STAの発生を抑制する方法の開発-STA発生防止のための研究-
SYNTHESIS OF HEMATITE NANOSTRUCTURES
FOR DYE-SENSITIZED SOLAR CELL APPLICATION

（色素増感太陽電池応用に向けたヘマタイトナノ構造の合成）

2016
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# TABLE OF CONTENTS

## CHAPTER 1 – INTRODUCTION

1.1 Dye Sensitized Solar Cell  
1.2 Common Photoanodes Used in DSSC  
1.3 Iron Oxide Nanostructure based DSSC  
1.4 Iron Oxide Nanostructures  
1.5 Common Iron Oxides (α-Fe₂O₃) Synthesis Methods  
   1.5.1 Thermal Oxidation  
   1.5.2 Hydrothermal Process  
   1.5.3 Solgel Method  
   1.5.4 Metallorganic Chemical Vapor Deposition  
1.6 Optical Properties  
   1.6.1 Electronic Transition in Hematite  
   1.6.2 Steady-state Absorption  
   1.6.3 Photoluminescence  
1.7 Charge Carrier Dynamic of Hematite Nanostructures  
1.8 Research Objectives  
1.9 References

## CHAPTER 2 – PREPARATION AND CHARACTERIZATION OF IRON OXIDE NANOFORLAKES

2.1 Introduction  
2.2 Thermal Oxidation Technique
2.3 Effects of Temperatures on Iron Oxide Nanostructures
   Synthesis by Oxidation
   2.3.1 Scanning Electron Microscopy Characterization
   2.3.2 Crystal Structure Characterization
2.4 Effects of Annealing Times on Iron Oxide Nanostructures
   Synthesis by Oxidation
   2.4.1 Scanning Electron Microscopy Characterization
   2.4.2 Crystal Structure Characterization
2.5 Transmission Electron Microscopy Characterization
2.6 Iron Oxides Nanoflakes Growth Mechanism
2.7 Conclusion
2.8 References

CHAPTER 3 – PREPARATION AND CHARACTERIZATION OF
IRON OXIDE NANOWIRES
3.1 Introduction
3.2 Two-step Oxidation Process
3.3 Effects of Oxidation Temperatures on Iron Oxide Nanowires
   Growth
3.4 Effects of Pre-annealing Temperatures on Iron Oxide
   Nanowires Growth
   3.4.1 Surface Morphology of Nanowires Growth in Dry Air
   3.4.2 Iron Oxide Nanowires Growth in Oxygen Gas
   3.4.3 Crystal Structure Characterization
   3.4.4 Elemental analysis
3.5 Discussion
3.6 Conclusion
3.7 References
CHAPTER 4 – PHOTOVOLTAIC PERFORMANCE OF IRON OXIDE BASED SOLAR CELL ON FE FOIL

4.1 Introduction 46

4.2 Iron Oxide Based Dye Sensitized Solar Cell Fabrication Procedure 47

4.3 Effects of Oxidation Temperatures on Iron Oxide Nanostructures 48
   4.3.1 Surface Morphology Characterization 48
   4.3.2 Crystal Structures Characterization 50

4.4 Photovoltaic Performance of Iron Oxide Nanostructures Based DSSC 51

4.5 Effect of Nanostructures Surface Area to Photovoltaic Characteristic 52

4.6 Discussion 53

4.7 Conclusion 54

4.7 References 55

CHAPTER 5 – OPTICAL PROPERTIES AND PHOTOVOLTAIC PERFORMANCE OF IRON OXIDE-BASED SOLAR CELL

5.1 Introduction 57

5.2 Iron Oxide Nanoflakes Based Electrochemical Solar Cell Fabrication Technique 58

5.3 Effects of Annealing Time on Iron Oxide Nanoflakes Preparation 59
   5.3.1 Surface Morphology Characterization 59
   5.3.2 Crystal Structure Characterization 61

5.4 Optical Properties of Iron Oxide Nanoflakes 61
   5.4.1 Absorption Spectra Characterization 61
   5.4.2 Transmittance Spectra Characterization 63
5.4.3 Reflectance Spectra Characterization 63
5.4.4 Optical Band Gap 64
5.5 Photovoltaic Characterization 66
5.6 Discussion 67
5.7 Conclusion 69
5.8 References 69

CHAPTER 6 – CONCLUSION

6.1 Overall Conclusion 70
6.2 Suggestions for Future Work 72
6.3 Acknowledgement 73
6.4 List of Publications 74
   6.4.1 Journals 74
   6.4.2 Conferences 75
CHAPTER 1

INTRODUCTION

1.1 Dye Sensitized Solar Cell

Rapid increases in world energy demand every year have become a worrying issue for world energy suppliers. In 2050, energy demand is expected to almost double from reported current energy consumption which is 13 to 23 terawatts (TW) [1]. Natural resources such as petroleum, gas and coal which cover about 80% world energy supplies are depleting rapidly. Intensive study and action are required in order to explore other energy sources such as renewable energy with high energy conversion to support world energy demand. In addition, an environmental issue caused by the burning of fossil fuel has become a major concern. Global warming due to increasing of dangerous carbon dioxide (CO₂) and carbon monoxide (CO) content in the atmosphere must be controlled. Safer and cleaner sources with high energy conversion are needed to support world energy consumption which now suffers from reduction of fuel reserves as well as environmental problems.

Several alternative energy sources have been commercially used such as hydroelectric, nuclear, geothermal, solar, wind and biomass. This energy meets 20% of world energy demand. Among these alternative sources, solar energy by employing photovoltaic technology has become the most efficient technology [2]. In addition, plenty of solar resources are available from solar radiation of the sun, with an approximate total of 3 x 10^{24} J per year, which is ten times the required world energy [3]. In 1954, the first commercial photovoltaic cell was fabricated by using diffused silicon p-n junction concept and achieved 6% efficiency [4]. The efficiency of silicon based solar cell has increased over the years, however the application of this device is limited by the high silicon cost and health risk in their production. This solar technology was commercially used in Germany (21%), China (16%), Japan (13%), United states
of America (11 %), Italy (10 %), Spain (4 %), France (3 %), United Kingdom (3 %) and rest of the world (19 %) [5]. Poor countries are not able to utilize this high cost silicon solar cell technology even though they have plenty of sunlight to harvest per year. Therefore, much of the current research that has been done has focused on clean and low cost solar cell such as organic solar cell and dye sensitized solar cell.

In 1991, inspired by O’Regan and Gratzel, a new low cost photovoltaic cell known as dye sensitized solar cell (DSSC) was been developed. By adapting the principle of plant photosynthesis, they successfully fabricated a photovoltaic cell by using the same basic mechanism. In this photovoltaic cell, colloidal titanium dioxide (TiO$_2$) particles were used as semiconductor material yielding overall light-to-electric energy conversion of 7.1-7.9 % [6]. In 2005, this DSSC efficiency was further increased to more than 11 % by using purified ruthenium sensitizer [7]. The performance of DSSC can be influenced by several factors or parameters that directly or indirectly contribute to the device fabrication process.

In common DSSC fabrication, there are several important materials involved such as working electrode consisting of conducting glass, photoanode and dye, electrolyte and cathode. The structure and working of DSSC is illustrated in Fig. 1. In this figure, S”/S+/S* is denoted as sensitizer in the ground state, oxidized state, and excited state.
Based on DSSC structure in Fig. 1.1, incidental light from the sun is converted to electricity by following a series of essential steps. First, photoanode will absorb incidental light from the sun consequently exciting the electrons in the dye. These excited electrons will be injected to the conduction band of the semiconductor due to different energy level. This condition leads to oxidizing of dye because of electron movement. These loss electrons will be restored by the electrolyte which is connected to the dye. The electrolyte will donate the electron and return the dye to initial state. Then, the electrolyte will go through reduction reaction in catalytic electrode and obtain electrons from the external circuit. This charge transfer processes occur in a complete cycle including backward electron transfer which will affect the performance of the solar cell.

There are several parameters involved in DSSC measurement such as short circuit current density ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF), conversion efficiency (%) and an incident photon to current efficiency (IPCE). The properties of
semiconductor, dyes and electrolyte will significantly affect this parameter. Equation (1) shows the relation between $J_{sc}$, $V_{oc}$, FF and $P_{in}$ to the power conversion efficiency [9].

$$\eta = \frac{V_{oc} \times I_{sc} \times FF}{P_{in}} \times 100$$  \hspace{1cm} (1)

Above equation suggested that it is important to improve the $J_{sc}$, $V_{oc}$ and FF of the device in order to increase the overall conversion efficiency. Han et al. investigated the series resistance of DSCs which focused on the sheet resistance of the transparent conducting oxide, ionic diffusion in the electrolyte resistance and interface resistance between counter electrode and the electrolyte [10]. They found that the FF increases with decrease in the internal resistance elements and consequently improve the overall efficiency.

1.2 Common Photoanodes Used in DSSC

Photoanode materials have become one of the important components in DSSC which significantly affect their overall performance. Normally referred to as semiconductor materials, this layer provides a surface area for the dye adsorption, taking and bringing the excited electron through its conduction band to the external circuit [11]. The efficiency of DSSC can be influenced by the surface morphology, crystal structure and surface area of semiconductor. Since 1991, TiO$_2$ with band gap of 3.2 eV is considered as an ideal photoanode materials due to their properties and surface morphology [6]. Nazeeruddin et al. successfully increased the efficiency of DSSC to 11.18 % by optimizing several ruthenium [12] sensitizers using purification process to form pure N-bonded isomers. In this study, the protonation of terminal carboxylic groups and the counterions on the electronic structure and optical properties of the dyes give significant effect to the conversion performance. Recently, this efficiency was increased to 13 % by Mathew et al., by applying porphyrin dye (SM315) with prototypical structure of a donor-$\pi$-bridge-acceptor [13]. This dye can optimize interaction between electrolyte as well as increase light-harvesting properties. From this
study, it is shown that the efficiency of DSSC can be further increased by modifying their light absorption properties.

In addition to TiO$_2$ semiconductor, widely study photoanode materials in DSSC are zinc oxide (ZnO), stannic oxide (SnO$_2$) [14, 15]. Mahmoud et al., in their study found that branched tetrapods ZnO nanostructures give the highest efficiency compared to ZnO and SnO nanorods, nanowires, nanobelts and nanoparticles. They also believed that semiconductor surface area, morphology and component combination will greatly influence the photoelectrochemical properties [15]. However, further studies are required since the efficiency achieved is lower as compared to TiO$_2$ based DSSC.

1.3 Iron Oxide Nanostructure Based DSSC

Iron oxide ($\alpha$-Fe$_2$O$_3$) or commonly known as hematite is a semiconductor material which has been extensively studied for many applications because it is a cheap, nontoxic, thermodynamically stable and abundant material with promising optical properties [16]. Having smaller optical band of 2.2 eV compared to TiO$_2$, ZnO and SnO$_2$ makes this material favourable for photocatalytic [17], photoelectrochemical [18, 19] and photovoltaic [20-22] applications. Agarwala et al. reported 0.8 and 1.8 % power conversion efficiency can be obtained by using Fe$_2$O$_3$ nanorods and nanoflowers respectively prepared by solution method as photoanode in DSSC [21]. In this study, higher surface area $\alpha$-Fe$_2$O$_3$ hybrid nanoflower morphology was synthesized to increase diffusion coefficient and improve their electron transport properties. In addition to nanorods and nanoflowers, Cavas et al. used Fe$_2$O$_3$ nanoparticles and nanocluster prepared by sol-gel method as photoanodes in Ruthenium solar cell [20]. With transmittance greater than 75 % in the wavelength range of 600-900 nm, they obtained the overall efficiency of 0.011 % at 100 mWcm$^{-2}$ light intensity and this efficiency is increased with increasing light intensity.

Recently, besides working electrode, Fe$_2$O$_3$ has also become a promising candidate for counter electrode in DSSC due to its interesting morphology. Shahpari et al. successfully synthesized Fe$_2$O$_3$ nanoparticles, nanofibers, nanoflowers and nanorods
through hydrothermal reactions and applied counter electrode by replacing expensive platinum (Pt) [23]. Among the nanostructures used, Fe$_2$O$_3$ nanoparticles give the highest efficiency of 4.6 % and this value is comparable to Pt. In this study, they suggest that larger surface are of nanoparticles with crystal structure grown on (012) and (104) directions have become the main factors in increasing solar cell performance. The previous study shows that Fe$_2$O$_3$ nanostructures can be explored as both working and counter electrode in DSSC because of their excellent properties and ability.

1.4 Iron Oxide Nanostructures

Iron oxides are chemical compounds consisting of iron and oxygen which can be obtained by various processes. There are sixteen common iron oxides and oxyhydroxides and the most important oxides structure is given in Table 1.1. Among the iron oxide compounds, α-Fe$_2$O$_3$ (hematite) offers the most thermodynamic stability compared to others.

<table>
<thead>
<tr>
<th>Oxides Formula</th>
<th>Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>5$H$</em>{6.4}$O$_8$.4H$_2$O</td>
<td>Ferrihydrite</td>
</tr>
<tr>
<td>α-Fe$_2$O$_3$</td>
<td>Hematite</td>
</tr>
<tr>
<td>γ-Fe$_2$O$_3$</td>
<td>Maghemite</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>Magnetite</td>
</tr>
</tbody>
</table>

Hematite (α-Fe$_2$O$_3$) is isostructural with corundum. The crystal structure of hematite is rhombohedral symmetry with lattice parameter given in hexagonal cell are: $\alpha = 5.0346$ Å, $c = 13,752$ Å. This structure is composed of dense arrangement of Fe$^{3+}$ ions in octahedral coordination with oxygen in hexagonal closest-packing similar to stacking of octahedral sheet. In hematite unit cell as shown in (Fig. 1.2), two types of Fe atoms are paired along the (111) axis consisting of short (type A) and larger (type B) Fe-Fe distance. It is also shown that a Fe atom is bonded to six O atoms, whereas each
O\textsuperscript{2} is bound to Fe\textsuperscript{3+}. In this structure, red big circle refers to oxygen atoms and blue small circle is Fe atoms.

**Figure 1.2:** Hexagonal unit cell of \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} (left) and rhombohedral primitive cell [25] [26].

Hematite can be obtained in various types of nanostructures by optimizing their synthesis parameter in several synthesis processes. Since 1990, one dimensional (1D) nanostructures such as nanowires [27-32], nanorods [33-35] and nanotubes [36, 37] have successfully synthesized on various substrates. Multidimensional hematite nanostructures are also extensively explored due to their larger surface area. For example, \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} nanoflakes [38-40], nanoflowers [21, 41], nanoparticles [42, 43], nanorings [44, 45] and nanocubes [46] were synthesized for electronic device applications.

### 1.5 Common Iron Oxides (\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}) Synthesis Methods

There are two general approaches for the formation of \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} nanostructures from Fe which are hydroxide route and oxide route. For hydroxide route, hematite formation occurs through iron hydroxide while in oxide route, the oxidation state of Fe slowly increase resulting in oxide layers with increasing oxidation [24].
1.5.1 Thermal Oxidation

Hematite nanostructures can be synthesized by heating Fe foil in ambient air [39] or an oxidizing atmosphere [47, 48]. Zheng et al. reported the synthesis of α-Fe₂O₃ nanoflakes by simply heating Fe foil on the hotplate under ambient condition [39]. They found that at temperature of 260 °C for 10 h, ultra-sharp α-Fe₂O₃ nanoflakes with 20 nm base-width and 5 nm at the tips with 1-2 μm in length was formed. It was believed that surface diffusion of iron atoms and iron oxides molecules are driven by oxygen rich and Fe deficient at low temperature.

In oxidizing condition, Fu et al. in their study successfully obtained large arrays of aligned α-Fe₂O₃ nanowires by oxidizing pure iron foil at 540-600 °C. Single crystalline of nanowires with diameters of 20-40 nm and lengths of 2-5 μm were synthesized by gas mixture of flows of 19.30% CO₂, 0.14% SO₂, 80.56% NO₂ and H₂O. Gas flow direction at 30-90° was found to form highly aligned nanowires as compared to parallel to the substrate. Nanowires diameter and length can be controlled by varying gas flowrate, temperature and annealing time during oxidation process. The formation of the nanowires is believed to be due to iron atom diffusion through the sides of the nanowire from the iron substrate to the nanowires tip.

Table 1.2 shows the summary of Fe₂O₃ nanostructures prepared by thermal oxidation process in ambient air, oxygen, and mixed gas. From the summary, it clear that Fe₂O₃ nanostructures mainly consisted of nanoflakes and nanowires successfully synthesized at temperature range 250 – 800 °C within 0.5 to 120 h. Different structure of Fe₂O₃ can be obtained by simply changing the oxidation temperature. Temperature becomes a significant parameter in growing Fe₂O₃ nanostructures in this process. In addition to temperature, annealing time also plays an important role in these nanostructures. Most of the study used longer annealing time of 10 h for the oxidation to take place. This time particularly depends on the oxygen supplier from which the gas used was obtained. Longer annealing time is required for oxidation to occur in open ambient air.
Table 1.2: Fe$_2$O$_3$ nanostructures prepared by thermal oxidation process

<table>
<thead>
<tr>
<th>Nanostructures</th>
<th>Temperatures (°C)</th>
<th>Annealing Time (h)</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanowires</td>
<td>550 – 650</td>
<td>10 – 120</td>
<td>Fu et al., 2001</td>
</tr>
<tr>
<td>Nanoflakes</td>
<td>300</td>
<td>0.75</td>
<td>Zhu et al., 2005</td>
</tr>
<tr>
<td>Nanowires</td>
<td>400 – 750</td>
<td>2 – 4</td>
<td>Srivastava et al., 2007</td>
</tr>
<tr>
<td>Nanoflakes</td>
<td>260 – 400</td>
<td>10</td>
<td>Zheng et al., 2007</td>
</tr>
<tr>
<td>Nanowires</td>
<td>350</td>
<td>10</td>
<td>Hsu et al., 2008</td>
</tr>
<tr>
<td>Nanowires and</td>
<td>300 – 800</td>
<td>10</td>
<td>Liao et al., 2008</td>
</tr>
<tr>
<td>nanoflakes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nanowires</td>
<td>375</td>
<td>0 – 1.67</td>
<td>Nagato et al., 2010</td>
</tr>
<tr>
<td>Nanowires</td>
<td>400 – 600</td>
<td>0.5 – 4</td>
<td>Yuan et al., 2012</td>
</tr>
<tr>
<td>Nanowires and</td>
<td>500 – 800</td>
<td>1</td>
<td>Grigorescu et al., 2012</td>
</tr>
<tr>
<td>nanoblades</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nanorods,</td>
<td>500 - 800</td>
<td>8 - 10</td>
<td>Vincent et al., 2012</td>
</tr>
<tr>
<td>nanocoral and</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nanoleafs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nanoflakes</td>
<td>375 – 450</td>
<td>10</td>
<td>Li et al., 2014</td>
</tr>
</tbody>
</table>

When pure or independent gas was used to supply oxygen in synthesis iron oxide nanostructures, oxidation process generally take place in oxidation furnace. Schematic diagram in Fig. 1.3 showed an experimental set up for copper oxide (CuO and Cu$_2$O) nanostructures prepared by thermal oxidation process. Gas from a cylinder gas is flown through the tube furnace and reacts with the substrate placed in the middle of tube furnace. In Fe$_2$O$_3$ nanostructure preparation, various gases can be employed such as pure oxygen [48] and mixed gas (19.3 % CO$_2$, 0.14 % SO$_2$, 80.56 % NO$_2$) [27] with specific flowrate. This furnace can also be used to synthesise Fe$_2$O$_3$ in ambient condition [18, 31]. For this purpose, both end caps should be removed and atmospheric air allowed entering the furnace for oxidation to occur. Many types of Fe substrate with various dimensions are applied for the initial precursor in this process such as Fe foil, wire and electroplating Fe layer on silicon. These Fe atoms easily react with oxygen in the gas to produce iron oxide. Synthesis processes by thermal oxidation process are simple, cheap and capable of high production.
Hydrothermal synthesis usually refers to low temperatures technique (< 300 °C) to prepare metal oxide nanostructures by hydroxide approach. In this process, nanostructure crystal growth occurs under high temperature and pressure water condition for substances which are insoluble in temperature and pressure of less than 100 °C and 1 atm respectively [50]. Hematite nanowires can be prepared by two step processes at which iron precursor such as FeCl$_3$ or Fe(NO$_3$)$_3$ form iron oxyhydroxides (β-FeOOH) and are then converted into hematite through annealing in air at high-temperature. Vayssieres et al. reported on hematite nanorod on FTO glass by immersing the substrate into 0.15 M ferric chloride hexahydrate (FeCl$_3$.6H$_2$O) and 1 M sodium nitrate and heated in oven at 100 °C for 24 h [51]. Eventhough this process allows the hematite grows on a conductive glass, the use of toxic, acidic and highly corrosive chemical is dangerous to human health. Extra care in the preparation process is required to avoid the consequent effect from the materials used.
1.5.3 Solgel Method

The solgel is another solution method employed for hematite nanostructures on the conducting substrate. Cavas et al. successfully synthesized hematite nanoparticles and nanoclusters on FTO glass by spin coating the substrate with a mixture of iron chloride (FeCl$_3$·6H$_2$O), ethanol and ethanolamine (C$_2$H$_7$NO.EA) at 1000 rpm for 30 s [20]. The sample was then thermally heated at 400 °C in air for 1 h for solid film preparation. Due to the same toxic chemical used in this method, additional precaution steps are needed for bulk production.

1.5.4 Metallorganic Chemical Vapor Deposition

Another synthesis method that has been used to prepare hematite nanostructures is metallorganic chemical vapour deposition (MCVD). Cha et al. reported the growth of hematite nanorod-thin film on catalyst-free silicon substrate by using vertical MCVD process [52]. In this process, iron acetylacetonate, Fe (acac)$_2$ or Fe((C$_5$H$_7$O$_2$)$_2$) was used as initial metal sources and high purity argon, nitrogen and oxygen as gas sources. The overall process takes place as shown schematically in Fig. 1.4. During the growth process, substrate temperature and pressure chamber become important parameters for vertically aligned hematite nanorod growth on the film. The temperature and pressure used is 600 °C and 400 Pa respectively and the process occurs over a period of 4 h. Compared to the previously discussed methods, MOCVD can yield high-quality and single crystal hematite nanostructures. However, this process is quite complicated and required a critical controlled parameter.
1.6 Optical Properties

Hematite has been extensively studied because of its promising optical properties which is suitable for many electronic applications.

1.6.1 Electronic Transition in Hematite

There are three types of Fe$^{3+}$ cations electronic transitions that develop within optical absorption spectra namely Fe$^{3+}$ ligand field transitions (d-d transitions), ligand-to-metal charge transfer transitions (LMCT) and pair excitations [53]. Sherman et al. in their study found that in corundum-type crystal structure hematite, the Fe 3d atomic orbitals are split into two sets specifically known as $e_g$ and $t_{2g}$ in a 10 Dq ligand crystal field splitting for d-d transitions. Furthermore, based on molecular orbital theory, in LMCT the transitions occur at energy higher than most ligand field transitions (with absorption >400 nm). For coordination polyhedron of (FeO$_6$)$^{6-}$ in hematite, the lowest energy occurred near the energy 40000 cm$^{-1}$ (250 nm) LMCT transitions from non-bonding O(2p) orbitals to the antibonding Fe(3d) orbitals. The third transition is pair excitation resulting in an additional absorption band corresponding to the simultaneous excitation of the Fe$^{3+}$-Fe$^{3+}$ pair. This transition is spin-allowed because the availability of the spin quantum number ($s$) of 0,1,2,3 in Fe$^{3+}$-Fe$^{3+}$ pairs.
1.6.2 Steady-state Absorption

Optical absorption properties in near UV to near IR are extensively studied in previous research [54, 55]. Hematite absorption bands can be observed in four main wavelength regions as shown in Fig. 1.5 (a) which is related to the previous discussed electronic transitions [56]. The regions are between 250-400 (combination of LMCT and Fe$^{3+}$ ligand field transitions), 400-600 (pair excitation transitions), 600-780 ($^{6}A_{1}(^{5}S)$ to $^{4}T_2(^4G)$ ligand field transitions) and 750-900 nm ($^{6}A_{1}(^{5}S)$ to $^{4}T_1(^4G)$ ligand field transitions) [16]. The strongest absorption band was found at about 535 nm resulting in interband transitions from double-exciton process which is corresponding to the red color of hematite [53]. The color of hematite nanostructures is significantly influenced by the phase, size and shape of the structure [16].

![Figure 1.5](image_url)

**Figure 1.5:** Absorption (a) and reflectance (b) spectra of hematite nanocrystals of different sizes [56].
1.6.3 Photoluminescence

Photoluminescence properties of hematite can be obtained from the self-trapped states in nanoscale structure and not in the bulk form. Hsu et al. studied the field emission characteristics of hematite nanowires by using two-parallel-plate system [57]. In this study they obtained the low turn-on field of 3.3 V/μm and a large current density of $10^{-3}$ A/cm$^2$ under an applied field about 7 V/μm by using optimal factors of population density of the nanowires per unit area. This property is varied by changing the thickness of Fe substrate that consequently affects the nanowires growth population. It is shown that emission property of hematite is highly dependent on their morphology and density.

1.7 Charge Carrier Dynamic of Hematite Nanostructures

Charge carrier dynamic property of most studied nanomaterials is influenced by their crystal structure and surface morphology. Cherepy et al. conducted an ultrafast charge carrier dynamic of hematite and maghemite by using 390 nm pump and several probes at 660, 720, 790 and 850 nm wavelength [58]. The results show both spherical and spindle nanoparticles give constant transient absorption decay pattern and were best fit with a triple exponential at time constant of 0.36, 4.2 and 67 ps. This quick decay progress is related to highly efficient nonradioactive relaxation caused by the dense band structure, trap states or tough coupling between trap states. They also found that this transition decay profile is not affected by other factors such as pump power, probe wavelength, pH and dopant materials applied. In addition to crystal structures and surface morphology, carrier dynamic is also studied by the change in their size, shape and doping materials [16]. Agarwala et al. tried to identify a way to increase hematite carrier mobility by using hematite nanorods and hybrid quasi-3D nanoflowers. They found that, hematite nanoflowers exhibit higher carrier mobility which is caused by larger surface area compared to the nanorods. Theoretically, the conversion efficiency of hematite based materials can be obtained by changing the shape, size, porosity and thickness of the nanostructures.
1.8 Research Objectives

Hematite nanostructures have become promising semiconductor materials due to its attractive electronic properties, abundance, low cost and environmental benign. Among the available synthesis methods, oxidation process shows some advantages as environmentally safe due to non dangerous chemical usage, low cost and easily controlled process parameter. Their synthesis processes are strongly dependent on the temperature and annealing time which result in different shape and density nanostructures. Previous reports show that longer annealing time is required for highly aligned and highly dense hematite nanostructure formation, especially when prepared in open air. Even though longer time is used, some of the nanostructures produced are not aligned and have low population. It is crucial to optimize the process parameter involve during the oxidation process for high quality nanostructure formation. Therefore, in this study, hematite nanostructures has been synthesized by oxidation process in high purity air focusing on nanoflakes and nanowires by changing process parameters such as temperature, annealing time and pre-annealing effect. This synthesis is started with the Fe foil as starting substrate and further enhanced on the FTO glass. Both hematite nanoflakes and nanowires on the foil and FTO glass were used as photoanodes in DSSC. The performances of the solar cell is further analysed and discussed in the following chapters.

1.9 References


CHAPTER 2

SYNTHESIS OF IRON OXIDE NANOFLAKES AT LOWER TEMPERATURE
BY AIR OXIDATION OF IRON FOILS

2.1 Introduction

Nanostructures are promising materials in modern science and technology owing to their large surface areas and possible quantum-confinement effects particularly in electronic, optical, mechanical, and thermal applications [1, 2]. Among various types of nanomaterials, metal oxide nanostructures have emerged as an important class of materials with great potential owing to their low dimensionality and device applicability. In previous studies, metal oxide nanostructures have been successfully tested for use in chemical and biological sensors [3], electron-field emitters [4], lithium-ion battery electrodes [5], lasers [6], solar cells and photocatalysts [6], piezoelectrics and nanogenerators [6], transparent electronics [6], field-effect transistors [6], and optical devices [7].

In recent years, magnetic nanomaterials such as hematite (α-Fe₂O₃), magnetite (Fe₃O₄), and maghemite (γ-Fe₂O₃) have emerged. They have novel properties and are widely used in many applications. For example, α-Fe₂O₃, which is an n-type semiconductor with a band gap of 2.1 eV and is thermodynamically the most stable of the iron oxides under ambient conditions, is attractive for many applications, particularly in electronic devices. Good sensitivity and selectivity to the ambient environment and directness of material synthesis and sensing device fabrication are the main factors desired in sensor exploration [3, 8, 9]. α-Fe₂O₃ also shows good electrochemical properties in lithium intercalation [5], in addition to being a promising photocatalyst candidate to resolve environmental problems and the energy crisis [6]. In recent years, α-Fe₂O₃ has attracted considerable attention as a solar energy conversion material owing to its small bandgap, high resistivity to corrosion, and its low cost [10,
11. Fe$_3$O$_4$ and γ-Fe$_2$O$_3$ have good tunable properties[12] and are widely used as catalysts [13], and in magnetic recording [14], high-performance electromagnetics such as for environmental remediation and biomedical applications, for example in magnetic resonance imaging (MRI) [15], cell and protein separations [16], and in drug delivery systems [17]. The size and shape of the iron oxide nanostructures are important properties in most applications.

In previous years, several techniques have been explored to produce iron oxide nanostructures such as liquid-solid solution methods [5], solution combustion [18], air oxidation [4, 10], thermal oxidation [19], vapor-solid techniques [20], thermal decomposition [21], template-based methods [22, 23], and the sol-gel process [14, 24]. Among these techniques, air oxidation of iron foil shows significant success for use in electron field emission and gas sensor applications. However, previously reported iron oxide nanostructures grown on iron foil were randomly aligned, which limited their performance. Yuan et al. succeeded in the synthesis of α-Fe$_2$O$_3$ nanoflakes at 650 °C in less than 10 s [19]. However, low-temperature synthesis will be required to enable the synthesis of α-Fe$_2$O$_3$ nanoflakes on a glass substrate in the future. Optimization of the synthesis parameters at low temperatures is crucial for further improvement of the nanostructure performance.

In this study, large quantities of iron oxide nanoflakes were synthesized at an optimum temperature and annealing period via the oxidation of iron foil at a low temperature. This optimization is aimed at gaining further understanding, particularly of the production of iron oxide nanostructures of high quality and in large quantities in controllable, simple, efficient, and commercially viable ways [25]. It is shown that iron oxide nanoflakes can be synthesized at 450 °C by increasing the oxidation period. The growth mechanisms for low-temperature synthesis are also described.

### 2.2 Thermal Oxidation Technique

Commercial iron foils (10x10x0.25 mm$^3$) with a purity of 99.99% were used as the initial substrates for α-Fe$_2$O$_3$ nanoflake growth. First, iron foils were cleaned in
acetone and deionized water for 5 min each. After drying with nitrogen gas, the samples were placed in the center of a horizontal tube furnace. High purity air (G3) flowed at 0.5 L/min through the tube furnace, and the temperature and time required were fixed. The samples were heated from 350 to 600 °C for several annealing periods from 1 to 6 h. After the oxidation process was completed, the samples were cooled naturally to room temperature. Rapid cooling may cause the samples to crack owing to thermal stress generated on the surface of the samples.

The samples were characterized using a scanning electron microscopy (SEM; Hitachi S-3000S) system, X-ray diffraction (XRD; Rigaku RINT-2100, 40kV, 30mA, Cu Kα radiation) system, and a transmission electron microscopy (TEM; JEOL JEM-2100F) system.

2.3 Effects of Temperatures on Iron Oxide Nanostructures Synthesis by Oxidation

2.3.1 Scanning Electron Microscopy Characterization

Figures 2.1(a) - (e) show SEM images of iron oxide nanostructures produced with a constant 1 h annealing period at different temperatures and Fig. 2.1(f) shows a low-magnification TEM image of the product. The surface of the substrate before the oxidation process is shown in Fig. 2.1(a). There are no nanostructures present. At 350 °C, small quantities of iron oxide nanoflakes were observed. These iron oxides nanoflakes have small diameters and do not greatly differ from the bottom to the top. When the temperature increased to 450 °C (Fig. 2.1(c)), many iron oxide nanoflakes with larger diameters appear on the substrate within 1 h. Some of the nanostructures have a larger diameter at the bottom than at the top. The shape of the flake is clearly shown in the low-magnification TEM image in Fig. 2.1(f). These particular nanoflakes have a diameter of 40 nm at the tips and 140 nm at the bottoms with an average length of 200 nm. With a further increase in temperature to 600 °C, the quantity of iron oxide nanoflakes was reduced and finally disappeared. At 600 °C and above, iron oxide
nanostructures were no longer observed. This result shows that iron oxide nanostructures can be obtained at a relatively low temperature in a short time compared with 10 h of oxidation in a box oven [10] and heating on a hot plate [4]. The oxidation temperature significantly affects the growth of iron oxide nanostructures.

Figure 2.1 SEM images of (a) pure iron and of iron oxide nanoflakes prepared with a fixed annealing time of 1 h at (b) 350, (c) 450, (d) 550, and (e) 600 °C. (f) Low-magnification TEM image of iron oxide nanoflakes prepared at 450 °C.
2.3.2 Crystal Structure Characterization

As revealed by the XRD patterns shown in Fig. 2.2, temperature plays an important role in iron oxide growth. Before oxidation takes place, pure iron foil exhibits three main peaks at 45°, 65°, and 77.5°. After oxidation at different temperatures, oxygen bonds are created leading to small amounts of Fe$_2$O$_3$ and a high intensity of Fe$_3$O$_4$. At 450 °C, the (110) peak at 35.5° becomes dominant and the intensity further increases almost threefold at 550 °C. The crystallinity decreases at 600 °C and more Fe$_3$O$_4$ is observed. The SEM and XRD results indicate that the largest quantities of iron oxide nanostructures were obtained at 450 °C, at which oxygen bonding favorably occurs at a lower surface energy.

**Figure 2.2** XRD patterns of pure iron oxide (before oxidation) and iron oxide nanoflakes annealed at different temperatures for 1 h.
2.4 Effects of Annealing Times on Iron Oxide Nanostructures Synthesis by Oxidation

2.4.1 Scanning Electron Microscopy Characterization

Figure 2.3 shows SEM images of large quantities of iron oxide nanoflakes produced at a fixed oxidation temperature of 450 °C for 1 to 6 h of annealing. These images show that the quantity of iron oxide clearly increased with increasing annealing time. Instead of a change in the flake quantity, the diameter at a short annealing time is smaller than that at a long annealing time.

![SEM images of iron oxide nanoflakes](image)

Figure 2.3 SEM images of iron oxide nanoflakes annealed at 450 °C for 1, 3, and 6 h.

2.4.2 Crystal Structure Characterization

The XRD patterns in Fig. 2.4 show that α-Fe₂O₃ and Fe₃O₄ groups exist in addition to the Fe component. The strongest peak appears at 35.5°, which corresponds
to α-Fe₂O₃ with lattice constants \( a = 0.5035 \text{ nm} \) and \( c = 1.3749 \text{ nm} \) [26]. The intensity increased when the annealing time was increased from 1 to 6 h. After 3 h of annealing, more Fe₃O₄ groups were observed on the substrate. After 6 h this peak decreases, indicating that Fe₃O₄ has been converted to Fe₂O₃.

**Figure 2.4** XRD patterns of iron oxide nanoflakes annealed at 450 °C for 1, 3, and 6 h.

### 2.5 Transmission Electron Microscopy Characterization

TEM analysis was conducted to further explain the formation and crystal structure of iron oxide nanoflakes. This nanostructure had a flaky appearance with a smaller diameter at the tips than at the bottoms as shown in Fig. 2.1(f). The selected-area electron diffraction (SAED) pattern of nanoflakes is shown in Fig. 2.5(a). Electron beams were focused on (110) spots. The typical high-resolution transmission electron microscopy (HRTEM) image in Fig. 2.5(b) confirms that the nanoflakes have a single-crystalline structure. The growth direction of the nanoflakes is (110) with a fringe spacing of 0.25 nm [4, 10].
2.6 Iron Oxides Nanoflakes Growth Mechanism

In this work, the growth temperatures of iron oxide nanoflakes are lower than 700 °C, at which the vapor pressure of iron is saturated [27]. Therefore, vapor phase mechanisms such as vapor-liquid-solid (VLS) and vapor-solid (VS) are not applicable. It is believe that the α-Fe$_2$O$_3$ nanoflake growth mechanism is based on the surface diffusion of iron atoms and iron oxide molecules [4, 10]. During the oxidation process, the iron surface is oxidized by oxygen contained in high-purity air to form a layer of α-Fe$_2$O$_3$ and Fe$_3$O$_4$. Initially, an Fe$_3$O$_4$ layer is produced and α-Fe$_2$O$_3$ appears as a result of the further oxidation of Fe$_3$O$_4$. A longer annealing period gives a higher probability of conversion to α-Fe$_2$O$_3$ at relatively low temperatures. The formation of α-Fe$_2$O$_3$ creates a pressure difference between the Fe$_3$O$_4$ layer and the top layer, which causes nanoflakes to grow from the bottom to the top in addition to an oxygen-rich and iron-deficient composition along the (110) direction [4, 10]. At this stage, a single-layer substrate changes to a triple layer consisting of Fe, Fe$_3$O$_4$, and α-Fe$_2$O$_3$. When the growth temperature increases to 600 °C, no nanoflakes are observed.
2.7 Conclusion

Large quantities of single-crystalline iron oxide nanoflakes were produced at a temperature of 450 °C with 6 h of annealing. The preferential growth direction was (110) with a 0.25 nm fringe spacing. The combination of the optimum temperature and annealing period in addition to a constant airflow resulted in high-quality iron oxide nanoflakes. The surface diffusion of iron atoms and iron oxide molecules is believed to be the nanoflake growth mechanism.

2.8 References

CHAPTER 3

SYNTHESIS OF ALIGNED $\alpha$-Fe$_2$O$_3$ NANOWIRES GROWTH VIA A TWO-STEP THERMAL OXIDATION

3.1 Introduction

Nanostructured materials have attracted the interest of researchers because of their promising and useful properties. Recently, synthesis of nanowires with excellent properties has become the focus of in-depth studies [1]. Adapting these types of materials into a device for application in instant solar cells requires an efficient technique, particularly for obtaining a highly aligned structure with a high quality of nanowires [1]. Various metal oxide nanowires have been produced by numerous techniques using zinc oxide (ZnO), titanium oxide (TiO$_2$), and stannic oxide (SnO$_2$). Together with these materials, hematite ($\alpha$-Fe$_2$O$_3$) nanowires have attracted interest because of their excellent optical properties in addition to their abundance, environmental friendliness, and magnetic and corrosion-resistant properties [2].

$\alpha$-Fe$_2$O$_3$, with a lower band gap of $\sim$2.2 eV compared with TiO$_2$, ZnO, and SnO$_2$, shows a capability to absorb a large portion of the visible solar spectrum (absorbance edge $\sim$600 nm). The potential to absorb light from the ultraviolet and visible regions has promoted the application of this semiconductor material in photocatalysis [3, 4], water splitting [5, 6], and photovoltaic cells [2, 7, 8]. When iron oxide nanowires are used in device applications, for instance in photovoltaic cells, aligned nanowires are preferable.

Previous studies have proven that several growth parameters critically influence the growth of iron oxide nanowires, such as the effects of oxidation temperature [9-13], annealing time, gas mixture ratio [10, 11, 14], surface roughness [15], and thickness of the substrates used [16]. Fu et al. reported that the growth of highly aligned single-crystal $\alpha$-Fe$_2$O$_3$ nanowires depends on the reaction temperature, time, and flow rate of the gases used in the thermal oxidation process [17]. They found that the nanowires
grow perpendicular to the local planar or spherical plane substrate surface at temperatures of 550–600 °C. At a higher oxidation temperature, Nasibulin et al. successfully synthesized α-Fe₂O₃ nanowires on iron wires by resistive heating at different potentials between 2.7 and 7.8 V [18]. This study showed that the growth of α-Fe₂O₃ nanowires is caused by the change of the oxidation state from 0 at the core to +3 at the upper layer. However, there are currently very few reports of the synthesis of high-density aligned nanowires.

In the thermal oxidation process, the substrate, which also acts as the precursor, plays an important role for aligned iron oxide nanowires to grow. Srivastava et al. successfully synthesized α-Fe₂O₃ nanowires in an ozone-rich environment at 700 °C for 4 h by using two different polycrystalline iron foil substrates [19]. They found that surface diffusion of iron was favorable in the (110) direction plane as body-centered cubic iron is more reactive and deficient in this particular plane. Furthermore, in another study, Srivastava et al. reported that the most favorable grain orientation of the substrate for the growth of hematite nanowires is on the (110) plane and controlling the substrate texture is important for the growth of nanowires [20]. In their study, the substrate texture was modified by filing the surface and annealing in vacuum conditions to obtain the desired crystal orientation. These methods are quite complicated and mechanical filing results in randomly oriented grains, which makes it difficult to obtain highly aligned nanowires. In this study, an easier method for growing highly aligned iron oxide nanowires on a textured Fe foil substrate were investigated by employing a two-step oxidation of the Fe foil with thermal pre-annealing at different temperatures. To the best of our knowledge, there are no reports on the effect of pre-annealing temperatures on the growth of iron oxide nanowires.

### 3.2 Two-step Oxidation Process

Commercial 99.99% pure iron foils (10×10×0.25 mm) were used as the substrate. The substrates were cleaned in acetone and deionized water for 5 min each. After cleaning, the samples were dried with nitrogen gas and placed at the center of a horizontal tube furnace. High purity air (G3) at 0.5 L/min was flowed through the tube
furnace, and the temperature and time required are fixed. For the first step of the oxidation, the samples were pre-annealed at a temperature between 100 and 400 °C for 30 min. For the second oxidation step, the samples were continuously heated at 550 °C for 3 h. The typical temperature profile with a pre-annealing temperature of 100 °C and oxidation temperature of 550 °C is shown in Fig. 3.1. After the second oxidation step was completed, the samples were cooled naturally to ambient conditions. The samples were characterized using scanning electron microscopy (SEM; Hitachi S-3000H), field emission scanning electron microscopy (FE-SEM, JEOLJSM7001FF) and X-ray diffraction (XRD; Rigaku RINT-2100, 40 kV, 30 mA, Cu-Kα radiation).

![Temperature profile of two-step thermal oxidation.](image)

**Figure 3.1** Temperature profile of two-step thermal oxidation.

### 3.3 Effects of Oxidation Temperatures on Iron Oxide Nanowires Growth

To identify the favorable temperature for iron oxide nanowires to grow, Fe foils were initially oxidized at different oxidation temperatures without pre-annealing. Fig. 3.2 (b) to (e) show iron oxide nanowires synthesized at fixed 3 h annealing period at different oxidation temperatures while Fig. 3.2 (a) shows surface morphology of iron foils before oxidation takes place. Before oxidation occurs, there are no nanowires observed on the substrate. At 350 °C, small amount of nanowires with small diameter and length were observed. The nanowires were spread randomly on the surface and the structure is not aligned. At 450 °C, many nanowires with flaky shape were produced. The nanoflakes diameters are in the range of 60 – 150 nm with length of 100 - 600 nm. When temperature increased to 550 °C, longer nanowires were produced with diameter
of 30 - 100 nm and 0.3 – 3.5 µm lengths. Aligned nanowires only grow at certain areas on the substrate and are not uniform in diameter and length. Nanowires are Fe₂O₃ as reported by several researchers [9, 11, 12, 15, 19] and XRD patterns are shown later. The nanowires start to disappear when temperature increased to 650 °C. These results demonstrate that the iron oxide nanostructure shape is strongly influenced by the oxidation temperatures. Oxidation temperature of 550 °C was selected for iron oxide nanowires grow by two-step oxidation process.

Figure 3.2 SEM images of iron oxide nanowires (a) before and (b-e) after oxidation at 350, 450, 550 and 650 °C for 3 h.
3.4 Effects of Pre-annealing Temperatures on iron oxide Nanowires Growth

3.4.1 Surface Morphology of Nanowires Growth in Dry Air

Figure 3.3 shows Fe₂O₃ nanowires oxidized at 550 °C for 3 h with different pre-annealing temperatures and without pre-annealing. Random growth of nanowires was observed on the substrate without pre-annealing, with an average diameter of 30.61 nm and a density of 5.0×10⁸ cm⁻². The density and diameter distribution of the nanowires for all the samples is given in Fig. 3.4. When the sample was pre-annealed at 100 °C, more uniform nanowires with a smaller diameter of 27.47 nm were produced but they were randomly aligned. The diameters of the nanowires increased to 29.64 nm after the sample was pre-annealed at 200 °C. Nanowires with a high density of 2.5×10⁹ cm⁻² and an average diameter of 17.0 nm were obtained when the pre-annealing temperature was increased to 300 °C. The inset in Fig. 3.3 (d) shows the FESEM image of the dense nanowires corresponding to the SEM image in Fig. 3.3 (d).
**Figure 3.3** SEM images of iron oxide nanowires oxidized at 550 °C for 3 h (a) without, (b)-(e) with pre-annealed at 100, 200, 300 and 400 °C for 30 min; (f) TEM image of nanowires in (d).
The nanowires produced are highly aligned with a preference to grow on the substrate. Nanowires with smaller diameters were synthesized in large quantities at this pre-annealing temperature. The low magnification TEM image in Fig. 3.3 (f) shows aligned nanowires prepared at pre-annealing 300 °C of diameter 20 nm. The nanowires again become non-uniform with a bigger average diameter of 43.0 nm when the pre-annealing temperature was increased to 400 °C. The quantity of nanowires decreased significantly to $6.0 \times 10^8$ cm$^{-2}$. These results indicate that the alignment and density of iron oxide nanowires have a great dependence on the pre-annealing temperature prior to the oxidation steps. Liu et al. also found that the annealing treatment of a ZnO seed layer has a significant effect on increasing the nanowire density of ZnO [21].

![Graph showing nanowire diameter and density distribution](image)

**Figure 3.4** Nanowires diameter and density distribution of iron oxide nanowires at different pre-annealing temperature.

Cross-sectional SEM images of corresponding SEM images in Fig. 3.3 are shows in Fig. 3.5. It is clearly shown that the nanowires alignment and density is improved when pre-annealing step was applied in thermal oxidation process. Without pre-annealing process, the nanowires is randomly aligned with non-uniform length. The nanowires density is increase with more uniform length when annealing process done at 100-200 °C. Further increases pre-annealing temperature to 300 °C, the nanowires become dense and highly aligned with uniform length. At higher pre-annealing temperature of 400 °C, the nanowires produced in lower density and randomly aligned.
This result indicated that pre-annealing in two-step oxidation process is significantly effects the iron oxide nanowires growth.

Figure 3.5 Cross-sectional SEM images of iron oxide nanowires oxidized at 550 °C for 3 h (a) without, (b-e) 100, 200, 300 and 400 °C.
3.4.2 Iron Oxide Nanowires Growth in Oxygen Gas

Another gas was used for oxygen supply to synthesis iron oxide nanowires on Fe foil by thermal oxidation rather than high purity air. The same experimental procedures for two-step oxidation in air were followed for the nanowires synthesis in oxygen. SEM images in Fig. 3.6 shows nanowires synthesized at different annealing time from 1-5 h. At 1 h annealing time, random with small diameter nanowires were observed. When the sample annealed to 3 h, high density with bigger diameter nanowires were synthesized. These nanowires are formed only at certain area on the substrate. Longer and dense nanowires are produced at 5 h annealing time. Iron oxide nanowires can be synthesized in high purity oxygen by two-step oxidation process but the due to the nanowires morphology is comparable to the nanowires synthesis in dry air, the optimization was done for dry air only.

![SEM images of nanowires prepared in oxygen gas at 550 °C for (a) 1, (b) 3 and (c) 5 h annealing time.](image)

**Figure 3.6** SEM images of nanowires prepared in oxygen gas at 550 °C for (a) 1, (b) 3 and (c) 5 h annealing time.
3.4.3 Crystal Structure Characterization

The X-ray diffraction patterns in Fig. 3.7 show the crystal structure and phase of the nanowires corresponding to the SEM images in Fig. 3.3 (a-e). The XRD pattern of the nanowires contains eight distinguishable peaks that correspond to pure rhombohedral $\alpha$-Fe$_2$O$_3$ structure based on JSPDS file no. 33-664. Strong peaks of (110) were detected at 35.5° for $\alpha$-Fe$_2$O$_3$ nanowires prepared without pre-annealing. This peak intensity further increased after the samples were pre-annealed at 100, 200, and 300 °C. The enhancement of the (110) peak in these nanowire samples is from the increase of the nanowire density, consistent with the SEM morphology in Fig. 3.3 (b–d). At 400 °C, a lower intensity of (110) and a broader peak is obtained, indicating a bigger and less oriented grain structure owing to a higher diffusion rate and a faster reaction at a higher temperature. Identical $\alpha$-Fe$_2$O$_3$ peaks were observed for all samples except for the samples that were pre-annealed at 200 and 300 °C. At these temperature, a peak at 38.41 appeared and was assigned as $\alpha$-Fe$_2$O$_3$ (200), which can be seen under high pressure.[22] The presence of this crystalline phase contributes to an improvement in the properties of the nanowires. This (200) peak is absent at 400 °C, indicating that the phase was fully converted to (110).

![Figure 3.7 XRD pattern of $\alpha$-Fe$_2$O$_3$ nanowires with and without pre-annealed at different temperature and oxidized at fixed 550 °C for 3 h.](image-url)
Several Fe$_3$O$_4$ peaks indexed based on JSPDS file no. 65-3107 were detected in all the samples, which indicates the presence of another layer below the Fe$_2$O$_3$ layer. [12, 15] Multiple layers consisting of Fe, Fe$_3$O$_4$, and Fe$_2$O$_3$ were formed after the two-stage oxidation process was completed. The density of the nanowires increased with increasing pre-annealing temperature up to 300 °C, which can be related to the high intensity of the Fe$_2$O$_3$ peak at (110).

To better understand the formation of aligned nanowires with pre-annealing, Fe foil was annealed at 100, 200, 300, and 400 °C for 30 min without oxidation. For comparison, pure Fe foil exhibited two main Fe peaks of (110) and (200) at 44.87 and 65.20°, respectively (Fig. 3.8). The peaks that were observed close to both of these peaks might be from a different Fe structure in the foil. After the sample was annealed at 100 °C, the intensity of the peaks changed but no other iron oxide peaks were detected. This indicated that no reaction had occurred between the iron foils and the air because the same peaks were present as for pure iron foils. At 200 °C, the first α-Fe$_2$O$_3$ peak of (200) was detected. The presence of this peak indicated that the reaction between the Fe foil and the oxygen molecules in the air had started forming an iron oxide layer. At 300 °C, two broad peaks corresponding to α-Fe$_2$O$_3$ phase (110) and (200) were observed. The crystallite sizes of α-Fe$_2$O$_3$ (110) and α-Fe$_2$O$_3$ (200), calculated by using Scherrer’s equation [23], were 14.82 and 18.95 nm, respectively. At a higher pre-annealing temperature of 400 °C, the (200) peak is slightly shifted to 38.21°, which corresponds to β-Fe$_2$O$_3$ (400) based on JSPDS file no. 39-238. The crystallite sizes of (110) and (400) were 25.49 and 35.39 nm, respectively. Bigger crystallite sizes were obtained when the sample was pre-annealed at a higher temperature. The preferred crystal direction (110) is favorable for high-quantity α-Fe$_2$O$_3$ nanowire growth.
3.4.4 Elemental analysis

To further confirm the nanowires produced are iron oxide, elemental analysis was conducted by using EDX. These measurements have performed on iron oxide nanowires pre-annealed at 300 °C as shown in FE-SEM images in Fig. 3.9. Graph (A) shows the spectra of iron oxide nanowires taken at A area. The results obtained show that this area contains Fe$_2$O$_3$ compound. And an EDX spectrum in graph (B) is taken at bottom layer (B) in the same SEM images. The atomic ratio shows this particular area is covered by Fe$_3$O$_4$ compound. EDX results obtained reveals that Fe$_2$O$_3$ nanowires prepared by thermal oxidation process grow on Fe$_2$O$_3$/Fe$_3$O$_4$ layer as reported in previous study [12, 15].
Figure 3.9 EDX spectra of $\text{Fe}_2\text{O}_3$ nanowires pre-annealed at 300 °C for 30 min and oxidized at 550 °C for 3 h.
3.5 Discussion

In this study, the effects of pre-annealing temperature from 100 to 400 °C on the substrate texture were analyzed and densely aligned α-Fe₂O₃ nanowires were obtained at a pre-annealing temperature of 300 °C (Fig. 3.3(d)). The XRD results (Fig. 3.8) show that crystalline α-Fe₂O₃ at (110) and (200) was formed with a small crystallite size of 14.82 and 18.95 nm, respectively. These broad peaks indicate the formation of a large amount of a small grain structure after pre-annealing. The presence of the α-Fe₂O₃ phase at (200) contributes to the improvement of the nanowire growth, which can easily transform to α-Fe₂O₃ nanowires at 550 °C. A large amount of α-Fe₂O₃ small grains allow a higher diffusion rate for nanowires to grow through the availability of plenty of grain boundaries. When the second oxidation step takes place at 550 °C, the surface substrate becomes more intensively stressed owing to a high diffusion rate. This condition provides a short path for the Fe cations to diffuse along the grain boundaries upward before they are deposited on the α-Fe₂O₃ grains through surface diffusion.[12] The volume change and interfacial reaction leads to the accumulation of stress and becomes a driving force for the growth of α-Fe₂O₃ nanowires.¹¹ A vapor-phase mechanism is not suggested in this study because the pre-annealing and oxidation temperatures used are below the melting points of Fe and Fe₂O₃ (1535 and 1350 °C, respectively). It is suggested that the formation of small and uniform crystalline α-Fe₂O₃ grains after pre-annealing at a favorable temperature contributes to the high-density nanowires. At a higher pre-annealing temperature of 400 °C, bigger α-Fe₂O₃ and β-Fe₂O₃ grains were formed with a (110) and (400) orientation, respectively, resulting in nanowires with a bigger diameter and a lower density (Fig. 3.3 (e)). Therefore, the formation of smaller textured grains of α-Fe₂O₃ after pre-annealing will result in highly aligned dense α-Fe₂O₃ nanowire growth by thermal oxidation.
3.6 Conclusion

The pre-annealing temperature significantly affects the density and alignment of α-Fe₂O₃ nanowires synthesized by thermal oxidation. Highly aligned and dense iron oxide nanowires were successfully obtained by modifying the substrate texture with pre-annealing at a temperature of 300 °C for 30 min and a second oxidation step at 550 °C for 3 h. These crystalline α-Fe₂O₃ nanowires have a diameter of 17 nm and density of $2.5 \times 10^9$ cm$^{-2}$. The XRD pattern shows that highly aligned nanowires are produced, with a preference for the α-Fe₂O₃ (110) phase. In the two-step oxidation, the pre-annealing temperature significantly influences the α-Fe₂O₃ nanowires growth by forming small α-Fe₂O₃ grains on the substrate, which become the seeds for the nanowires.

3.7 References


CHAPTER 4

EFFECTS OF NANOSTRUCTURES ON IRON OXIDE BASED DYE SENSITIZED SOLAR CELLS FABRICATED ON IRON FOILS

4.1 Introduction

Hematite (α-Fe₂O₃) is one of metal oxides that is extensively studied for many applications because it has attractive optical properties, low cost, is nontoxic and thermodynamically stable. Favourable semiconducting properties of 2.1 eV and antiferromagnetic has been verified in various applications [1-10]. Acting as n-type semiconductor with favourable band gap shows it can be applied in electronic device applications specifically in photo electrochemical and solar cells.

In devices applications, iron oxide nanostructures were prepared on indium doped tin oxide [11, 12] and fluorine doped tin oxide (FTO) [3, 11, 13-16] substrate. Several types of nanostructure were applied in DSSC such as nanoflowers, nanoparticles and nanocluster. Previous research shows several types of α-Fe₂O₃ nanostructure were used in DSSC applications. Agarwala et al., reported hybrid α-Fe₂O₃ flower-like morphology as a working electrode in DSSC which contribute 1.8 % power conversion efficiency [3]. A three-dimensional (3D) nanostructure was developed in this study to improve surface area, diffusion coefficient and electron transport of the solar cells. Cavas et al. proved that Fe₂O₃ nanoparticle and nanocluster can be used in ruthenium DSSC and the photocurrent of the sample is increased with light illumination intensity [13]. Niu et al. successfully used flower-shaped hematite as a photoanode in DSSC with energy conversion efficiency of 0.94 % [14]. Recently, biohybrid hematite and titanium oxide (TiO₂) nanostructure was used as anodic component in biohybrid DSSC [15]. Solar conversion efficiency of this photovoltaic is below that required for practical use but it has been proposed that it can be used in biohybrid solar-to-fuel nanodevices. However, the performance of α-Fe₂O₃ nanowires and nanoflakes in DSSC have not been reported yet. The synthesis highly aligned and high density α-Fe₂O₃
nanowires and nanoflakes on FTO or ITO glass will be challenging to improve the solar cell performance.

In previous research, α-Fe$_2$O$_3$ nanostructures were synthesized on FTO or ITO glass when applied in device applications. Most of the synthesis methods employed to produce good quality nanostructures normally require high temperature. Hiralal et al. were successful in synthesizing nanostructured hematite thin film on FTO glass by thermal oxidation process at low temperature of 255 °C for 24 hours [16]. However, α-Fe$_2$O$_3$ nanowires produced are not highly aligned and this condition might affect the performance of the nanostructures. Most reported highly aligned and high quantity α-Fe$_2$O$_3$ nanostructures are from thermal oxidation directly on the Fe foils [17-19]. However, it was difficult to synthesize the same quality nanostructures on FTO or ITO glass by using the same method. Therefore, it is important to examine the performance of highly aligned and high quantity α-Fe$_2$O$_3$ nanostructures prepared on the Fe foils in device applications.

In this study, α-Fe$_2$O$_3$ nanowires, nanoflakes and film were synthesized on Fe foil by simple air oxidation method by merely changing the temperature. The performance of these nanostructures were examined as photoanodes in DSSC and compared to the film under back-side illumination. To the best of our knowledge, there are no reports on the α-Fe$_2$O$_3$ morphology changes at different oxidation temperature. It is crucial to determine the performance of α-Fe$_2$O$_3$ nanostructures photoanodes directly prepared on the foils in order to fully utilise their ability.

4.2 Iron Oxide Based Dye Sensitized Solar Cell Fabrication

Commercial iron foils (20x20x0.25 mm$^3$) with a purity of 99.99% were used as the initial substrate for Fe$_2$O$_3$ nanowire growth. First, iron foils were cleaned in acetone and deionized water for 5 min each. After drying with nitrogen gas, the samples were placed in the center of a horizontal tube furnace. High purity air (G3) flowed at 0.5 L/min through the tube furnace, and the temperature and time required were fixed. Then, the samples were pre-annealed at 300 °C for 30 minutes. After that, the samples
were continuously heated to 450, 550 and 650 °C for a fixed 6 h. After the oxidation process was completed, the samples were cooled naturally to room temperature. The samples were characterized using a scanning electron microscopy (SEM; Hitachi S-3000H) system, X-ray diffraction (XRD; Rigaku RINT-2100, 40kV, 30mA, Cu Kα radiation) system.

For solar cell fabrication, all iron oxide samples were immersed in a ruthenium dye (ruthenium-535 bis TBA, Solaronix) for 12 h. After that, the sample was cleaned in methanol and dried in air for several minutes. Semi-transparent platinum electrode (Transmittance ~ 78 %) was inserted into the sample and electrolyte (iodide/triiodide redox, Iodolyte AN-50, Solaronix) was dropped in between them. Schematic structure of DSSC layer is shown in Fig. 4.1. DSSC performance was then measured by using solar simulator (100 mWcm⁻², AM 1.5 illumination) in air with specific area of 2.0 cm².

Figure 4.1 Dye-sensitized solar cell schematic structures.

### 4.3 Effects of Oxidation Temperatures on Iron Oxide Nanostructures

#### 4.3.1 Surface Morphology Characterization

SEM images of iron oxide synthesized at 450, 550 and 650 °C are shown in Fig. 4.2 (a), (b) and (c) respectively. At 450 °C, iron oxide nanoflakes were obtained and have average diameter of 40 nm at the tips and 140 nm at the bottoms with average length of 1.28 μm. These nanoflakes grew in high quantity and covered the entire
surface of the substrate. When temperatures increased to 550 °C, aligned iron oxide nanowires were produced with average diameter of 17 nm and average length of 4.8 μm. Smaller diameters, longer average length and high density of nanowires were obtained at this particular temperature. At higher temperatures of 650 °C, no nanostructures were observed and only iron oxide film was present. These results show oxidation temperatures have a significant effect on the growth of multidimensional and one dimension iron oxide nanostructures.

Zheng et al. reported that under atmospheric condition, ultra sharp α-Fe₂O₃ nanoflakes can be obtained by oxidation process and successfully applied in electron field emission [20]. In this study, at 450 °C, broader flaky shape iron oxides were obtained whereas during oxidation, α-Fe₂O₃ nanoflake grows on the top of a thin α-Fe₂O₃ layer. With continuous heating, thermal stress is expected to be accumulated on the top of thin α-Fe₂O₃ layer and relaxed by slipping in α-Fe₂O₃ crystal. At the same time screw dislocation might occur at a specific crystal direction causing Fe atom and iron oxide molecules at the surface to move upward and stack in the same plane before finally become a flake. By increasing the oxidation temperature to higher temperature of 550 °C, aligned and high density α-Fe₂O₃ nanowires can be obtained. Fu et al. also obtained highly aligned and high density α-Fe₂O₃ nanowires at 600 °C in atmospheric condition. Within these temperatures, higher stress gradient will accumulate on the top of the α-Fe₂O₃ thin layer surface due to the interfacial reaction, volume changes and thermal expansion mismatch between the iron oxide layer and substrate [18]. This stress gradient acted as a driving force for oxide nanowires growth. At higher oxidation temperatures of 650 °C, no nanowires were observed due to high thermal stress. Grigorescu et al. also found that at oxidation temperature greater than 600 °C, neither flakes nor wire morphology can be observed [19].

In this study, different structures of α-Fe₂O₃ were successfully obtained by changing oxidation temperatures by following the above mentioned mechanism. These morphology transformations might be influenced by the initial nucleation produced after first-step oxidation in addition to the stress-driven formation mechanism at elevated temperatures.
4.3.2 Crystal Structures Characterization

XRD pattern in Fig. 4.3 shows that Fe₂O₃ and Fe₃O₄ compounds are present in addition to Fe component. The dominant peak of (110) appears at 35.5° in all temperatures which correspond to α-Fe₂O₃ with lattice constants a = 0.5035 nm and c = 1.3749 nm. At 450 °C at which Fe₂O₃ nanoflakes were formed, combination peak of Fe₂O₃ was observed with the strongest peak of (110). This peak becomes more intense when temperature increased to 550 °C where nanowires were produced. Weak (220) peak of Fe₃O₄ was also detected at 30.15° in both nanoflakes and nanowires samples. More iron oxide groups were detected in iron oxide nanowires and nanoflakes which increases their crystallinity as compared to the film. These results also indicate that Fe₂O₃ nanostructures were grown on the Fe₃O₄ layer by thermal oxidation process [18].

Figure 4.2 SEM images of iron oxide synthesized at 450 °C (a), 550 °C (b) and 650 °C (c).
Triple iron and iron oxide layer consisting of Fe$_2$O$_3$/Fe$_3$O$_4$/Fe were formed after thermal oxidation with Fe$_2$O$_3$ nanostructures on the top layer.

4.4 Photovoltaic Performance of Iron Oxide Nanostructures Based DSSC

Photovoltaic performance of synthesized iron oxide nanowires, nanoflakes and film were examined by applying them as photoanodes in DSSC. $J$-$V$ curves in Fig. 4.4 show the effects of iron oxide structures on the performances. Short circuit current, open circuit voltage, fill factor and efficiency of iron oxide nanowires, nanoflakes and film are given in Table 4.1. The performance of the $\alpha$-Fe$_2$O$_3$ based DSSC increases sharply from films, nanoflakes and finally nanowires. $\alpha$-Fe$_2$O$_3$ nanowires give the highest photovoltaic performance as compared to others due to the high current density generated in the cells. This value was increased from about 0.01 to 0.08 mA/cm$^2$ when $\alpha$-Fe$_2$O$_3$ nanoflakes were used as photoanodes. When 1-dimensional nanowires were used, current density is further increased to 0.25 mA/cm$^2$ significantly affecting the efficiency of the solar cells.
Table 4.1: Photovoltaic characteristic of DSSC for different iron oxide nanostructures

<table>
<thead>
<tr>
<th></th>
<th>Nanowires</th>
<th>Nanoflakes</th>
<th>Film</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Short circuit current density,</strong> $J_{sc}$ (mA/cm²)</td>
<td>0.25</td>
<td>0.08</td>
<td>0.01</td>
</tr>
<tr>
<td><strong>Open circuit voltage, $V_{oc}$ (V)</strong></td>
<td>0.42</td>
<td>0.36</td>
<td>0.26</td>
</tr>
<tr>
<td><strong>Fill factor</strong></td>
<td>0.38</td>
<td>0.25</td>
<td>0.27</td>
</tr>
<tr>
<td><strong>Efficiency (%)</strong></td>
<td>0.04</td>
<td>0.007</td>
<td>0.0007</td>
</tr>
</tbody>
</table>

4.5 Effect of Nanostructures Surface Area to Photovoltaic Characteristic

In order to discuss the variation of solar performance for different nanostructures, the surface area per unit area of $\alpha$-Fe$_2$O$_3$ nanostructure was calculated from the SEM images. The surface area of nanowires and nanoflakes is 25 and 16 nanowires/μm² respectively. In this calculation, $\alpha$-Fe$_2$O$_3$ films were assumed to be a flat surface with 1.00 surface area for comparison. The higher surface area of nanowires is because of smaller diameter and longer of the wire produced as compared to nanoflakes. Iron oxide nanostructures distributions were determined by estimate the number of
nanowires and nanoflakes grow on the substrate. Graph in Fig. 4.5 shows the relationship between current density and the surface area. The graph shows that α-Fe$_2$O$_3$ nanowires with 6.34 cm$^2$ surface area give the highest current density of 0.25 mA/cm$^2$. α-Fe$_2$O$_3$ nanoflakes and films with surface area of 2.87 and 1.00 cm$^2$ give the current density of 0.08 and 0.01 mA/cm$^2$ respectively. The result clearly shows that current density increased with increasing the surface area of photoanodes. Agarwala et al. in her study also found that increasing the surface area of the nanoflower could improve the current density and photovoltaic performance in DSSC applications [3]. Low efficiency in α-Fe$_2$O$_3$ films is because of high oxidation temperature of 650 °C was used where at higher temperature, the migration of iron oxide is promoted by the thermal energy of the heated substrate [11]. Therefore, the surface of the top layer becomes smoother and resulting in small surface area. This smaller surface area will give lower photovoltaic performance in DSSC.

![Figure 4.5](image)

**Figure 4.5** Current density versus surface area graph of iron oxide films, nanoflakes and nanowires.

### 4.6 Discussion

In this study, the highest photovoltaic performances of α-Fe$_2$O$_3$ nanowires can be related to the highest nanowires surface area on the substrate which will affect the light collection rate in the DSSC active area. Niu et al. found that α-Fe$_2$O$_3$ nanoflower
as photoanode will enhance the charge transfer rate to prevent the charge recombination in addition to increase light collection efficiency [14]. In this study, 1-D α-Fe₂O₃ nanowires with high surface area give the highest charge transfer rate which can slow the charge recombination as compared to nanoflakes and films. Even though α-Fe₂O₃ nanoflakes have a bigger diameter compared to nanowires, the lower nanoflakes length and density will limit the charge transfer rate within these structures. Bigger nanoflakes diameter might be limited the charge carrier mobility through the nanostructure because of trap densities contain in the structure [3]. α-Fe₂O₃ films give the lowest performance due to the low light collection caused by the low surface area as compared to other structures. Iron oxide in nanoscale significantly increases the properties of this material for photovoltaic applications [3].

Table 4.1 shows α-Fe₂O₃ nanostructures synthesized by thermal oxidation process on Fe foils give lower photovoltaic performance if compared to solution [3, 14] synthesis method. This is because of hematite nanostructures synthesis by oxidation process will result not only in a α-Fe₂O₃ layer, but contains Fe₃O₄ as shown in Fig. 4.3 [18] previously. Appearance of these layers might affect the performance of α-Fe₂O₃ in DSSC. Although metal substrate can form a conducting layer, the usage of Fe foil as the substrate will be limited the DSSC performance. This is because of higher optical loss which attributed by the reflection at the Pt electrode and adsorption at the electrolyte. However, the advantage of thermal oxidation process is we can produce highly aligned in high quantity iron oxide nanostructures directly on the metal substrate in addition to this being a very easy process.

4.7 Conclusion

In summary, we have succeeded in the synthesis of nanoflakes, nanowires and films of α-Fe₂O₃ by changing the oxidation temperatures. We have obtained the highest photovoltaic characteristic for α-Fe₂O₃ nanowires if compared to nanoflakes and film with short circuit current, open circuit voltage, fill factor and efficiency of 0.25 mA/cm², 0.42 V, 0.38 and 0.04 % respectively. 1-D α-Fe₂O₃ nanowires with dense nanowires distribution give the highest surface area that can increase the charge transfer
rate which can slow the charge recombination as compared to others. Increasing in this photovoltaic performance is significantly associated with the surface area of $\alpha$-Fe$_2$O$_3$ nanostructure used.

4.8 References

CHAPTER 5

FABRICATION OF Fe$_2$O$_3$ NANOFLAKES BASED ELECTROCHEMICAL SOLAR CELLS PREPARED BY FACILE THERMAL OXIDATION

5.1 Introduction

Recently, hematite nanostructure-based solar cells have been widely explored owing to their excellent properties, especially improved by the reduction to the nanoscale. The narrower band gap of 2.1 eV and broader photoresponse compared with those of TiO$_2$ has motivated the use of hematite as a photoanode in solar cells. However, the production of a high photocurrent is a great challenge with hematite photoanodes owing to its poor hole collection ability. One suggested way to overcome this problem is to control the morphology, size, and porosity of the hematite layers [1].

Previously, Somekawa et al. successfully increased the performance of Fe$_2$O$_3$ film solar cells by improving the interaction between the Fe$_2$O$_3$ and fluorine-doped tin oxide (FTO) by altering the calcination temperature using laser ablation [2]. Dye wetting in dye sensitized solar cells (DSSCs) can be enhanced by increasing the surface area of nanostructured hematite photoanodes using a chemical solution method [3]. Recently, Niu et al. reported a broad photoresponse spectral region of up to 700 nm for a nano-flower hematite photoanode prepared using a chemical approach [4]. It has been reported that the use of nanostructured semiconductor materials could enhance the low energy conversion efficiency of DSSCs [5]. In the previous paper, the synthesis of Fe$_2$O$_3$ nanoflakes by thermal oxidation of iron foil through the optimization of the annealing temperature has been reported [6]. In this study, this method was applied to synthesize Fe$_2$O$_3$ nanoflakes for the fabrication of an electrochemical solar cell on FTO glass. The focus is on the effect of annealing time on the structure of the Fe$_2$O$_3$ nanoflakes and the corresponding effect on the photovoltaic performance of the
resulting electrochemical solar cell. This work represents the first report on a Fe$_2$O$_3$ nanoflakes-based electrochemical solar cell prepared by thermal oxidation.

5.2 Iron Oxide Nanoflakes Based Electrochemical Solar Cell Fabrication Technique

The thermal oxidation process was employed for growing Fe$_2$O$_3$ nanoflakes on the fluorine doped tin oxide (FTO) glass. Before the oxidation process, a thin layer of Fe was deposited onto FTO glass using vacuum electron beam evaporation. The FTO glass was cut to 20 × 20 mm$^2$, cleaned in methanol for 5 min, and dried in a nitrogen flow. A 99.9% purity Fe block was used as the source for the deposition process. A Fe thin film of 300 nm thickness was deposited on the surface of the FTO substrate at a deposition rate of 2.0 Å/s.

For the oxidation process, the sample with thin Fe layer was placed in the middle of a horizontal tube furnace. High purity air (G3) was flowed through the furnace at 0.5 L/min. The temperature of the oxidation process was set to 450 °C. To study the growth of the nanoflakes, samples were heated to the set point and then annealed for 0 to 6 h. After the annealing, the samples were allowed to cool to room temperature naturally. The samples were characterized using scanning electron microscopy (SEM; Hitachi S-3000H), X-ray diffraction (XRD; Rigaku RINT-2100, 40 kV, 30 mA, Cu Kα radiation), and ultraviolet-visible spectroscopy (UV-Vis; JASCO V-570).

For solar cell fabrication, the samples were dipped into ruthenium dye (ruthenium-535 bis TBA, Solaronix SA) for 12 h. The samples were then cleaned in ethanol and dried in air for several minutes. Next, semi-transparent platinum was deposited onto the sample to form a sandwich structure. Finally, the space between the Fe$_2$O$_3$-dye surface and the Pt electrode was filled with electrolyte (iodide/triiodide redox, Iodolyte AN-50, Solaronix). The performance of the solar cells was measured
under solar simulated illumination (100 mW cm\(^{-2}\), AM 1.5) in air with a specific area of 2.0 cm\(^2\). The light was illuminated from the glass side.

5.3 Effects of Annealing Time on Iron Oxide Nanoflakes Preparation

5.3.1 Surface Morphology Characterization

To investigate the effect of oxidation time, the samples were annealed at different times and SEM images of Fe film before and after annealing are shown in Fig. 5.1. Fe grain with diameter range of 70 – 600 nm were observed after deposited by vacuum electron beam evaporation (Fig. 5.1 (a)). After the samples were annealed at elevated temperature including at lower temperature whereas the sample was directly cooled to room temperature after heating to 450 °C, the color remarkably changed which indicates the presence of hematite. Nanoflakes with average length of 236.5 nm were grown on the substrate (Fig. 5.1(b)). For sample annealed at 1, 2 and 6 h the average length is gradually increased to 308.5, 318 and 321.5 nm, respectively. The density of the nanoflakes is almost constant when increasing the annealing time.
Figure 5.1 SEM image of (a) as deposited Fe film and (b-e) Fe$_2$O$_3$ nanoflakes prepared at 0, 1, 2 and 6 h annealing time.
5.3.2 Crystal Structure Characterization

The XRD patterns in Fig. 5.2 reveal that pure hematite was obtained for all samples, with four Fe$_2$O$_3$ peaks of (012), (104), (110), and (214) reflections. The sample marked 0 h was heated to 450 °C and then cooled to room temperature without holding of the temperature. Weak and broad Fe$_2$O$_3$ peaks were detected for this 0 h sample. These peaks remarkably increased in intensity as the annealing time was increased. At less than 2 h annealing time, the (104) Fe$_2$O$_3$ peak was dominant, while the (110) peak became dominant and its FWHM became narrower at annealing time longer than 2 h. This result indicates that the crystal growth of the Fe$_2$O$_3$ nanoflakes increased along the (110) plane with annealing time.

![XRD pattern of Fe$_2$O$_3$ nanoflakes at different annealing time at 450 °C.](image)

Figure 5.2 XRD pattern of Fe$_2$O$_3$ nanoflakes at different annealing time at 450 °C.

5.4 Optical Properties of Iron Oxide Nanoflakes

5.4.1 Absorption Spectra Characterization

Figure 5.3 (a) and (b) show the optical absorption spectra of unmodified samples and samples dipped into ruthenium dye, respectively. These spectra show that the Fe$_2$O$_3$ nanoflakes absorbed light from the UV region to the visible region [7]. The sample pre-annealed at 6 h exhibited broader photon absorption compared with that of the others. It
is noted that the absorption spectrum recorded at greater wavelengths (more than 700 nm) might be affected by scattering from the Fe$_2$O$_3$ nanostructure [4]. The absorption spectra did not change after dye loading. This is because the optical properties, such as the band gap, of the dye were the same as those of Fe$_2$O$_3$ [8]. The absorption spectrum of ruthenium dye is strongest between 400–600 nm. Therefore, the very thin layer of dye absorbed on the surface of the Fe$_2$O$_3$ nanoflakes did not much affect the absorption spectra of the samples.

![Absorption spectra of Fe$_2$O$_3$ nanoflakes at different annealing time at 450 °C](image)

**Figure 5.3** Absorption spectra of Fe$_2$O$_3$ nanoflakes at different annealing time at 450 °C (a) without dye and (b) with dye.
5.4.2 Transmittance Spectra Characterization

Transmittance spectra of Fe$_2$O$_3$ nanoflakes corresponding to the SEM images in Fig. 5.1 are measured and shown in Fig. 5.4. It can be seen that the sample annealed at 0, 1 and 2 h have higher transmittance with shorter-wavelength absorption edges. The transmittance is initially increased with increasing wavelength up to ~ 600 nm and become constant. The average transmittance of Fe$_2$O$_3$ nanoflakes prepared by this method is within 60-70 %. This value is in agreement with previous reported study [3, 7, 9]. Longer annealing time increased the size of the nanoflakes and might also increase the grain size of iron oxide layers at the nanoflakes base. These factors will enhance the scattering of light and reduce the light transmitted through the sample [9].

![Transmittance curve](image)

**Figure 5.4** Transmittance of Fe$_2$O$_3$ nanoflakes at different annealing time at 450 °C.

5.4.3 Reflectance Spectra Characterization

Figure 5.5 shows the variation of reflectance as a function of wavelength of Fe$_2$O$_3$ nanoflakes at different annealing time. The light has been reflected about 7 % at lower wavelength range from 400-550 nm. These values then further increased to 9 % and fluctuate in the range 8-18 %. Reflectance obtained for Fe$_2$O$_3$ prepared on the FTO glass by this method is higher as compared to solution method [7]. The reflectance pattern is more similar to α-Fe$_2$O$_3$ thin film synthesis by reactive evaporation process.
[9]. However the average reflectance values they obtained are higher as compared to this study.

![Figure 5.5 Reflectance of Fe₂O₃ nanoflakes at different annealing time at 450 °C.](image)

### 5.4.4 Optical Band Gap

Optical properties of Fe₂O₃ nanoflakes such as transmittance and reflectance measured by UV-Vis spectroscopy were applied in band gap calculation. Tauc plots of Fe₂O₃ nanoflakes at different annealing time are shown in Fig. 5.6 (a) for indirect and (b) for direct band gaps. In order to calculate the optical band gap of Fe₂O₃ nanoflakes semiconductor, absorption coefficient (α) is required. This value can be obtained from the following relation,

\[
\alpha = \frac{1}{d} \ln \left( \frac{(1 - R)^2}{T} \right)
\]

(1)

where R is the reflectance, T is transmittance, d is the thickness of the film. From the fundamental absorption region, the absorption coefficient can be related to the energy band gap as shown in equation (2).

\[
\alpha = \frac{\alpha_s}{E} (E - E_g)^{\delta}
\]

(2)
where $\alpha_0$ is a constant with values between $10^5$ and $10^6$ cm$^{-1}$[10]. The constant $\eta$ depends on the type of transitions including direct ($\eta=0.5$) and indirect ($\eta=2$). For band gap determination, $(\alpha E)^{1/\eta}$ is plotted as a function of photon energy.

Indirect transition which refer to $(\alpha \nu \nu)^{1/2}$ versus photon energy graph were obtained by extrapolating the photon energy to $\alpha \nu \nu = 0$. From extrapolation the band gap obtained is between 1.77-2.08 eV and comparable with the previous studies [9]. This indirect band gap allows absorption in the UV and the blue part of the visible light region, and it will affect the physical color of Fe$_2$O$_3$ nanoflakes, turning them a reddish-brown color.

For direct band gap determination, $(\alpha \nu \nu)^2$ versus photon energy is plotted and the same procedure by extrapolating $\alpha \nu \nu = 0$ is applied. The band gap yield is in the range of 2.3-2.52 eV and is comparable with previous reported hematite thin film prepared by reactive evaporation process [9]. Variations in band gap values are observed for Fe$_2$O$_3$ nanoflakes at different annealing time.
5.5 Photovoltaic Characterization

The Fe$_2$O$_3$ nanoflakes samples were used as photoanodes to fabricate electrochemical solar cells and the schematic diagram of working electrode is shown in Fig. 5.7 (a). The performances of the Fe$_2$O$_3$ based solar cells with and without dye measured using a solar simulator as shown in Fig. 5.7 (b)-(d). It is clear that short circuit current density ($J_{sc}$) of the cells increased gradually with annealing time, and these values were improved significantly when the photoanode samples were dipped in ruthenium dye. The highest $J_{sc}$ obtained for dipped and not dipped in dye sample are 26.54 and 4.21 $\mu$A/cm$^2$ respectively. The open circuit voltages ($V_{oc}$) increased greatly to
0.01 V at 1 h and then remained constant at with annealing time. The same trend with higher $V_{oc}$ values was obtained with dye. These $V_{oc}$ and $J_{sc}$ characteristics affected their overall solar cell performance (Fig. 5.7 (d)).

![Diagram](image)

**Figure 5.7** Schematic diagram of the working electrode (a), (b) open circuit voltage, (c) short circuit current density and (c) efficiency of Fe$_2$O$_3$ based solar cell.

**5.6 Discussion**

In this study, the photovoltaic performance of nanostructured Fe$_2$O$_3$-based electrochemical solar cells was analyzed as a function of annealing time. The $J_{sc}$ and $V_{oc}$ of the cells was increased rapidly at 1 h annealing time owing to formation of longer nanoflakes, which increased their surface area. At longer annealing time, the length of the nanoflakes slightly increased while their density roughly remained constant. This
improvement also increased the surface area. With larger surface area, more electrolyte can be penetrate between the nanoflakes, resulting in a greater Fe$_2$O$_3$/electrolyte interface. Furthermore, the formation of crystalline Fe$_2$O$_3$ grains with (104) and (110) planes on the substrate (Fig. 5.2) may have contributed to an improved interaction between semiconductor and electrolyte [8]. From 1 h annealing time, the crystal quality of the nanoflakes were improved, with increasing (110) peak intensity and the appearance of more Fe$_2$O$_3$ peaks. The intensity of this particular peak was noticeably increased at 6 h annealing time. Oxidation for longer periods may have enhanced the reaction between the iron oxide molecules and oxygen in the air and result in more crystalline Fe$_2$O$_3$. Even though the density of the nanoflakes was almost constant at longer annealing time, their nanoflakes surface area was increased and surface crystal structure became more crystalline. Therefore, each nanoflake would have generated more electron-hole pairs under absorption, increasing the photocurrent [7]. In contrast, $V_{oc}$ was saturated beyond 1 h annealing time because the same nanoflake structure was obtained in all samples.

Additionally, the overall photovoltaic performance was increased by the loading of dye onto the surface of the Fe$_2$O$_3$ nanoflakes (Fig. 5.7). This is because the Fe$_2$O$_3$ surface is passivated by dye, resulting in the suppression of carrier recombination at the surface [9]. When the rate of this recombination is reduced, $J_{sc}$ increases and consequently improves the solar cell performance. However, the absorption spectra of the samples were not changed after dye loading (Fig. 5.3), because the optical properties, such as the band gap, of the dye were the same as those of Fe$_2$O$_3$. Assuming that the dye is not adsorbed at the surface, the improvement of $J_{sc}$, $V_{oc}$ and efficiency with dye cannot be explained. These observations show that the dye is adsorbed at the surface of nanoflakes.
5.7 Conclusion

In summary, electrochemical solar cells based on a Fe$_2$O$_3$ nanoflake photoanode were successfully prepared by a thermal oxidation process for the first time. The photocurrent of the cells was found to increase with annealing time. Improvement in the surface area and crystal quality of the (110) plane of the nanoflakes were believed to be factors that enhanced electron transfer in the solar cells. The application of ruthenium dye significantly enhanced the photovoltaic performance of the Fe$_2$O$_3$ nanoflake-based solar cell.

5.8 References

CHAPTER 6

CONCLUSION

6.1 Overall Conclusion

This thesis described the synthesis of iron oxide (α-Fe₂O₃) nanostructures by thermal oxidation process of iron foil and deposited iron layer on FTO glass. The morphology and crystal structures of this nanostructures material are characterized and discussed. Their performances also evaluated as photoanodes in DSSC on Fe foil or FTO glass substrate.

Iron oxide (α-Fe₂O₃) nanoflakes have been synthesized on iron foil by simple air oxidation technique. The effects of oxidation temperatures between 350-600 °C and annealing time from 1-6 h to grow the nanoflakes has been studied. The study indicated that the α-Fe₂O₃ nanostructure shape is influenced by the growth temperature while their density is affected by annealing time. Different pressure gradient created at different temperature contributed to the grain size effect and results in wire-like or flaky shape nanostructures. When exposed to longer annealing time, dense nanoflakes can be obtained because of the possible occurrence of more oxidation reaction converting Fe atom to iron oxide molecules. XRD patterns prove that crystal structure of the α-Fe₂O₃ nanoflakes formed consists of Fe₂O₃ and Fe₃O₄ molecules. This result indicated that the oxidation of iron foil in the high purity air at 450 °C will form two oxide layers. The preferential growth direction of the nanoflakes is found at (110) with a fringe spacing of 0.25 nm.

From single heating step synthesis methods, another additional step is introduced by employing pre-annealing step in α-Fe₂O₃ nanowires formation. The effect of pre-annealing temperature on the nanowires alignment and density has been studied. Pre-annealing in two-step oxidation process will modify the crystal structure and grain
orientation on the substrate before nanowires grow. XRD results show iron oxide molecules at (110) and (200) direction is formed at pre-annealing at 300 °C for 30 min. The results indicate that iron oxide layer which act as seed layer is formed with smaller Fe$_2$O$_3$ grains of good crystallinity is produced and second oxidation occurred on these grain structures at 550 °C for α-Fe$_2$O$_3$ nanowires synthesis. Substrate modification by pre-annealing at 300 °C led to the formation of grain structure at (110) direction which significantly contribute to the highly aligned and high density α-Fe$_2$O$_3$ nanowires at the same preferential growth direction. Pre-annealing temperature has become an important parameter in the grain structure modification for α-Fe$_2$O$_3$ nanowires synthesis on Fe foil.

As semiconductor materials, the performance of Fe$_2$O$_3$ nanoflakes and nanowires is investigated as photoanodes in DSSC. Two different dimension nanostructures of Fe$_2$O$_3$ nanoflakes and nanowires prepared on Fe foil at 450 and 550 °C, respectively, are used as photoanodes and compared to Fe$_2$O$_3$ films. SEM images shows high alignment of high density Fe$_2$O$_3$ nanoflakes and nanowires are synthesized. XRD pattern reveal Fe$_2$O$_3$ nanoflakes and nanowires are prepared at oxidation temperature below than 570 °C, in which the crystal structure consists of Fe$_2$O$_3$ and Fe$_3$O$_4$ layer. Single Fe$_2$O$_3$ layer is formed for oxidation temperature higher than 570 °C. The study indicated that short circuit current density is increased with increasing nanostructures surface area. Fe$_2$O$_3$ nanowires with 6.34 cm$^2$ give the highest power conversion efficiency of 0.04 % as compared to nanoflakes and films. Surface area of nanostructures used as photoanodes significantly influence the photovoltaic performance in DSSC.

Fe$_2$O$_3$ nanoflakes are grown on FTO glass by oxidizing Fe layer deposited by vacuum electron beam evaporation system. Oxidation temperature of 450 °C is chosen for growing the nanoflakes on the FTO substrate based on the Fe$_2$O$_3$ nanoflakes grown on the foil. Effect of annealing time on the nanoflakes grown on the FTO glass has been studied and their application as photoanodes in electrochemical solar cell has been analysed. SEM images shows aligned flaky nanostructure is formed on thin Fe layer of 300 nm. Increasing annealing time is found to have little effect on nanoflakes density but give some effect to the crystal structure. XRD pattern indicated that pure Fe$_2$O$_3$
group is produced at various annealing time applied. The optical band gap calculated give 1.77-2.08 eV for indirect and 2.3-2.5 eV for direct energy gap. As photoanodes in electrochemical solar cell, the power conversion efficiency is increased with increasing annealing time. Suppression of recombination of carriers at the surface caused the overall photovoltaic performances to increase with dye loaded onto the Fe$_2$O$_3$ nanoflakes surface. When surface recombination is reduced, the $J_{sc}$ will be increased and consequently improve the solar cell performance. This study has shown that Fe$_2$O$_3$ nanoflakes based electrochemical solar cell performances is affected by the nanostructure crystallinity and application of ruthenium dye.

6.2 Suggestions for Future Work

Hematite nanostructures are promising semiconductor and their application in DSSC and electrochemical solar cell shows it can be used as photoanodes even if prepared directly on the foil or conducting glass substrate. There are some factors which can contribute to the low solar cell performance in this study such as the compatibility of ruthenium dye used with the surface of $\alpha$-Fe$_2$O$_3$ nanostructures. More study focusing on the dye which can adhere and function properly is required to further improve the interaction between these two materials.

In addition, the surface morphology of the nanostructures prepared especially on the FTO glass needed to be optimized. In this study, Fe layer is deposited by vacuum electron beam evaporation method, and other Fe seed layer deposition techniques can be explored for example electrodeposition, electroplating or combination of these. Highly aligned and high density $\alpha$-Fe$_2$O$_3$ nanostructures are needed for further improvement of their performance in solar cell.

The application of $\alpha$-Fe$_2$O$_3$ nanostructures as other functions such as for counter electrode for Pt replacement in DSSC should be explored. And because of dye compatibility problem in liquid solar cell, these nanostructures can be applied in other solid solar cell types such as quantum dot of organic solar cell.
6.3 Acknowledgement

I am most grateful to Allah Almighty for giving me a chance to continue my study in Phd in Nagoya Institute of Technology (NIT) and for giving me the strength and determination to pursue this work. My greatest appreciation is to the Malaysia Government for the financial support and promotion for my Phd study in Japan.

I would like to express my gratitude to my supervisors, Prof. Tetsuo Soga from Department of Frontier Materials, NIT for giving me the opportunity to study under his supervision, and for his unflinching encouragement, indispensable help and inspiration to carry out this study. My sincere thanks also go to Dr. Naoki Kishi from Department of Frontier Materials, NIT for his valuable guidance, suggestion and support through my Phd journey.

I would like to thank the committee member, Prof. Masaya Ichimura and Prof. Yo Ichikawa, Nagoya Institute of Technology for giving their comments and suggestions for improving my thesis.

I am also thankful to my wonderful family, my husband Mohd Nazri and my son Muhammad Irfan Hadi for their prayers, support and sacrifice. I really appreciate it. To my beloved parents, Mohamed Rashid and Halijah, my siblings and my family-in-laws, thank you very much for your prayers and never ending support.

Last but not least, I really appreciate to my friends in Nagoya and Malaysia who always encourage and pray for me. I would also like to thank all friends in my laboratory and visiting professors who helped me in this work.

Finally, I wish to acknowledge all those who have been directly or indirectly involved the completion of my Phd and this thesis.
6.4 List of Publications

6.4.1 Journals

1. Norhana Mohamed Rashid, Xuyang Li, Naoki Kishi, and Tetsuo Soga “Synthesis of iron oxide nanoflakes at lower temperature by air oxidation of iron foils”
   DOI.org/10.7567/JJAP.53.11RE04

2. Norhana Mohamed Rashid, Naoki Kishi, and Tetsuo Soga “Synthesis of high-density aligned Fe$_2$O$_3$ nanowires via two-step thermal oxidation”
   DOI 10.3139/146.111303

3. Norhana Mohamed Rashid, Naoki Kishi, and Tetsuo Soga “Effect of pre-annealing temperature on aligned α-Fe$_2$O$_3$ nanowires growth via two-step thermal oxidation”
   *Surface Reviews and Letters* (accepted).

4. Norhana Mohamed Rashid, Naoki Kishi, and Tetsuo Soga “Effect of nanostructures on iron oxide based dye sensitized solar cells fabricated on iron foils”
   http://dx.doi.org/10.1016/j.materresbull.2016.01.028

5. Norhana Mohamed Rashid, Naoki Kishi, and Tetsuo Soga “Fabrication of Fe$_2$O$_3$ nanoflakes based electrochemical solar cells prepared by facile thermal oxidation”
6.4.2 Conferences

