

**SYNTHESIZE OF ALUMINUM ZINC OXIDE NANOWIRES FOR DYE
SENSITIZED SOLAR CELL APPLICATION**

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SYNTHESIZE OF ALUMINUM ZINC OXIDE NANOWIRES FOR DYE
SENSITIZED SOLAR CELL APPLICATION

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Dedicated to

My beloved family especially my wife and my son and my parent's soul. Thank you very much for being supportive, helpful and understanding.

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ABSTRACT

Zinc oxide nanowires (ZnO NWs) have evoked extensive attention in recent years because of their potential technological applications. Aluminum (Al-ZnO) doped ZnO NWs have been deposited onto indium tin oxide (ITO) glass substrate, by using sol-gel spin coating and hydrothermal methods. Al-ZnO NWs with the percentage of Al content up to 6% were annealed at 450–600 °C. The structural, electrical and optical properties of the samples were characterized with X-ray diffraction (XRD), Energy-dispersive X-ray (EDX) spectroscopy, Field-emission scanning electron microscope (FE-SEM), atomic force microscope (AFM), and UV-Visible spectrophotometer and photoluminescence (PL) spectrometer. Meanwhile, the Al-ZnO NWs conductivity level was determined by Van der Pauw method. XRD analysis confirmed a single phase spinel structure with the crystallite size between 20-50 nm calculated using the Scherrer's formula. The highest main diffraction peak corresponding to the (002) orientation was due to the dominant phase of Al-ZnO at annealing temperature of 550 °C. The FE-SEM and AFM micrographs displayed the formation of well-defined and homogenous crystallite grains. The biggest grain size of 37 nm was observed for Al-ZnO NWs prepared with 6% Al concentration and annealed at 550 °C. The samples showed a high transmittance of more than 85% in the visible region, with energy band gap in the range of 3.25 to 3.35 eV. In addition, the electrical measurement result of the Al-ZnO NWs showed the lowest conductivity value of 2.49×10^{-4} S/cm with the activation energy $E_a = 27$ meV. A dye sensitized solar cell (DSSC) with this design showed a high short-circuit current density of 3.94 mA/cm² and open circuit voltage of 0.48 V. A DSSC with efficiency of 0.72% was achieved using this photo-anode.

ABSTRAK

Dawai nano zink oksida (ZnO NWs) telah mendapat perhatian meluas dalam tahun kebelakangan ini kerana potensi yang tinggi dalam penggunaan teknologi. ZnO NWs berdop aluminum (Al-ZnO) telah dimendapkan ke atas substrat kaca indium Stanum oksida (ITO) menggunakan kaedah pelapisan putaran sol-gel dan hidroterma. Al-ZnO NWs dengan kepekatan Al sehingga 6% telah disepuhlandap pada 450-600 °C. Pencirian sifat struktur, elektrik dan optik sampel telah dibuat menggunakan pembelauan sinar-X (XRD), spektroskop sinar-X tenaga-serakan (EDX), mikroskop elektron pengimbasan medan pancaran (FE-SEM), mikroskop daya atom (AFM), spektrofotometer UV-cahaya nampak dan spektrometer kefotopendarcahayaan (PL). Sementara itu, tahap kekonduksian Al-ZnO NWs ditentukan menggunakan kaedah Van der Pauw. Analisis XRD mengesahkan sampel berstruktur spinel fasa tunggal dengan saiz hablur antara 20-50 nm dikira menggunakan formula Scherrer. Puncak pembelauan utama tertinggi sepadan dengan orientasi (002) adalah berpunca daripada fasa dominan Al-ZnO pada suhu penyepuhlandapan 550 °C. Mikrograf FE-SEM dan AFM memaparkan pembentukan butiran hablur yang sekata dan homogen. Saiz butiran terbesar 37 nm diperhatikan bagi Al-ZnO NWs yang disediakan dengan kepekatan 6% dan disepuhlandapkan pada 550 °C. Sampel menunjukkan kehantaran tinggi melebihi 85% dalam rantau cahaya nampak dengan jurang jalur tenaga antara 3.25 hingga 3.35 eV. Disamping itu, hasil pengukuran elektrik Al-ZnO NWs menunjukkan nilai kekonduksian terendah 2.49×10^{-4} S/cm dengan tenaga pengaktifan $E_a = 27$ meV. Solar sel terpeka pewarna (DSSC) dengan reka bentuk ini menunjukkan kepadatan arus litar pintas yang tinggi 3.94 mA/cm^2 dan voltan litar terbuka 0.48 V. DSSC dengan kecekapan 0.72% telah terhasil dengan menggunakan foto-anod ini.

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LIST OF ABBREVIATIONS

| | | |
|--|---|---|
| AFM | - | Atomic Force Microscope |
| Al Cl ₃ -6H ₂ O | - | Aluminum Nitrate Hexahydrate |
| DC | - | Direct Current |
| DEA | - | Diethanolamine |
| DSSC | - | Dye-Sensitized Solar Cell |
| EDX | - | Energy dispersive X-ray |
| FESEM | - | Field emission scanning electron microscopy |
| FPP | - | Four point probe |
| FWHM | - | Full width at half maximum |
| HMTA | - | Hexamethylenetetramine |
| ITO | - | Indium Tin Oxide |
| IPCE | - | Incident-Photon-to-electron Conversion Efficiency |
| NaOH | - | Sodium Hydroxide |
| NW | - | Nanowire |
| PL | - | Photoluminescence |
| SC | - | Solar cell |
| UV-VIR | - | Fourier transform Infrared |
| XRD | - | X-ray Diffraction |
| Zn (CH ₃ COO) ₂ ·2H ₂ O | - | Zinc Acetate Di-hydrate |
| Zn (NO ₃) ₂ ·6H ₂ O | - | Zinc Nitrate Hexahydrate |
| ZnO | - | Zinc Oxide |

LIST OF SYMBOL

| | | |
|---------------------|---|--|
| μ_0 | - | Permeability |
| \AA | - | Angstrom |
| A | - | Area |
| a, c | - | lattice constant |
| $a,$ | - | Lattice parameter |
| P_{in} | - | Input Power [mW/cm^2] |
| $\text{Cu K}\alpha$ | - | Copper K-alpha line |
| d | - | Inter planar distance |
| D | - | Crystallite |
| FF | - | Fill Factor [dimensionless] |
| J_{sc} | - | Short Circuit Current Density [A/cm^2] |
| I | - | Current [A] |
| I_0 | - | Incident Photon Flux [$\text{cm}^{-2}\text{s}^{-1}$] |
| IPCE | - | Incident Photon-To-Electron Conversion Efficiency [%] |
| J | - | Current Density [A/m^2] |
| V | - | Voltage [V] |
| V_{oc} | - | Open Circuit Voltage [V] |

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CHAPTER 1

INTRODUCTION

1.1 Background of study

In twenty first century a wide interest to fabricate nanostructure materials and devices. These materials and devices have structures with nano-scale dimensions. One of the main reasons for interesting to nano-materials is because of different properties from those bulk materials. These properties such as large surface area have applications for various uses. Specially, Zinc oxide (ZnO) nanostructures are attracting interest since the techniques used to fabricate them are largely correspondent with available semiconductor production processes. ZnO nanostructures properties are different from that bulk ZnO.

ZnO is a key technology material with numerous applications ranging from chemical sensors to optoelectronics because of unique optical, electronic, and chemical properties [1-5]. The lattice parameters of ZnO are $a=0.3249$ nm and $c=0.5206$ nm at temperature room (300K), with a c/a ratio of 1.602. Moreover, ZnO has a wide band-gap 3.37 eV II-VI compound semiconductor that is suitable for short wavelength optoelectronic applications [6-9]. ZnO has an effective electron mass of $\sim 0.24 m_e$, and a large exciton binding energy of 60 meV at temperature room [10-13]. In addition, ZnO is a transparent material to visible light; also, it can be highly conductive by doping. The intrinsic defect levels that lead to n -type doping lay approximately 10– 50 meV below the conduction band [14, 15]. The reliable and reproducible p -type conductivity has not yet been achieved due to many issues. The

compensation of dopants by energetically favorable native defects such as zinc interstitials or oxygen vacancies is one of the obstacles [16]. The low dopant solubility is another issue. One of the optical properties of ZnO is extensively studied because of their promising applications in optoelectronics. Furthermore, the lasing conditions can be further improved with low dimensional ZnO structures, which enhance the excitation oscillator strength and quantum efficiency [17,18]. Therefore bulk ZnO has a small exciton Bohr radius (~ 2.34 nm). The Quantum Confinement effect in ZnO nanowires could be observable at the scale of an exciton Bohr radius. It has been reported by Guet *al.* [19] that the excitation binding energy is significantly enhanced due to size confinement in ZnO nano-rods with diameter of ~ 2 nm. Various types of solar cell, such as silicon-based, GaAs and organic have recently been developed [19, 20]. Semiconductor nano-wires (NWs) have been proposed as basic “building blocks” in a variety of devices, for example, photonics, electronics, and chemical sensing [20].

Nowadays, one-dimensional (1D) nano-wires and nano-rods have attracted a lot of attention. Compared to thin-film and bulk devices, 1DNW devices are expected to have a larger response to light due to the high length-to-diameter aspect ratio and high surface-to-volume ratio of 1D-NWs. Investigations into semiconductor nano-material systems have demonstrated that ZnO is a promising material for application in various devices because it is a chemically and thermally stable and n-type semiconductor with a large band-gap energy and a large exciton binding energy at room temperature. ZnO nano-structures can be synthesized using different techniques. Vapor phase deposition [21] and hydrothermal synthesis [22] are the most commonly used low-temperature synthesis techniques for zinc oxide nanostructures.

In particular, dye-sensitized solar cells (DSSCs) of the third generation of solar cells have become a very interesting and practical alternative for advances in solar cell technology. The working mechanism of the DSSC is unique in that it does not follow the principles of the traditional p-n junction solar cell. The dye sensitizer absorbs the photons, while the role of the semiconductor film is to facilitate charge transport to the collecting transparent conductive oxide glass substrate. Since its

introduction into the science community in 1991, the nanocrystalline photoanode in DSSC have predominantly been comprised of nanoparticles. With efficiencies reaching a plateau of 11-12% for TiO₂ nanoparticle-based dye sensitized solar cells [6, 9], many researchers became very interested in studying the dye-sensitized solar cell performance of alternative semiconducting nanomaterials. Specifically, ZnO has been an ideal alternative to TiO₂ because ZnO has a similar conduction band edge that is appropriate for proper electron injection from the excited dyes; moreover, ZnO provides better electron transport due to its higher electronic mobility.

Over the past decade, there has been a heightened interest in using ZnO NWs as the semiconducting photoanode in dye-sensitized solar cells. Utilizing wide-band gap semiconductor nanowires (e.g., ZnO NWs) instead of TiO₂ nanoparticles has been thought to be very advantageous because i) the NW morphology allows for electrons to travel a more direct 3 conduction path from the point of injection to the point of collection, and ii) the NW possess a large enough surface area for adequate dye adsorption [9]. The NW photoanode has a very fast electron injection rate and the electron diffusivity in crystalline wires (ZnO NW) has been reported as several orders of magnitude larger than electron diffusivity within TiO₂ nanoparticles [17]. The superior electron transport within the NW photoanode can be attributed to its higher crystallinity and the presence of an internal electric field that facilitates electron transport to the collecting glass substrate by effectively separating the injected electrons from the oxidized species of the electrolyte; this, in turn, improves the charge collection efficiency [17]. Furthermore, NWs can be synthesized at low temperatures, which allow the use of various substrates including polymers, and the employment of low temperatures greatly reduces energy costs. However, researchers have yet to fabricate ZnO NW-based DSSC with efficiencies similar or higher than TiO₂ nanoparticle-based DSSCs. Although the vertical NW morphology has many advantages, there is also a critical disadvantage. Compared to the closely packed nanoparticle thin film, more uncovered substrate surface between the NWs is present in the vertical NW array. These open spaces lead to direct contact between the electrons at the conducting glass substrate and either the oxidized dye molecules or oxidized species in the electrolyte during the charge transport process. This phenomenon is known as either electron recombination or electron back transfer. Interestingly, many have referred to the occurrence of electron back transfer as the

most crucial limitation of DSSC as it severely affects its performance by short-circuiting the cell. It is thought that by placing a barrier layer between the conducting glass substrate and the NWs, the contact at the conducting substrate-electrolyte interface can be significantly reduced or avoided completely. Another major challenge of ZnO NW-based dye sensitized solar cells stems from the lower surface area of the ZnO NW array to that of the network of TiO₂ nanoparticles on the substrate. By having a larger surface area, the nanocrystalline photoanode is able to absorb a greater amount of the incoming light. Thus, improvements in the surface area of the ZnO NWs array used for the DSSC will significantly enhance the light harvesting efficiency, which in turn results in an overall increase in the power conversion efficiency of the cell. In addition to providing better charge collection, the use of very long and dense ZnO NW arrays results in a greater surface area that is necessary for an increase of adsorbed dye molecules, which leads to improved light harvest efficiency [17]. As an alternative to synthesizing longer NWs, the concept of producing dense hierarchal NW structures should also yield larger surface areas needed to improve the conversion efficiency of ZnO NW-based DSSC.

1.2 Problem statement

This research shows that ZnO NWs have been studied almost two decades, to emphasize generally on their synthesis and properties [23]. Most of the techniques employed are based on chemical methods comprising of electrochemical and chemical bath deposition (CBD) [24-25]. The second methods appeared to be more reliable in terms of its ease of use, less expensive and the ability for commercial production [26-27].

Synthesis and Controlled growth using different techniques and using Al instead of Pt in ZnO NWs by easy and economic method is demanding for optoelectronic application. since many techniques, are for fabricate Solar Cell technique including advantages for large scale, and high density fabrication of Al-ZnO NWs. However, we achieved this method with various growth conditions to

study the role of annealing, a variation of substrate temperature, annealing time, and another growth parameter on sample morphology.

However, there is No progress of works using the conventional bath techniques which revealed the formation of ZnO NWs with less defines the structures. Further examination showed that the NWs the same ZnO appeared as simple and short, ascribed by their non-random orientations via chemical bath deposition [29]. A CBD method is proposed which will result in quality of ZnO NWs. The novel corresponding structural and optical properties are expected to improve significantly. And the following method of preparation and optimum synthesis of Al-ZnO NWs by presented method can approach to optimum nanostructure for semiconductor application.

1.3 Research Objectives

This study presents the following objectives:

- I. To fabrication photo anod of ZnO NWs
- II. To determine the structure of Al-ZnO by chemical deposition method in different temperature and ratio and protract employing XRD and EDX.
- III. To analyze of surface morphology such as ZnO roughness, number density, ratio of grain area, shape and size of the ZnO NWs by AFM and FE-SEM.
- IV. To determine the optical properties of nanowire ZnO in different annealing temperature (value of 450-600 °C) and concentration by UV-visible and photo-luminance (PL).
- V. To determinate effects of the current density of ZnO NWs arrays on the overall DSSC power conversion efficiency by designing a one-

dimensional ZnO NWs that increases the NWs density and enhances surface area, and thus enhances light absorption.

1.4 Scope of research

This project aims to synthesize and investigation of structural, optical and electrical properties of ZnO NWs. The concentrations of Al- ZnO seeded catalyst expressed as were (0 – 6 %).

This material is selected for this study in view of their technological importance. The crystallinity of the film is developed by calcinate at 450 - 600 °C. To growth ZnO NWs, several steps must be taken, which each step is depend on benefits and builds on the information found in the previous steps. These are reflected in the experimental approach. Sol-gel and Chemical Bath Deposition (CBD) methods are employed to prepare ZnO nanowire on Indium-tin-Oxide (ITO) glass substrate, ZnO bilayer, and glass/ITO/AZO/ ZnO heterostructure. Different deposition parameters such as; time deposition, substrate temperature and treatment that in different temperatures and times are applied to investigate the growth process and surface evolution of zinc oxide nano-wires. Energy dispersive X-ray diffraction (EDX) and field emission scanning electron microscopy (FE-SEM)are used to characterize the surface morphology of samples.

Optical properties of samples and the effect of growth parameter, ZnO space layer thickness and ITO substrate thickness on the optical behaviour are studied by photoluminescence (PL) and UV-Visible. This project involves the preparation and characterization of ZnO nanostructure.

1.5 Significant of study

Nano-structuring of semiconductors is a novel device of developing new electronic and optoelectronic devices. Particularly, it is one of the discoveries of room-temperature (RT) visible photoluminescence (PL) from ITO and ZnO. Furthermore, nanostructures have very much interest in these particular kinds of Nanoclusters and small semiconductor nanoparticles. Setting the optical response of ITO and zinc oxide nanomaterial by changing their size to become also a the most challenging aspects of recent research on semiconductors.

Easy and economical fabrication technique would be developed. The instrumentation for large-scale fabrication has socio-economic impact. The fundamental physics behind the growth would be understood. The data generated throw this research will be published in high impact factor journal, and research data would be presented in conferences, workshops, and seminars. Ph.D. and Masters Research Scholar can be trained using this methodology to pursue their future research.

The high quality of the sample needed for the optoelectronic industries can be supported by using rf magnetron sputtering method. The device would be cheaper and economic. A set of characterization, which we propose, would be able to measure the band gap, right sample structure, and right physics. An extension of this research is that these methodologies are not just limited to the Zinc, another semiconductor nanostructure like ZnO and other also can be grown by using this method. This method can be extended and become versatile for nanostructure growth.

1.6 Organization of research

This research is concluding of five chapters. Chapter 1 begins with the introduction, followed by the research background, the statement of the problem,

research objective, research questions, and the scope of the study, research hypothesis, and the organization of the study.

Chapter 2 provided an extensive literature review that had been done serve as a guide for understanding the following chapters. This detailed review will be based primarily on, **i)** the properties, characteristics, and attractive uses of ZnO and its nanomaterials; and **ii)** the fundamental principles of photovoltaic and particularly advancements of dye-sensitized solar cells within the nanotechnology field.

Chapter 3 focused on, **i)** the fabrication of ZnO nanowires based on a hydrothermal process synthesis; **ii)** an investigative study of ZnO morphology based on varied synthesis conditions and **iii)** examined various methodologies to improve the overall power conversion efficiencies of ZnO nanowires based dye-sensitized solar cells via the fabrication of a one-dimensional solar cell design.

Chapter 4 described the basic recipe used to grow ZnO NWs. To grow these nanowires successfully, various growth parameters were studied. The growth mechanism was explained, and structural characterizations on grown ZnO NWs were performed.

Lastly, Chapter 5 concludes all major findings and rationalizations from this research project.

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