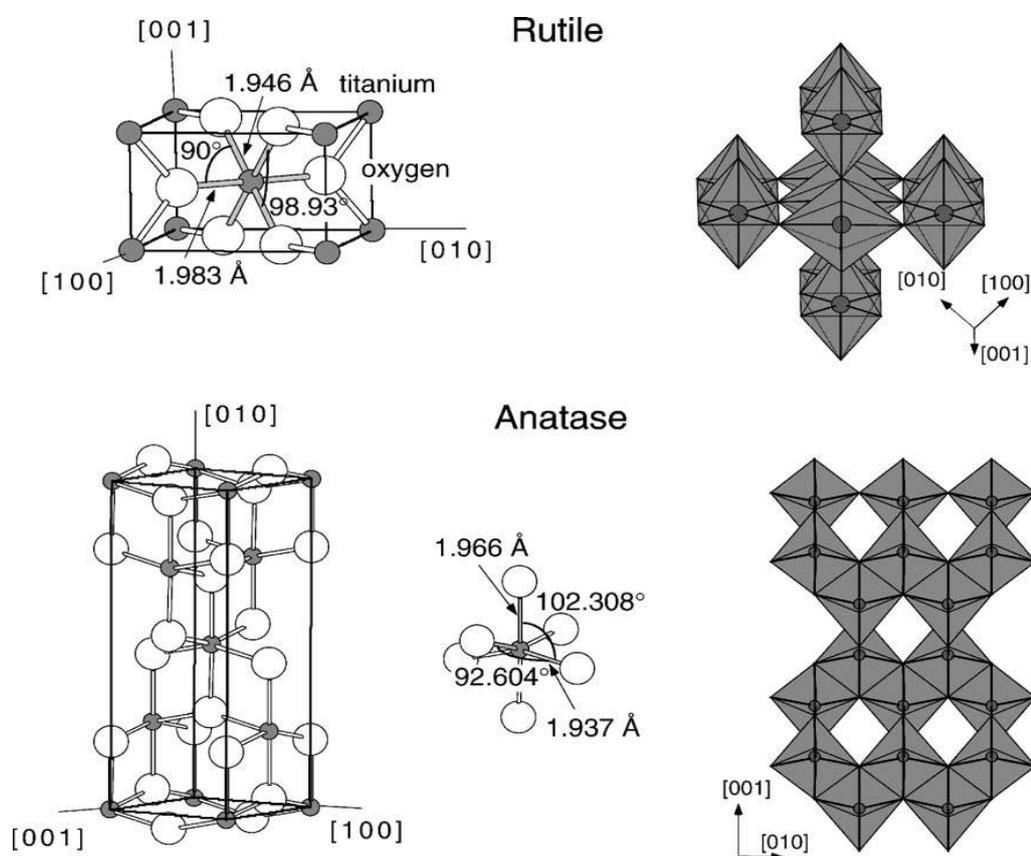


Figure 2.6: The structure bonding of rutile and anatase of  $\text{TiO}_2$  thin films [94]

This phase also has high stability at 0 K as compared to the rutile even the energy between two phase is small [95]. Anatase  $\text{TiO}_2$  as a chemically stable material due to high conduction band edge energy of 3.2eV and more prefer to be used in DSSC than rutile  $\text{TiO}_2$  which has low band edge energy [96].

The rutile is stable in high temperature region, whereas anatase and brookite was metastable phase and transformed to the rutile phase by annealing at high temperature. The electron transport process in rutile was also slower when compared to anatase due to the high packing density [97]. Beside, brookite  $\text{TiO}_2$  has larger cell volume and more complicated than the two phase of  $\text{TiO}_2$  and it is not commonly used in photovoltaic research [85].

There were a lot of findings which described the fabrication of anatase  $\text{TiO}_2$  pertaining to the variation of morphology such as nanoparticles, nanorod, nanoflower, nanofiber, hollow sphere, and hollow semisphere. [98-100]. Overall, nanoparticle  $\text{TiO}_2$  film has been considered as an ideal nanostructure semiconductor in photovoltaic application based on improvement of the attaching geometry of the dye on  $\text{TiO}_2$  surface due to the increment of surface quality which will led to faster electron injection [92].

E. V. Premalal et al. [26] reported using nanoparticle of  $\text{TiO}_2$  would be able to reach 6.48% of efficiency of DSSC. It was small in grain size that consisted of high surface area and made it possible for higher dye adsorbed at the surface of  $\text{TiO}_2$ , for boosting light harvesting and conversion of solar cell efficiency.

The fabrication of  $\text{TiO}_2$  almost similar to TCO fabrication such as hydrothermal, spray pyrolysis deposition, electrochemical method, sol gel method and chemical vapour deposition [101]. These methods fabricated different surface morphology of  $\text{TiO}_2$ .

## 2.4.2 Dyes

Dye adsorption was the most important part in DSSC. The function of dye adsorbed is to convert the light (photon) and transfer the electron into conduction band in the semiconductor material [102]. This molecular dye is chemically coated on the surface of  $\text{TiO}_2$  before DSSC is prepared by immersing deposited  $\text{TiO}_2$  on FTO surface in dye solution for 15 hours. The three groups of dyes are metal complex, metal-free organic and natural dye. Among of these dyes, metal complex dyes have high efficiency output [103].

Ruthenium (II)-polypyridyl complex was the metal complex dye group with the most efficient dye due to its numerous advantageous features, such as good

absorption, long excited-state lifetime and highly efficient metal-to-ligand charge transfer [103]. It consists of N3, N719, Z709 and black dye [87, 104, 105]. The molecular structure of dyes are as shown in Figure 2.7 [106]. However, these metal-complexes absorber are expensive materials that required a complicated preparation technique.

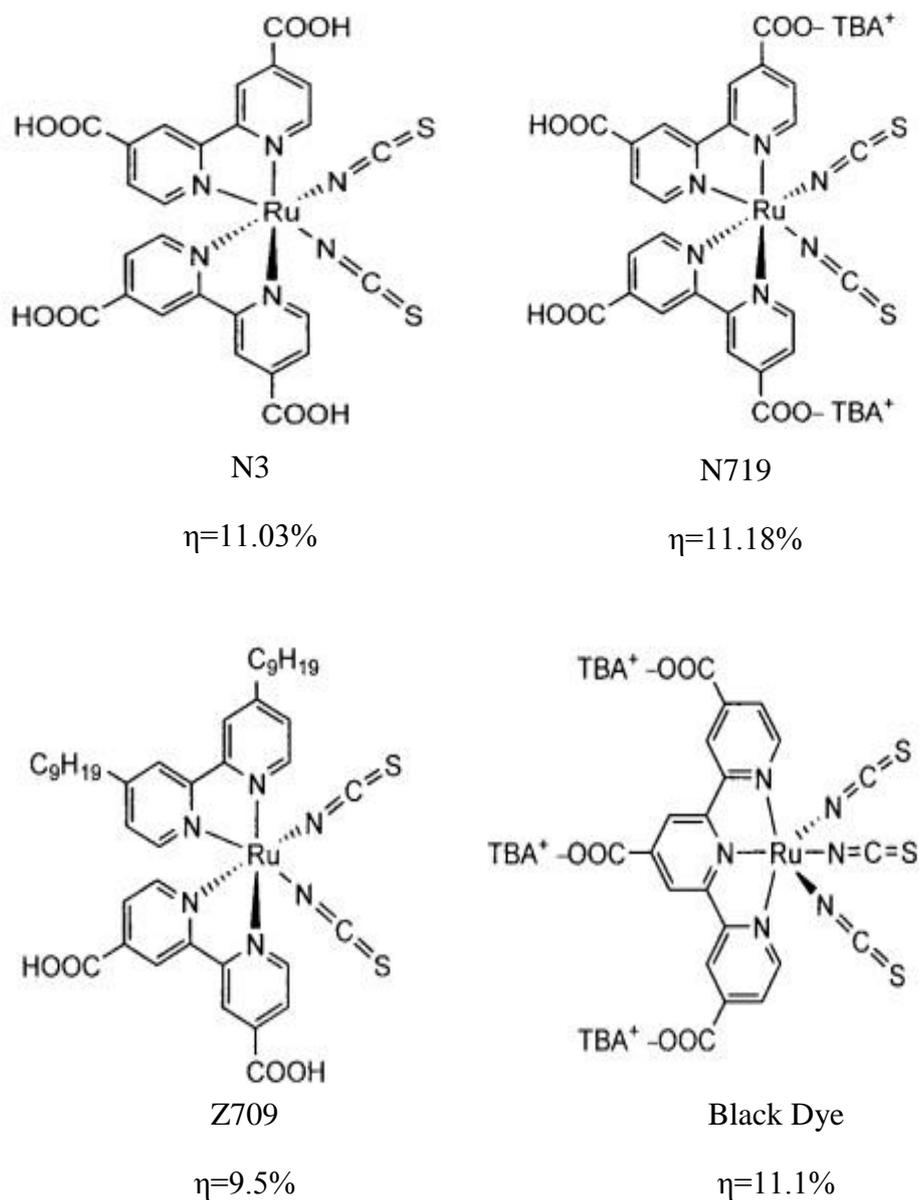


Figure 2.7: Molecular structure of various of metal-complexes dye with efficiency [106]

Metal-free organic dye was one of the promising materials to replace the expensive Ruthenium based sensitizer. The mechanism works through the donor and the acceptor which separated by  $\pi$ -bridge as shown in Figure 2.8 [106]. The  $\pi$ -bridge with high polarizability act as a backbone to enhance the efficiency of DSSC. As reported in [107], using the donor group of coumarin and acceptor group of cyanoacry acid with  $\pi$ -bridge system would be able to achieve 8.2% of efficiency. However, the efficiency of this dye is lower than synthetic dye due to the lack of absorption ability in visible region [108].

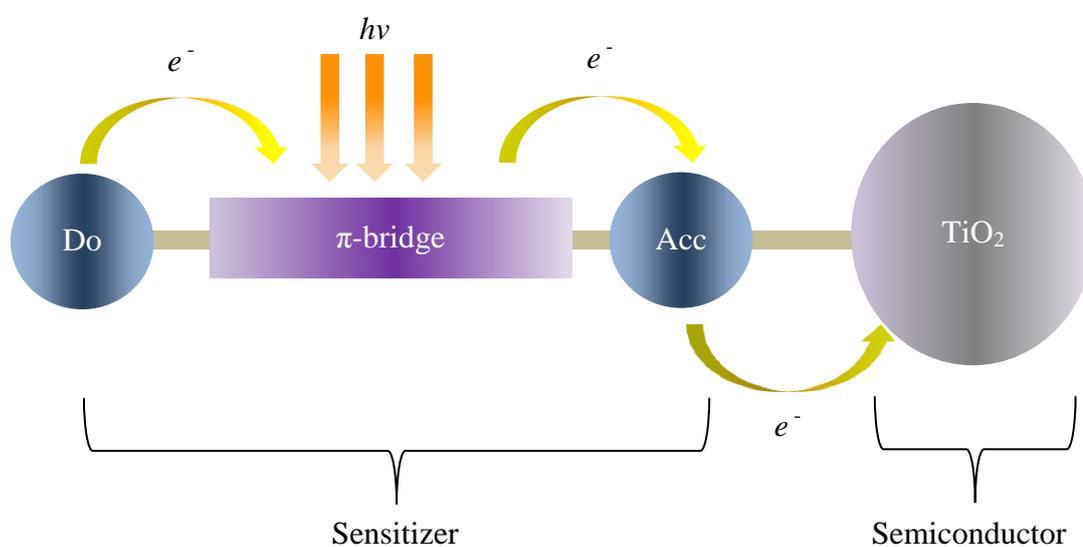


Figure 2.8: Working mechanism of metal-free organic dye. Do and Acc denote donor and acceptor, respectively

Another promising candidate that could cut down the cost compared to Ruthenium based complex dye is from natural dye. Natural dye as light harvesting elements in DSSC which have the potential to reach similar performances and stability as metal complexes dyes. They are easy to extract, non-toxicity, and environmental friendly [109]. There were four classes of plant pigments such as chlorophyll, flavonoids, anthocyanins, and carotenoids that could be obtained from different parts of plant such as roots, stems, fruits and flower petals [108]. The maximum absorption in the visible light range has been recorded by extraction of anthocyanins group [110]. There was a report indicated that efficiency from extraction of anthocyanins and carotenoids group which have not exceed 1% value

[86]. Literature survey found various types of natural dyes that have been extracted as shown in Table 2.2.

Table 2.2: I-V measurement of DSSC based on various types of natural dye [86]

Dye	$J_{SC}$ (mAcm <sup>2</sup> )	$V_{OC}$ (V)	Fill Factor	Efficiency
Wormwood	0.196	0.585	0.47	0.54
Purple Cabbage	0.208	0.660	0.53	0.75
Turmeric	0.288	0.529	0.48	0.03
Morinda Lucida	0.256	0.440	0.47	0.53
Wild Silican Prickly Pear	7.320	0.400	0.41	1.21
Red Turnip	9.500	0.450	0.37	1.70
Bougainvillea	2.100	0.300	5.7	0.36

### 2.4.3 Electrolytes

Sensitizer release electrons to the conduction band of porous semiconductor, then it was in the excited state. The electrolyte regenerates excited dye (oxides dye) into stable state. The main role of the electrolyte was to transfer positive charges toward the counter electrodes and reduce the oxides dye. The ideal electrolyte must has several characteristics to ensure good performance of DSSC such as [103]:

- (a) Good conductivity and low viscosity for enhancing the diffusion rate of electron.
- (b) The surface contact between the semiconductor and the counter electrode must in good condition.

(c) Not effecting the desorption of the sensitizer from oxidized surface and the degradation of the sensitizer.

(d) It is not absorbing light in visible wavelength.

Three classes of electrolyte for DSSC are as shown in Figure 2.9 [111]. The power energy conversion efficiency reached up to 11% with the liquid electrolytes based on acetonitrile solvent, a low-viscosity volatile solvent, and by using comparatively low iodine concentration [112]. As reported by Kusama et al. [112] addition of organic compound in electrolyte solution could enhance the efficiency of solar cells.

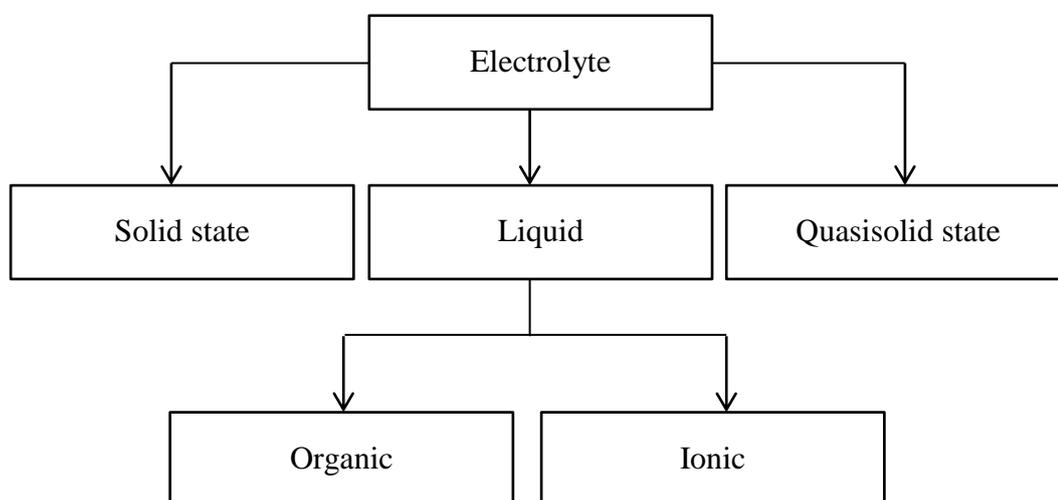


Figure 2.9: Classification of electrolyte for DSSC

#### 2.4.4 Counter Electrode

The enhancement of charge transfer was related to the catalytic activity and electrical conductivity. Based on this consideration, platinum (Pt) with high catalytic activity and low resistance was preferable to be used [113]. Platinum was a superior catalyst that has been used as a counter electrode for process reduction because it has high exchange current density, good catalytic activity and reflective material but the disadvantage of platinum was easy to disperse in electrolyte which caused degradation of DSSC. Furthermore, platinum is a high cost material [114]. Instead of

platinum, there were several materials like graphene and conductive polymer also have been used as counter electrode even the efficiency for those material were much lower compared to platinum but it would able to reduce the cost [88]. To overcome the costing problem of platinum, Qi et al. [115] deposited polyaniline (conductive polymer) on the stainless steel 304 (SS) for enhancing electrochemical activity. The conductivity of the catalyst also has been improved by deposits polyaniline on the graphitized polyimide carbon films thus exhibits the high open circuit-voltage and efficiency of DSSC [114]. The counter electrode of DSSC should be of high conductivity.

## **2.5 Summary of literature review**

The hydrothermal process is an attractive method to growth the nanostructured FTO films with high homogeneous. By forming the 3D structure of FTO films, it would able to enhance its light scattering ability. Then, among chemical precursors, such as  $\text{SnCl}_4$  and  $\text{NH}_4\text{F}$  in molar ratio 1:3 provided high surface area and low resistivity of thin films. This organic solvent (acetone) that has low viscosity produced a better single crystal and increase the reaction in solution. To avoid the formation of nanoparticle, the hydrothermal temperature must be exceeded  $120^\circ\text{C}$ . The irregular nanoparticles were obtained when the reaction was carried out at low temperature such as  $120^\circ\text{C}$  and below as discussed in Section 2.2.

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