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

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A thesis submitted in
fulfillment of the requirement for the award of the
Degree of Master in Electrical Engineering

Faculty of Electrical and Electronic Engineering
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January 2017

*To my beloved parents*

## ACKNOWLEDGEMENTS

My most humble and sincere thanks to my supervisor Dr Mohd Khairul Ahmad, Head of Solar Cell laboratory, MiNT-SRC, University Tun Husseein Onn Malaysia for his advice and guidance me entire in this research work.

The entire team at MiNT-SRC with very special thanks especially to Pn Faezahana and Miss Esri Hetti for their efforts and energy, all my samples experiment were able to be characterized on time.

To the incredible labmates, I would like to thank Pn Sakinah, Pn Kamalia, Asyikin Syasya, Fatin Izyani, Salina Mokhtar, Liyana and Kim Seng for all their support on me. Last, I'm very gratefull to my family for their patience that always supported me to finish this research.

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## 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 ($SnCl_4$), ammonium fluoride ($NH_4F$), acetone, deionized water and hydrochloric acid (HCl). The compound was prepared in an autoclave at 150°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°C, 140°C, 150°C, 160°C, and 170°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°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 disintesiskan 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 mengoptimumkan 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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| | | |
|---|---|---|
| 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 |
| $SnCl_4$ | - | Tin (iv) chloride |
| TCO | - | Transpaerent conducting oxide |
| $TiO_2$ | - | 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 ($SnO_2$) is a n-type semiconductor with band-gap energy of 3.6eV. A thin films of $SnO_2$ 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 $SnO_2$ 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 flourine because of the fact that the resultant flourine 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 posseses 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-butyll)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 $SnO_2$ film and they have studied the initial growth mechanism of $SnO_2$ formed and the thermal decomposition of DBTDA [21, 22]. $SnCl_2$ as tin precursor also has been used in fabrication of $SnO_2$ layer via hydrothermal method as been reported by Wang et al. [23]. The aligned $TiO_2$ nanorods and nanoflower on FTO substrate using hydrothermal method at low temperature as low as 150ºC were grew [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 of 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 grow

## 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, Flourine-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 $SnO_2$ films was performed by Ming et al. [31] by using $SnO_2$ 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 $SnO_2$ nanosheet films with 1 μm of thickness and second layer was $SnO_2$ hierarchical microspheres attached on nanosheets. The first synthesis of double layer $SnO_2$ film without $SnO_2$ seed layer was performed by Wang et al. [23] using direct growth from FTO substrates. This work was able to produce double layer of $SnO_2$ nanoflower on $SnO_2$ nanosheets films. This formation was synthesized by using $SnCl_2$, 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 examing 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]

| Materials and Process | Reference |
|---|---|
| Ag by **chemical-bath deposition** | Unknown Venetian |
| $SnO_2$:Sb by **spray pyrolysis** | J.M. Mochel , 1947 |
| $SnO_2$:Cl by **spray pyrolysis** | H.A. McMaster 1947 |
| $SnO_2$:F by **spray pyrolysis** | W.O.Lytle and A.E. Junge 1951 |
| $In_2O_3$:Sn by **spray pyrolysis** | J.M. Mochel , 1951 |
| $In_2O_3$:Sn by **sputtering** | L.Holland and G.Siddall, 1955 |
| $SnO_2$:Sb by **CVD** | H.F. Dates and J.K. Davis, 1967 |
| $Cd_2SnO_4$ by **sputtering** | A.J. Nozik , 1974 |
| $Cd_2SnO_4$ by **spray pyrolysis** | A.J. Nozik and g Haacke 1976 |
| $SnO_2$:F by **CVD** | R.G. Gordon , 1979 |
| Tin by **CVD** | S.R. Kurtz and R.G. Gordon, 1986 |
| ZnO:In by **spray pyrolysis** | S.Major , 1984 |
| ZnO:Al by **sputtering** | T.Minami, 1984 |
| ZnO: In by **sputtering** | S.N. Qui , 1987 |
| ZnO:B by **CVD** | P.S. Vijayakumar, 1988 |
| ZnO:Ga by **sputtering** | B.H. Choi, 1990 |
| ZnO:F by **CVD** | J.Hu and R.G. Gordon, 1991 |
| ZnO:Al by **CVD** | J.Hu and R.G. Gordon, 1992 |
| ZnO:Ga by **CVD** | J.Hu and R.G. Gordon , 1992 |
| ZnO:In by **CVD** | J.Hu and R.G. Gordon, 1993 |
| $Zn_2SnO_4$ by **sputtering** | H.Enoki , 1992 |
| $ZnSnO_3$ by **sputtering** | T.Minami, 1994 |
| $Cd_2SnO_4$ by **pulsed laser deposition** | 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.

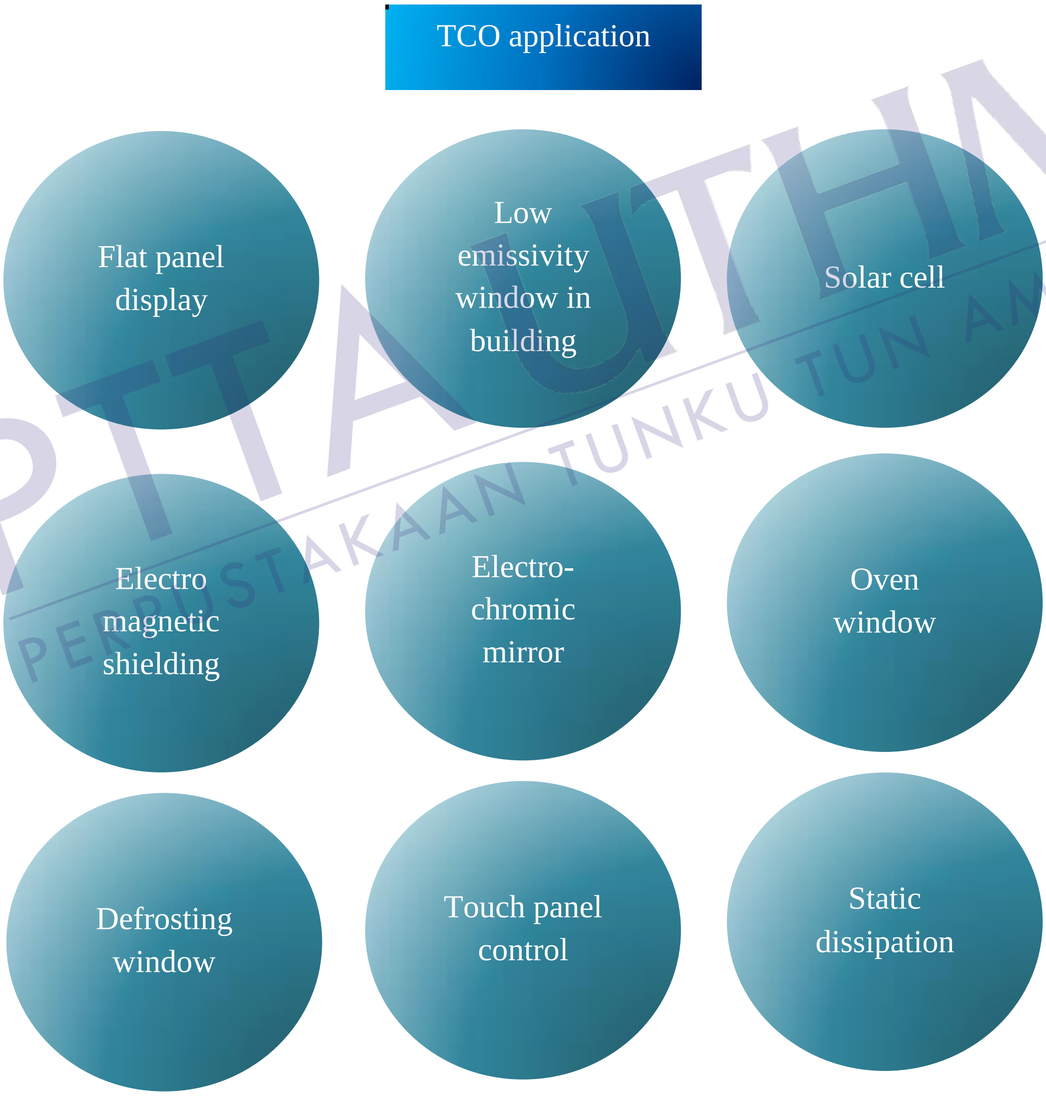


Figure 2.1: The applications of TCO

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