The American University in Cairo
The Graduate School
The Nanotechnology Program

ZIRCONIUM-BASED PHOTOANODES
FOR THE PRODUCTION OF SOLAR FUEL

A Thesis in
Nanotechnology

By
Ahmad Waleed Amer

©2015 Ahmad Waleed Amer

Submitted in Partial Fulfillment
of The Requirements
for The Degree of Masters of Science in Nanotechnology

September 2015
Abstract

With global climate change becoming a chronic situation, humanity needs to come up with efficient, sustainable, and clean alternative energy sources that can truly create markets capable of competing with the fossil fuel industry. Being one of the fundamental constituents of the greater part of the planet, Hydrogen emerges as one of the best alternative fuels, offering comparable –or higher- energy levels, as well as cleaner combustion results, when compared with our everyday sources of energy. Also, water is both the primary source and resultant, which means full sustainability. The process of producing Hydrogen gas, however, is not as giving. Huge amounts of energy are consumed daily to produce amounts of Hydrogen gas that can barely cover the currently-low market demand. Thus, the need to develop more efficient Hydrogen production systems is dire.

Being the gigantic nuclear fusion reactor it is, the Sun supplies our planet with more energy per day than all of industrial energy sources combined. Harvesting such energy is made available by pyroelectric as well as semiconducting materials. With the invention of the transistor, the world’s focus on the latter materials increased greatly, and huge amounts of research has been taken out ever since. It is now a global ultimatum to develop semiconducting systems that can efficiently convert the energy of the Sun to electrical energy to be used in the electrolysis of water for the production of Hydrogen gas. In this thesis, an Earth-abundant material, Zirconium, was used to develop semiconducting electrodes for that exact purpose.

Because nanostructuring offers new properties un-attainable at the macro scale, in the first part of this thesis, a comprehensive study was taken out to develop protocols for the synthesis of semiconducting Zirconium Oxide nanotubes (NTs) with
different lengths, diameters, wall thicknesses, and morphologies. It was shown that, using the cheap electrochemical anodization method, Zirconia NTs with hexagonal as well as circular cross sections were synthesized, depending on the concentrations of water and etchant in the electrochemical bath. The control of length, diameter, and wall thickness was also attained through controlling the applied potential, anodization time, as well as the solvent composition of the electrolyte. With the aims of using these NTs in solar water splitting, the smallest wall thickness, as well as the best structure, were the main drives behind choosing the optimum electrolyte-potential-time combination for NT synthesis. Thus, the synthesis of semiconducting, widely stable Zirconia NTs was successful.

Zirconia NTs are wide band gap semiconductors, limiting their optical absorption to the Ultra Violet region (<10%) of the solar spectrum. Thus, their use in solar water splitting proves to be inefficient. It was, thus, the aim of the second part of this thesis to cheaply modify the synthesized nanostructured electrodes. Atomic Layer Deposition (ALD) was used to deposit very thin layers of Zirconium Nitride, another Earth-abundant compound, to drive Oxygen/Nitrogen diffusion, and eventually attain an oxynitride layer on the surface of the oxide NTs. This so-called Zirconium Oxynitride layer is known to have visible-light absorption characteristics, which would greatly increase the efficiency of the resulting photoanodes. Indeed, the chemical composition was proven to be a mixed oxide-nitride layer through X-ray Photoelectron Core and Valence Band Spectroscopy. UV-Vis and Tauc optical analysis proved the shift in the optical band gap of the oxide NTs from 3.8 to 2.4 eV. Photoelectrochemical analysis showed a higher catalytic activity for the composite photoanodes as compared to the bare oxide NTs. Electrochemical Impedance Spectroscopy showed that the increase in photogenerated carriers, as well as the
decrease in the hole potential barrier at the photoelectrode/electrolyte interface in the composite electrodes, may be the main reasons behind the performance enhancement witnessed in these electrodes.
The thesis of Ahmad Waleed Amer was reviewed and approved* by the following:

Nageh K. Allam  
Associate Professor, Physics Department  
Director, Energy of Materials Laboratory (EML).  
The American University in Cairo  
Thesis Advisor  
Chair of Committee

Joumana El-Rifai  
Assistant Professor, Physics Department  
The American University in Cairo  
Internal Examiner

Adel B. El-Shabasy  
Professor, Design and Production Engineering Department  
Director, Materials Engineering and Metallurgy Consultancy Unit  
Faculty of Engineering, Ain Shams University.  
External Examiner

Ahmed El-Gendy  
Visiting Associate Professor, Department of Construction and Architectural Engineering, The American University in Cairo  
Defense Moderator

*Signatures are on file in the Graduate School.
# TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................................................... viii

LIST OF TABLES .................................................................................................................................................. xi

LIST OF ACRONYMS ......................................................................................................................................... xii

ACKNOWLEDGMENTS ....................................................................................................................................... xiii

Chapter 1 Introduction and Scope of Thesis ................................................................................................. 1

1.1 Fuel Alternatives ...................................................................................................................................... 3
1.2 Production of Solar Fuel ............................................................................................................................ 5
1.3 Towards Efficient Solar Water Splitting ..................................................................................................... 6
1.4 Zirconium Dioxide Semiconductors ........................................................................................................... 8
1.5 Scope of Thesis ......................................................................................................................................... 8

References ......................................................................................................................................................... 11

Chapter 2 Background .................................................................................................................................... 13

2.1 Thermodynamics of Water Splitting .......................................................................................................... 13
2.2 Photoelectrochemical Cells ........................................................................................................................ 14
2.3 Materials Selection Criteria ........................................................................................................................ 18
   2.3.1 Semiconductor Band Gap ....................................................................................................................... 18
   2.3.2 Band Edge Positions ................................................................................................................................. 19
   2.3.3 Semiconductor Stability ........................................................................................................................ 20
   2.3.4 Charge Carrier Dynamics ....................................................................................................................... 21
2.4 Experimental Considerations ....................................................................................................................... 24
   2.4.1 The Solar Spectrum ................................................................................................................................. 25
2.5 Atomic Layer Deposition ............................................................................................................................. 27

References ......................................................................................................................................................... 28

Chapter 3 Literature Review .......................................................................................................................... 30

3.1 Fabrication of ZrO\textsubscript{2} NT Arrays ..................................................................................................... 30
   3.1.1 Anodization Variables .......................................................................................................................... 31
   3.1.2 Anodization Mechanism ....................................................................................................................... 38
3.2 Zirconium Oxynitrides for Photocatalysis ................................................................................................... 40

References ......................................................................................................................................................... 44

Chapter 4 Materials & Experimental Procedures .......................................................................................... 50

4.1 Photoanode Fabrication ............................................................................................................................... 50
   4.1.1 Synthesis of ZrO\textsubscript{2} NT Arrays ................................................................................................... 50
   4.1.2 Fabrication of ZrN/ZrO\textsubscript{2} Composite Photoelectrodes ............................................................... 51
4.2 Morphological, Crystalline Structure, and Chemical State Analyses ......................................................... 51
4.3 Optical and Photoelectrochemical Characterization .................................................................................. 51
Chapter 5 Fabrication of ZrO$_2$ Nanotube Arrays

5.1 Effect of Solvent Composition
5.2 Effect of Etchant & Water Contents
5.3 Effect of Anodization Duration
5.4 Effect of Anodization Potential
5.5 Point Defect Model on Anodization of Zr Metal
5.6 Thermodynamic Analysis of Anodization of Zr Foils
5.7 Annealing of ZrO$_2$ NT Arrays
5.8 Optical Analysis of ZrO$_2$ NT Arrays
5.9 Conclusions

References

Chapter 6 ZrN/ZrO$_2$ Composite Photoanodes

6.1 Morphological and Structural Analysis
6.2 Optical Characterization
6.3 Photoelectrochemical Characterization
6.4 Conclusions

References

Chapter 7 Suggestions for Future Work

7.1 Optimization of Zirconia NT Arrays for Water Splitting
7.2 Optimization of ZrN Layer Thickness

PUBLICATIONS
LIST OF FIGURES

Figure 1-1: The current routes for production of Hydrogen gas as well as their percentages.8 ......................................................................................................................................................4

Figure 1-2: A capacity comparison between the different available energy sources by the year 2050. The figure also shows the global consumption in TW/year in 2009 and 2050.15 ......................................................................................................................................................5

Figure 1-3: The three possible setups for solar water splitting cells.16 .................................................7

Figure 2-1: Energy diagrams showing an n-type semiconductor/electrolyte junction on initial contact (a), and at equilibration (b). Panels (c,d) show the effect of illumination on a semiconductor having a $V_{FB}$ that is more anodic than the water reduction potential, thus requiring overpotential to drive the reaction forward. Panel (e) shows another case of illuminated semiconductor but having a $V_{FB}$ that is more cathodic than the water reduction potential.4 ......................................................................................................................................................15

Figure 2-2: Band edge positions for selected semiconductors vs NHE. The water redox potentials are also indicated.5 ......................................................................................................................................................20

Figure 2-3: Electron (solid circles) and hole (hollow circles) pathways after excitation in planar (A) and 1-D (B) electrodes. $L_d$ is the hole diffusion length ($\sim \lambda$), and $\alpha$ is the absorption coefficient of the material.14 ......................................................................................................................................................23

Figure 2-4: A schematic of a laboratory one-compartment PEC cell. WE, RE, and CE stand for the Working, Reference, and Counter Electrodes, respectively. A circulation system maybe used to refresh the electrolyte.15 ......................................................................................................................................................24

Figure 2-5: The spectral irradiance of the three standardized AM numbers.15 ......................................................................................................................................................26

Figure 2-6: A comparison between the photon fluxes of Xenon arc lamps and AM1.5 G sunlight. All measurements were normalized to 1000 W/m².6 ......................................................................................................................................................26

Figure 2-7: Schematic explaining the steps involved in depositing one cycle of material in ALD.25 ......................................................................................................................................................27

Figure 3-1: The effect of switching between organic and inorganic electrolytes on the rate of etching NT arrays in Zr foils.13 ......................................................................................................................................................32

Figure 3-2: ZrO$_2$ NTs synthesized in electrolytes with etchant being (a) HCl,26 (b) HF,20 (c) NaF,16 and (d) NH$_4$F.17 ......................................................................................................................................................34

Figure 3-3: The rates of Hydrogen and Oxygen gas evolution over Pt-ZrON and ZrON catalysts, respectively, versus the wavelength of the incident light. Absorbance is also presented.61 ......................................................................................................................................................43
Figure 4-1: A schematic showing the anodization setup and the method of formation of NT arrays ................................................................. 50

Figure 5-1: FESEM images of as-grown ZrO$_2$ nanotube arrays via anodic oxidation for 3hrs @50V in glycerol electrolytes containing 4wt% H$_2$O and 1wt%NH$_4$F, along with (a) 0% FA, (b) 10% FA, (c) 20% FA, (d) 30% FA, and (e) 40% FA. Panel (f) shows the variation of the ZrO$_2$ NT dimensions with FA content ................................................................. 56

Figure 5-2: FESEM images of as-grown ZrO$_2$ nanotube arrays via anodic oxidation for 3hrs @50V in glycerol electrolytes containing 20% FA, along with (a) 0.5wt% NH$_4$F and 2wt% H$_2$O, (b) 0.5wt% NH$_4$F and 3wt% H$_2$O, (c) 0.5wt% NH$_4$F and 4wt% H$_2$O, (d) 1wt% NH$_4$F and 2wt% H$_2$O, (e) 1wt% NH$_4$F and 3wt% H$_2$O, (f) 2wt% NH$_4$F and 2wt% H$_2$O, (g) 2wt% NH$_4$F and 3wt% H$_2$O, and (h) 2wt% NH$_4$F and 4wt% H$_2$O .................................................. 58

Figure 5-3: The variation in average NT diameter with changing NH$_4$F and H$_2$O contents in the anodization bath ................................................................. 59

Figure 5-4: FESEM images of as-grown ZrO$_2$ nanotube arrays via anodic oxidation @50V in glycerol electrolytes containing 20% FA, 4wt% H$_2$O and 1wt%NH$_4$F, for a duration of (a) 1, (b) 2, (c) 4, (d) 5, (e) 6, and (f) 16 hrs. Panel (g) illustrates the change in NT length, diameter and wall thickness with increasing anodization duration ................................................................. 61

Figure 5-5: FESEM images of ZrO$_2$ NTs anodized for 3 hrs in GE-based electrolytes containing 20% FA, 1wt% NH$_4$F and 4wt%H$_2$O at (a) 10, and (b) 30V ................................................................. 62

Figure 5-6: (a) Schematic illustrating the anodization of Zr foils in fluoride-rich electrolytes. (b) EDX spectra of the bottoms of detached nano-tubes showing a F$^-$ ion at% almost double that of Zr ................................................................. 65

Figure 5-7: (a) FESEM image of ZrO$_2$ NT arrays as-annealed at 500°C for 4 hrs. (b) XRD spectra of (I) as-annodized and (II) as-annealed arrays ................................................................. 70

Figure 5-8: (a) ZrO$_2$ NT arrays after annealing at 350°C for 4 hrs. (b) XRD spectra for (I) the as-anodized and (II) the as-annealed arrays ................................................................. 71

Figure 5-9: (a) Schematic showing the model built for the FDTD calculations, (b) a plot showing the incident, reflected, and transmitted electromagnetic fields in the time domain. (c) Dependence of the relative permittivity of ZrO$_2$ on the frequency of the incident field. (d and e) A comparison between the measured and simulated transmittance and absorbance, respectively, for NTs having a length of 18 mm, a diameter of 64 nm, and a wall thickness of 12 nm. (f and g) Simulated data for transmittance and absorbance of nanotubes having different lengths. (h) Simulated data for transmittance of nanotubes having different wall thicknesses ................................................................. 73
Figure 6-1: FESEM images of ZrO$_2$ samples having (a) 5, (b) 10, (c) 20, (d) 48, and (e) 200 ALD cycles of ZrN.................................81

Figure 6-2: XPS (a) N 1s, (b) Zr 3d, and (c) O 1s core spectra of bare ZrO$_2$ NTs samples, and NT samples with 10, 48, 95, and 142 ALD cycles of ZrN..83

Figure 6-3: XPS VB spectra for samples with different number of deposition cycles of ZrN on ZrO$_2$ NTs. A Zr foil having 600 ALD cycles of ZrN was added for reference............................................................87

Figure 6-4: UV-Vis spectra of ZrO$_2$ NTs having 0 and 95 ALD cycles of ZrN. (b and c) Tauc plots for the same samples, respectively. (d) An empirical relationship between the band gap of the samples and the number of ALD cycles as extracted from Tauc analysis....................................................88

Figure 6-5: (a) Photocurrent density-voltage curves for bare ZrO$_2$ NTs, and ZrO$_2$ NTs having different ALD cycles of ZrN. (b) A plot showing the change in the OCP with increasing number of ALD cycles.........................90

Figure 6-6: (a) Illuminated Nyquest plots for the Bare NTs and the NTs with 95 ALD cycles. (b) and (c) Simplified circuit elements for both samples respectively.................................................................92

Figure 6-7: (a) Area-corrected Mott Schottky plots for the bare NTs and the NTs having 95 ALD cycles. (b) Band Allignment diagram for both samples with respect to the water splitting redox potentials.................................98
LIST OF TABLES

Table 1-1: Shares of CO₂ emissions (in million tons) from 1971-2020.4 .................................................................................................................................2

Table 3-1: A summary of experimental conditions and results of some of the most important literature on the anodization of Zirconium........................................33

Table 5-1: ZrO₂ NT lengths, diameters, and wall thicknesses with varying FA contents in electrolytes........................................................................................................57

Table 5-2: Average ZrO₂ NT (length-wall thickness) with varying NH₄F and H₂O weight contents in the anodization electrolytes.......................................................59

Table 6-1: The chemical states, Zr 3d, O 1s, and N 1s peak binding energies (+/- 0.05 eV) of bare NTs and NTs having 10, 48, 95, and 142 ALD cycles, as extracted from XPS data.........................................................................................................................86

Table 6-2: Values of resistances (in Ω) and capacitances (in μF) in the suggested circuits as extracted from impedance spectra for both bare NTs and NTs with 95 ALD cycles of ZrN......................................................................................................94
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALD</td>
<td>Atomic Layer Deposition</td>
</tr>
<tr>
<td>AM</td>
<td>Air Mass number</td>
</tr>
<tr>
<td>ASPO</td>
<td>Association for the Study of Peak Oil &amp; Gas</td>
</tr>
<tr>
<td>CBM</td>
<td>Conduction Band Minimum</td>
</tr>
<tr>
<td>CPS</td>
<td>Counts Per Second</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectra</td>
</tr>
<tr>
<td>FA</td>
<td>Formamide</td>
</tr>
<tr>
<td>FDTD</td>
<td>Finite Difference Time Domain</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field Emission Scanning Electron Microscope</td>
</tr>
<tr>
<td>GCP</td>
<td>Global Carbon Project</td>
</tr>
<tr>
<td>GE</td>
<td>Glycerol</td>
</tr>
<tr>
<td>IC</td>
<td>Integrated Circuit</td>
</tr>
<tr>
<td>IPCE</td>
<td>Incident Photon Conversion Efficiency</td>
</tr>
<tr>
<td>MMTs</td>
<td>Million Metric Tons</td>
</tr>
<tr>
<td>MOMR</td>
<td>Monthly Oil Market Report</td>
</tr>
<tr>
<td>MS</td>
<td>Mott-Schottky</td>
</tr>
<tr>
<td>NHE</td>
<td>Normal Hydrogen Electrode</td>
</tr>
<tr>
<td>NTs</td>
<td>Nanotubes</td>
</tr>
<tr>
<td>OPEC</td>
<td>Organization of the Petroleum Exporting Countries</td>
</tr>
<tr>
<td>PBE</td>
<td>Perdew–Burke–Ernzerhof</td>
</tr>
<tr>
<td>PDM</td>
<td>Point Defect Model</td>
</tr>
<tr>
<td>PEC</td>
<td>Photoelectrochemical Cell</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated Calomel Electrode</td>
</tr>
<tr>
<td>US EPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultra Violet - Visible</td>
</tr>
<tr>
<td>VBM</td>
<td>Valence Band Maximum</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectrometer</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

The only true provider of success and straightness in one’s path is ALLAH subhanahu wa ta’ala. However, because causality is a fundamental concept in the creation of this world, ALLAH renders humans, and other, the main causes behind one’s success. This being said, I owe all my success in taking out this study to my advisor, Dr. Nageh Allam. I am indeed grateful to his constant financial and logistical support to my project, including buying all the materials I used to finish my studies, as well as obtaining access for me to work at the Laser Dynamics Lab (LDL) at the Georgia Institute of Technology to take out critical experiments. I am also indebted to him for his extreme care to teach me, as well as all other group members, and constantly drive us towards better status, even if this often caused him great distress. In this sense, I am thankful to Prof. Mostafa El-Sayed, as well as his only Egyptian PhD student, Mustafa, for making life extremely easy for me and my peers at the US.

Coming second to Dr. Nageh’s support is the support by my father, mother, brother, and my wife. Indeed, my upper family was always beside me whenever I needed support throughout my studies, even if it sometimes irritated them, or made them fall into a financial dilemma, or simply angered them. Also, my wife; what she endured during my three-year experience was not part of our vows. Her constant support, positivity, and ingenious sink of technical and social ideas that saved a lot of my days are truly invaluable. Of course, our baby son, Malek, also had to endure a lot. May ALLAH make it easy upon them all. I am forever indebted to them.

I’d also like to specially mention my quarter back: Ahmad Mohyeldin. Meeting at the Fellowship’s office before starting our first semester, Ahmad and I grew very strong ties until we travelled together to the US, where we became true brothers. Ahmad has always been there for me to set up that elusive experiment, or
take out that anodization or photoelectrochemical experiments when I was absent. This work owes much to Ahmad. I hope I can join him with my PhD studies to always be fellows in this grand journey of life.

I would also like to thank all my peers at the Energy Materials Lab and beyond, especially Basamat, Hafez and Ali, for helping me achieve this degree, whilst providing the friendliest working atmosphere. In addition, the constant support of Justin, Mike, Steven, and Paul from LDL is gratefully acknowledged.

Indeed, the generous acceptance of the respected members of my examination committee: Prof. Adel El-Shabasy, Dr. Joumana El-Refai, and Dr. Ahmed El-Gendy, is well acknowledged. I thank them all for being very facilitating throughout the process of submission and defense, as well as for their valuable advice and constructive criticism before and after the defense.

Finally, the financial support by the American University in Cairo, as well as the US National Science Foundation, are also acknowledged.
Chapter 1

Introduction and Scope of Thesis

With the limits in worldly resources emerging as a global crisis, humanity is faced with its toughest challenge yet. Throughout human history, war has been the eminent solution to such earthly dilemmas. However, innovation remained the safe house to which we often sheltered as a refuge from undesired events. Consequently, ever since Fire was discovered, humans have grown a habit of dealing with problems only as opportunities for engineering breakthroughs. Equipped with such intellectual positivity, our race remains in an ever-developing state, God willing, towards the more advanced, better equipped, and most importantly, truly ethical civilizations. Today, the crisis of diminishing resources is most dramatic in the energy industry: the remaining life-line to which humans are holding, fossil fuels, may not be around by the end of the 21st century.

Analyzing the oil industry, the Monthly Oil Market Report (MOMR) produced by OPEC (Organization of the Petroleum Exporting Countries) on the 16th of March 2015 shows an increase in world oil demands in 2014 just above 1% from past years. Fortunately, the same MOMR shows a total of about 2% increase in global oil supplies in the same year. In addition, OPEC’s Annual Statistical Bulletin presents an 0.4% increase in global proven crude oil reserves (and an 0.4% decrease in the proven natural gas reserves) between 2012 and 2013. OPEC’s analysis delivers a reassuring message. However, on the other, darker side of reality, the Association for the Study of Peak Oil & Gas (ASPO), using a modified Klass model, predicted the lifetime of the 2008 reserves of oil and gas to be 35 and 37 years, respectively, while coal was estimated to last for a longer 107 years. All in all, by 2112, none of the three fossil
fuels would exist. This study, although theoretical, predicts a possible crisis around the turn of the century.

Indeed, neither OPEC’s nor ASPO’s studies can be deemed innocent of political tendencies. However, other chapters remain in the case of the problematic dependence on fossil fuels: namely, the ill-famed carbon footprint, which originates from burning fossil fuels, and is one of the main reasons behind global warming. This effect is traced back to the emission of greenhouse gases. In particular, Carbon Dioxide gas (CO₂) is responsible for more than 70% of the greenhouse effect.¹ The United States Environmental Protection Agency estimates Carbon Dioxide emission in 2013 from US territories in the Energy sector alone as about 5331.5 million metric tons (MMTs), compared to the 871 MMTs decrease in the same year because of increased forestry.⁵ The 2013 data shows a 3.3% increase in CO₂ emissions from 2012. On a global scale, Table 1.1 shows the different shares of CO₂ emissions in the world from 1971 up to the projected shares in 2020. Just last year, the Global Carbon Project⁶ estimated the yearly increase in global CO₂ emissions from the use of fossil fuels as 2.5%. This sustained release of CO₂ into the atmosphere is projected to cause an average of 4.3°C increase in the planet’s temperature by 2100, compared to pre-industrial times.⁷ With certainty, this latter projection clarifies the reasons behind the current impact of using fossil fuels on deteriorating global life cycles and increased natural disasters (e.g. Tsunamis).

Table 1.1: Shares of CO₂ emissions (in million tons) from 1971-2020.⁴

<table>
<thead>
<tr>
<th>Region</th>
<th>1971</th>
<th>1995</th>
<th>2010</th>
<th>2020</th>
</tr>
</thead>
<tbody>
<tr>
<td>Members of OECDᵃ</td>
<td>9031</td>
<td>10763</td>
<td>13427</td>
<td>14476</td>
</tr>
<tr>
<td>Rest of World</td>
<td>1436</td>
<td>4791</td>
<td>8034</td>
<td>11163</td>
</tr>
<tr>
<td>Worldᵇ</td>
<td>14732</td>
<td>22150</td>
<td>31189</td>
<td>37848</td>
</tr>
</tbody>
</table>

ᵃOrganization for Economic Co-operation and Development.
ᵇNumbers for total global emissions gathered from a different resource.
From the aforementioned emerges the bottleneck of the energy crisis. Humanity’s current reserves of fossil fuels are being quickly depleted, leaving no backup plans for that unfortunate generation that will be dwelling this planet by the time earth runs out of fossil fuels. Furthermore, the planet’s climate is being changed by humans burning fossil fuels for energy. It is, thus, a global ultimatum to devise new sustainable sources as well as means of producing energy, to get rid of the global warming leash that is currently tightening around humanity, as well as the energy crisis bottleneck that would eventually, and very soon, hinder the advancement of the human race.

1.1 Fuel Alternatives

Amongst the replacement fuels that have emerged recently is Hydrogen. Hydrogen is a light gas and is one of the most abundant elements in the planet.\(^8\) When ignited in the presence of an oxidant (Air, O\(_2\)...etc), one gram of it (gas or liquid) would easily result in a little less than triple the amount of energy when compared to one gram of crude oil or natural gas.\(^9\) In fact, when compared to any alternative fuel, Hydrogen has the highest mass energy density.\(^10\) Also, it is 8 times lighter than Methane, which can facilitate logistics to a great extent.\(^9\) Judging on an energy basis, Hydrogen is the best available fuel that can replace fossil fuels today, and still provide higher efficiencies. On another hand, the combustion products of Hydrogen are almost fully composed of pure H\(_2\)O. The Hydrogen market is thus a very promising one, especially when considering the other strategic uses of Hydrogen such as fuel cells and production of Ammonia gas. Today, there are many routes for the production of Hydrogen gas. Figure 1-1 shows a summary of these routes as well as percentages of the most important ones.
As shown in Figure 1-1, 96% of all Hydrogen production routes depend on fossil fuels; only about 3.9% of the current production of Hydrogen comes from the electrolysis of water, a surprising figure when put next to the 71% indicating the terrain of planet Earth that is covered with water. Indeed, water electrolysis is a facile route to obtain Hydrogen gas, in which electricity is used to split water molecules into \( \text{H}_2 \) and \( \text{O}_2 \) gases through a two-step redox reaction. However, as will be shown in Chapter two, splitting water molecules is an energy-consuming process. As shown in Figure 1-1, the electricity needed for such an operation comes from non-fossil fuel sources, namely: hydro, tidal, wind, solar, and nuclear energies.

Figure 1-1: The current routes for production of Hydrogen gas as well as their percentages.\(^8\)
1.2 Production of Solar Fuel

Looking onto the aforementioned renewable energy sources for the electricity needed in water electrolysis, and others, Figure 1-2 shows a comparison between the capacities of the different energy sources by the year 2050. Thus, a direct comparison of the full capacities of these particular sources used in water electrolysis is possible:\textsuperscript{11}

- Hydro-energy: a capacity of 1.5 TW/year given dams are built on all rivers on the planet.
- Wind energy: a practical capacity of 2 TW/year given all available class 3 land areas (producing about 300 W/m\textsuperscript{2} at 50 m) are utilized.
- Nuclear Energy: a capacity of 10 TW/year given a new reactor is constructed every other day for the next 50 years.\textsuperscript{12}
- Solar Energy: a capacity of at least 60 TW/year given only 10% conversion efficiency (current commercial efficiencies round to 17%).

![Image of energy comparison chart](image)

Figure 1-2: A capacity comparison between the different available energy sources by the year 2050. The figure also shows the global consumption in TW/year in 2009 and 2050.\textsuperscript{15}
It is thus apparent that solar energy emerges as the most promising renewable and clean route to produce Hydrogen gas through water electrolysis.

Indeed, approaching its estimated middle ages, the 1.4 million Km-wide nuclear furnace that is the Sun produces about 386 billion billion MW every second. About 176 billion MW of this energy reach the earth’s surface. In addition, solar energy is clean, free, and would remain at least as long as our species persist on earth. The use of Solar energy to produce Hydrogen gas emerges as a great opportunity to gain the best of both worlds: Production of the clean and energetic Hydrogen, as well as the possibility to store solar energy into a fully-transferrable gas that can power the darker, colder, or simply less advanced parts of the planet.

Solar water electrolysis can be performed through two routes, as shown in Figure 1-1: 1) Use of photovoltaics to produce electricity that is then connected to the grid and used in water electrolysis. 2) Direct Photolysis where photoactive electrodes are directly used in water electrolysis. The latter is comprised of a cheaper single system, while the former includes two systems connected together. Thus, for the purposes of achieving cheap, high-efficiency systems, this thesis will only focus on Photolysis (herein referred to as solar water splitting).

1.3 Towards Efficient Solar Water Splitting

In solar water splitting, a cell composed of an electrolyte, a photoanode and a photocathode (or only one of these with another metallic counter electrode) is used to transform solar energy into chemical bonds of Hydrogen (at photocathode) and Oxygen (photoanode), schematically shown in Figure 1-3. More details about the process are discussed in Chapter 2. In general, to demonstrate good stance for the
Hydrogen economy, the solar water splitting process must be competitively efficient. Issues of cost, stability, and overall performance must all be targeted when developing highly efficient systems.

Figure 1-3: The three possible setups for solar water splitting cells.\textsuperscript{16}

The use of solar energy to efficiently produce Hydrogen gas through water splitting has been a global aim since the oil crisis preceding the Ramadan war in 1973, where Japanese scientists developed the water splitting cell using a Titanium Dioxide (TiO\textsubscript{2}) photoanode and a Platinum counter electrode.\textsuperscript{17} Although the efficiency of their cell rounded to 0.1\%, their successful demonstration of the concepts of solar water splitting lead to a gold rush towards developing more and more efficient systems. The present endeavors in achieving high-efficiency systems focus on the development of materials that can absorb most of the spectrum of sunlight (fundamental property), can efficiently separate excited electrons from holes, is earth-abundant and stable in the changing environments of water electrolysis.\textsuperscript{18} To conclude, the burden of pushing humanity forward away from the energy bottleneck falls now on the shoulders of Materials scientists.
1.4 Zirconium Dioxide Semiconductors

In recent years, and since the Honda-Fujishima experiment, metal oxide nanotubes have been gaining attention due to their high stability, wide abundance, and intrinsic n-type semiconducting behavior i.e. electrons are abundant with no need for extra dopant materials such as in the case of Silicon (Si). For such reasons, the use of metal oxide semiconductors in water splitting has shown high competitiveness with the use of the more conventional n-type Si. Zirconium Dioxide (ZrO$_2$), in particular, has been shown to have the ability of overall water splitting, where it acts as both the photoanode and the photocathode with no need for an extra counter electrode, given its favorable band edge positions. Furthermore, it mainly comes from Zircon and badeleyite, making it more abundant than Copper in the Earth’s crust. ZrO$_2$ also shows high stability in a wide range of media, stepping out as one of the most promising metal oxide semiconductors for solar water splitting. It is, however, a wide bandgap semiconductor, which limits its absorption capabilities to the UV region of the solar spectrum, thus rendering its use in solar applications inefficient.

1.5 Scope of Thesis

The aims of this study is to modify the band gap of ZrO$_2$ facilitating visible light absorption, whilst producing a photoelectrode that is made of highly-ordered, vertically-oriented nanotube arrays. This way, the high stability, great catalytic activity, and earth-abundance of ZrO$_2$, combined with the modified band gap, would meet the strong charge carrier dynamics of the ordered nanotubular structures. As described in chapter 1, the thesis is planned to include two parts:
1. **ZrO$_2$ Nanotube Fabrication:** developing a protocol for the control of length, diameter, wall thickness, as well as cross section of ZrO$_2$ nanotubes (NTs) fabricated via cheap anodic oxidation.

2. **Fabrication of ZrO$_2$ NT/ZrN Composites:** depositing thin ZrN layers on top of the ZrO$_2$ NT arrays. Given the thickness of the coating layer is thin enough, the ZrN would be oxidized to produce ZrON species, which are known to have a theoretical band gap of 1.9-2.1 eV.$^{27}$ This wide-band gap/small band gap combination should promote good charge dynamics, where more carriers would be photogenerated in the small band gap material, and then injected into the CB of the wide band gap material, the large gap of which should provide barriers for recombination of charge carriers. This latter effect of the wide band gap ZrO$_2$, combined with the nanotubular structure, should provide excellent charge carrier dynamics that would serve well as a water splitting photocatalyst.

**Chapter 2** presents the background needed for the thesis by discussing the different concepts of solar water splitting such as solar radiation, semiconductor/electrolyte junctions, and cell analysis.

**Chapter 3** contains a synthesis of some of the available literature on ZrO$_2$ NT fabrication, and optical modification routes, shedding some light on the use of Atomic Layer Deposition (ALD) in electrode modification.

**Chapter 4** summarizes the experimental setups used for the fabrication of the NTs as well as the composite electrodes. The optical, spectroscopic, and photoelectrochemical analyses are also presented.

**Chapter 5** discusses the details of developing the ZrO$_2$ NTs fabrication protocols by presenting the results and conclusions of the studied variables. The energy
consideration for the fabrication process and optical analysis of the NTs are also presented.

**Chapter 6** presents the results and discussion for the optical, spectroscopic, and photoelectrochemical analyses of the synthesized ZrO$_2$/ZrN composite photoelectrodes.

**Chapter 7** concludes the thesis, and presents possible future work that should render this study vastly comprehensive.
References


5. Greenhouse Gas Inventory Data Explorer | US EPA. 


7. Carbon Dioxide Emissions from Fossil Fuels and Cement Reach Highest Point in Human History | World Resources Institute. 


11


Chapter 2

Background

2.1 Thermodynamics of Water Splitting

As mentioned in Chapter 1, water splitting is an energy-demanding process. The overall reaction of the decomposition of water goes as follows:

\[ H_2O(l) + \text{energy} \rightarrow \frac{1}{2}O_{2(g)} + H_2(g) \]  \[ 2.1 \]

The Gibb’s free energy for the overall water splitting redox reaction \((\Delta G^\circ_{H_2O})\) equals 237.14 kJ/mol for an open cell configuration at standard temperature and pressure. This number indicates the amount of energy needed to split one mole of water. Considering that one mole of matter contains Faraday’s number of Columbs \((F)\), and that two electrons are involved in the overall water splitting reaction, the electrochemical potential needed to drive the overall water decomposition reaction forward \((E_{\text{Cell}})\) is given by the following equation:

\[ E^\circ_{\text{Cell}} = \frac{\Delta G^\circ_{H_2O}}{2F} \]  \[ 2.2 \]

Plugging in the numbers, equation 2.2 yields about 1.23 V, which translates into 1.23 eV (about 1.97x10^{-19} in Joules) when considering the energy needed to drive one electron in the reaction. Analyzing these numbers and comparing to the amount of heat energy supplied to a semiconductor at room temperature (~300 K) of about 0.0816x10^{-19} J, it is clear that the energy supplied will not drive the reaction forward. Thus, an external energy source must be present to supply the required energy for water decomposition. In fact, due to many losses such as charge carrier recombination, electrolyte and contact resistances, as well as other sources of energy
dissipation, the external energy source would need to supply more than 1.23 eV (~2 eV).\textsuperscript{1,2} Considering solar energy, a photon with an energy of 2 eV lies within the visible range of the solar spectrum, which constitutes about 60% of sunlight.\textsuperscript{3} Indeed, the immense amount of energy that can be taken from the sun daily (see Chapter 1), results in an abundance of such energetic photons all around us.

2.2 Photoelectrochemical Cells

Industrial water splitting occurs using electrolyzers. Those are generally composed of two Platinum (Pt) electrodes, an electrolyte, and huge power supplies. In the case of solar water splitting, a Photoelectrochemical Cell (PEC) is used instead.\textsuperscript{1} For the purposes of this thesis, only PECs with photoactive anodes and metallic cathodes (Figure 1-3a) will be discussed. Figure 2-1 shows an energy diagram of such a PEC. A typical n-type semiconductor would have a Fermi level close to the Conduction Band Minimum (CBM), giving it a cathodic potential, due to the increase in the number of electrons in the CBM as compared to the number of holes in the Valence Band Maximum (VBM). For the electrolyte, the Fermi level lies within the redox potentials of the water splitting reaction.\textsuperscript{4} As will be discussed later, one of the requirements of a PEC is that the Fermi level of the semiconductor be more cathodic (more negative) than that of the electrolyte (Figure 2-1a). Thus, once the semiconductor is inserted into the electrolyte, electrons start to move from the CB of the semiconductor to the electrolyte having a more anodic (more positive) Fermi level. Because electrons in the CB of the semiconductor are finite, their transfer renders the CBM with a more anodic potential, causing what is known as band bending (Figure 2-1b).
Figure 2-1: Energy diagrams showing an n-type semiconductor/electrolyte junction on initial contact (a), and at equilibration (b). Panels (c,d) show the effect of illumination on a semiconductor having a $V_{FB}$ that is more anodic than the water reduction potential, thus requiring overpotential to drive the reaction forward. Panel (e) shows another case of illuminated semiconductor but having a $V_{FB}$ that is more cathodic than the water reduction potential.4
The semiconductor surface is thus depleted of electrons forming what is called the depletion region (or space charge region). This positively-charged region attracts negative ions in the electrolyte towards the semiconductor/electrolyte interface forming the Helmholtz layer. Because the space charge region is responsible for separating the excited electrons form the holes, its width \( W_{SC} \) is an important parameter in water splitting:

\[
W_{SC} = \sqrt{\frac{2eN_D\varepsilon_0}{\varepsilon\varepsilon_r}} \sqrt{(V_{applied} - V_{FB})}
\]  \[2.3\]

where \( e \) is the elementary charge; \( N_D \) is the charge carrier density; \( \varepsilon \) and \( \varepsilon_0 \) are the permittivities of the material and of free space, respectively; \( V_{applied} \) is the applied potential; and \( V_{FB} \) is the flat-band potential, which is the potential of the Fermi level when there is no band bending in the CBM. Given the fact that the space charge and Helmholtz layers both resemble capacitors, the semiconductor/electrolyte interface can be simulated as a grouping of circuit elements such as resistors and capacitors. From such models, the total impedance of the interface can be measured (using Electrochemical Impedance Spectroscopy); \( N_D \) and \( V_{FB} \) can then be calculated using the Mott-Schottky relation:

\[
\frac{1}{C_{SC}^2} = \left( \frac{2}{eN_D\varepsilon\varepsilon_r} \right) \left( V_{applied} - V_{FB} - \frac{kT}{e} \right)
\]  \[2.4\]

where \( C_{SC} \) is the space charge capacitance, \( k \) is Boltzmann’s constant, and \( T \) is the absolute temperature. Once the semiconductor is illuminated (Figure 2-1c), electrons get excited from the VB to the CB, thus increasing the negative charges in the CB, pushing it again to the cathodic direction and decreasing the band bending phenomenon. Saturating the CB with electrons will push it to its original ‘flat’ position i.e. the CBM will be said to have reached the flat-band potential \( (V_{FB}) \). This will cause electrons to start moving through the wire to the metallic cathode as long as
the anode is illuminated.

Metals have what is called work functions (metallic equivalent of Fermi levels). If the metal’s work function is low enough i.e. more cathodic than the water reduction potential (which is 0 V vs Normal Hydrogen Electrode), then the electrons will be able to transfer to the cathode/electrolyte interface, and drive the water reduction reaction evolving H₂ gas. Depending on the original position of the CBM of the semiconductor, the position of the metallic work function maybe still more anodic than the water reduction potential (Figure 2-1c), and thus an overpotential maybe required to drive the reaction forward. In this case (Figure 2-1d), an applied anodic bias (overpotential) will raise the Fermi level of the metallic cathode and allow continuous water splitting.⁴ In another case (Figure 2-1e), where the $V_{FB}$ of the semiconductor is initially more cathodic than the water reduction potential, then shining the semiconductor with enough light to completely flatten the CBM will be sufficient to raise the Fermi level of the cathode and allow for spontaneous water splitting without an external applied bias.⁴

Thus, a typical PEC would be comprised of a number of components and would undergo the following steps in order to split water using solar energy:⁵

- A semiconducting photoanode marks the only photoactive component; light energy absorbed by it causes the excitation of electrons from the VBM to the CBM leaving positive holes behind. Thus, electron-hole pairs are formed, i.e.

$$2hν \rightarrow 2e^- + 2h^+ \quad [2.5]$$

- The positive holes travel to the semiconductor/electrolyte to react with water causing its oxidation and producing O₂ gas, i.e.

$$H_2O_{(l)} + 2h^* \rightarrow \frac{1}{2}O_2(g) + 2H^+ \quad [2.6]$$

- The excited electrons travel through the wire to the metallic cathode, where they
diffuse to the cathode/electrolyte interface, reducing H⁺ atoms into H₂ gas, i.e.

\[ 2H_{(i)}^+ + 2e^- \rightarrow 2H_{2(g)} \]  

[2.7]

Looking onto these steps, the efficiency of a PEC depends on many factors, the most important of which are materials-based properties, such as the semiconductor band gap, the percentage of absorbed light, and the efficiency of charge carrier separation.⁶

### 2.3 Materials Selection Criteria

Turning to the materials used in PECs, there exist criteria for selecting n-type semiconductors for use as photoanodes in PECs:⁷

- **Semiconductor Band Gap**: The semiconductor must have a band gap that enables it to absorb most of the visible light spectrum that is the greatest portion of sunlight.³

- **Band Edge Positions**: The potentials of the semiconductor’s VBM and CBM must straddle the water redox potentials.

- **Semiconductor Stability**: The electrode must be stable in a wide range of electrolytes. Also the free enthalpies of oxidation and reduction must be appropriate with respect to the VBM and CBM of the semiconductor, respectively, to avoid photocorrosion.

- **Charge Carrier Dynamics**: The structure of the semiconducting electrode must allow for efficient charge carrier separation and reduced recombination.

#### 2.3.1 Semiconductor Band Gap:

A semiconductor’s band gap is the energy required to excite an electron form the VBM to the CBM. Because energy is quantized, 2 photons having half the energy
of the band gap will not excite an electron from the VBM; one photon having the energy of the band gap or higher will. The solar spectrum is comprised of 60% visible light, the wavelength of which stretches from about 400 nm to 700 nm. Wavelength of incident light ($\lambda$) is related to energy ($E$) through the following relation:

$$E = \frac{h\nu}{\lambda}$$

[2.8]

where $h$ is Planck’s constant and $\nu$ is the frequency of the incident light. Thus, most of the photons coming from the Sun would have energies within the visible range (1.7-3.1 eV). Thus, it is a requirement that the semiconductor has a band gap that is less than 3 eV so at least some of the abundant visible light photons would have enough energy to excite the electrons within the semiconductor.

### 2.3.2 Band Edge Positions

Figure 2-2 schematically presents the band edge positions of a number of semiconductors as compared to the water oxidation and reduction potentials versus the Normal Hydrogen Electrode (NHE). Given the band gap criterion, semiconductors such as Si, CdSe, MoS$_2$, WO$_3$, GaP and Fe$_2$O$_3$ have band gaps that are small enough to allow the absorption of most of the solar spectrum. However, there exists a second criterion for the semiconducting materials that makes the use of such materials inefficient. Namely, for the photo-generated holes to travel to the photoanode/electrolyte interface and take part in the water oxidation reaction, the VBM of the semiconductor must be more anodic than the water oxidation potential (1.23 V vs NHE); otherwise, holes would never travel to a more anodic potential to take part in the reaction (e.g. all materials in Figure 2-2 have this condition except CdSe, GaP, and Si). Another part of the band edge positions criterion was mentioned in section 2.2: the CBM must be more cathodic than the water reduction potential to
avoid the need to apply overpotential to drive the reaction forward (e.g. all materials surveyed in Figure 2-2 have this condition except MoS$_2$, WO$_3$, and Fe$_2$O$_3$). This leaves only materials that cover both conditions available for use in solar water splitting.

![Figure 2-2: Band edge positions for selected semiconductors vs NHE. The water redox potentials are also indicated.](image)

2.3.3 Semiconductor Stability

Re-examining Figure 2-2 at this step reveals that, because of its suitable band gap, only CdS may have the required properties to allow self-sustained water splitting. Unfortunately, besides the high toxicity of Cd, CdS is not stable in aqueous electrolytes. This demonstrates the third criterion for semiconductors that are suitable for efficient water splitting; stability. A semiconductor must demonstrate resistance to photocorrosion. Photocorrosion occurs when the photo-generated electron-hole pairs reduce or oxidize the semiconductor itself, respectively, instead of taking part in the water splitting reaction, rendering the material unstable in aqueous electrolytes.
The free enthalpies of oxidation \((E_{p,d})\) and reduction \((E_{n,d})\) of the semiconductor must fulfill the following criteria in order to inhibit photocorrosion:\(^{12}\)

- The water oxidation potential \([\text{O}_2/\text{H}_2\text{O}]\) must be more anodic than \(E_{p,d}\) of the material.
- The water reduction potential \([\text{H}^+/\text{H}_2]\) must be more cathodic than \(E_{n,d}\) of the material.

With the above criteria set, it is a challenging task to select single materials covering all conditions. Wide-band gap semiconductors are the most stable in aqueous electrolytes, and show band edge positions that are favorable for water splitting, whilst small-band gap semiconductors have stability problems (see Figure 2-2). Looking at durability of operation, the modification of wide-band gap semiconductors stands out as a great opportunity to reach high efficiencies in solar water splitting.

**2.3.4 Charge Carrier Dynamics**

Another important criterion for enhancing the efficiency of PECs is the dynamics of photogenerated charge carriers inside the semiconductor. Upon excitation, electrons have to travel a distance within the semiconductor before reaching the electrical contacts. During this journey, bulk defects such as vacancies, interstitials, and grain boundaries form defect energy states that can trap the electrons before reaching the metal contact.\(^{11}\) This decreases the photocurrent that can be extracted from the semiconductor. Another type of such trap states lie on the surface, where the unfulfilled bonds, or adsorbed electrolyte species act as electron sinks. All these types of defects can form electronic states that lie within the forbidden band
These states may also act as hole recombination sites preventing the photogenerated holes from reaching the electrolyte. Furthermore, too many surface states can cause Fermi level pinning, which prevents band bending from occurring, and thus increasing recombination due to the absence of the electric field separating electrons from holes. Perfecting the structure of the semiconductor should more or less decrease the defect density inside the bulk and on the surface of the material, which would in turn decrease the probability of occurrence of trap states. This is where the control of the fabrication process emerges as the most important factor controlling the density of trap states.

In order to quantify the effect of recombination to be able to diminish it, a Debye diffusion length ($\lambda_D$) is defined as the maximum distance across which charge carrier recombination can be avoided. With holes being much heavier than electrons, hole diffusion lengths are rate determining i.e.

$$\lambda_D = \left(\frac{kT\varepsilon\varepsilon_r}{N_D e^2}\right)^{\frac{1}{2}} \quad [2.9]$$

As shown in equation [2.9], the Debye length depends on the charge carrier concentration ($N_D$), and is thus material-dependent. In addition, given the fact that $N_D$ changes with changing structure (e.g. decreases with increasing surface states), $\lambda_D$ also depends on the structure of the semiconductor. With $N_D$ being in the range of $10^{17}-10^{19}$, the Debye length is usually in the range of ten nanometers or less. In principal, if the semiconductor is fabricated to a thickness within that diffusion length, hole recombination, and in turn, electron recombination, will be greatly diminished. Thus, the need for nanostructuring the semiconductor photoelectrodes is very important in order to achieve that aim. However, the thinner the semiconductor is, the less the percentage of incident light that it can absorb. This would decrease the
number of electrons that can be extracted from the electrode. As a possible solution to
the delimma of these two competing factors, vertically-oriented one-dimensional
nanostructures (nanotubes, nanowires, nanorods...etc) are fabricated.\textsuperscript{14} Figure 2-3
schematically shows the difference between planar and one-dimentional structures. In
planar structures, the photogenerated electron-hole pair move along the same axis
increasing the chances for recombination, while in 1-D structures, holes move
horizontally to the interface with the electrolyte, while electrons move vertically
towards the metallic contact at the bottom of the 1-D structure. In addition, as
mentioned above, making planar structures as thin as the hole diffusion length would
decrease light absorption. On the other hand, 1-D nanotubes, for example, with wall
thicknesses equal or less than the diffusion length may have lengths up to hundreds of
micrometers. Light falling on these nanotubes would remain trapped inside the tubes
reflecting between its inner walls until it gets entirely absorbed. Thus, light-trapping,
charge path decoupling, and the ability to make wall thicknesses as thin as the
diffusion length, or thinner, render 1-D nanotubes promising for enhanced charge
carrier dynamics.

Figure 2-3: Electron (solid circles) and hole (hollow circles) pathways after excitation
in planar (A) and 1-D (B) electrodes. $L_D$ is the hole diffusion length ($\sim \lambda_D$), and $\alpha$ is
the absorption coefficient of the material.\textsuperscript{14}
From the aforementioned, ZrO$_2$ nanotube arrays seem very promising if the band gap is modified. This is where the scope of the thesis fits within water splitting research.

2.4 Experimental Considerations

Inside the lab, water splitting is performed under very controlled conditions. Figure 2-4 shows a schematic diagram of a one-compartment design for a lab PEC cell. A cell with a Quartz window is used to build the PEC. A potentiostat is connected to the photoanode (the semiconductor), the cathode (a Pt foil/wire or another semiconductor), and a reference electrode. Through the potentiostat, various techniques can be used to determine the different indicators of water splitting performance in dark and illuminated conditions.

Figure 2-4: A schematic of a laboratory one-compartment PEC cell. WE, RE, and CE stand for the Working, Reference, and Counter Electrodes, respectively. A circulation system maybe used to refresh the electrolyte.\textsuperscript{15}
2.4.1 The Solar Spectrum

The total solar irradiance reaching the surface of the Earth is about 1366.1 W/m\(^2\). This power density depends on the concentrations of gases, particulates and aerosols in the atmosphere, which scatter or absorb parts of the spectrum.\(^6\) This makes sunlight quite variable according to the atmospheric conditions.\(^6\) One of the most important parameters, which is also the easiest to define, that affects the variability in the power density of sunlight is the amount of atmosphere through which light must travel to reach the surface of Earth.\(^15\) This variable is termed the Air Mass number (AM). This number can be calculated from the Zenith angle of the sun (at which the sun is directly above the examiner) as follows:

\[
AM \# = \frac{1}{\cos\theta_{\text{zenith}}} \tag{2.10}
\]

where \(\theta_{\text{zenith}}\) is the angle between the vector pointing towards the sun, and the vertical to the surface at the zenith of the sun. There exists three known standards for spectra that can be simulated in the lab, namely: AM0, AM1, and AM1.5.\(^15\) Figure 2-5 shows the spectral irradiance of the three air masses. AM0 indicates the spectrum of sunlight just above Earth’s atmosphere. AM1 indicates that at sea level. AM1.5 indicates the average annual irradiance in the United States (\(\theta_{\text{zenith}} = 48.1^\circ\)). The standard indicates the total intensity falling on a plate tilted at 37\(^\circ\) with the horizontal (which resembles the latitude of most states in the US).\(^15\) It is now accepted that the total irradiance of an AM1.5 spectrum is 1000 W/m\(^2\) (100 mW/cm\(^2\)). The term AM1.5 global sunlight (or AM1.5 G) is used to indicate the AM1.5 spectrum that takes into consideration both: direct light (90%), and scattered light (10%).\(^15\)
Inside the lab, a number of arc or filter lamps can be used to simulate the solar spectrum, most of which would have some discrepancies, thus an AM 1.5 filter is used. Figure 2-6 shows the spectral irradiance of a Xenon arc lamp (similar to the one used in this thesis) without a filter, as well as with a water filter to absorb infrared radiation, and that of AM1.5G sunlight.

Figure 2-5: The spectral irradiance of the three standardized AM numbers.

Figure 2-6: A comparison between the photon fluxes of Xenon arc lamps and AM1.5G sunlight. All measurements were normalized to 1000 W/m².
2.5 Atomic Layer Deposition

Atomic Layer Deposition (ALD) is a state-of-the-art technique designed for the controlled deposition of ultra thin (~0.5 Å) films, with good conformity and adhesion.\textsuperscript{16} It involves the controlled pulses of precursors into the atmosphere of the reaction chamber. Designed to have good chemisorption onto the used substrate, as well as vigorous reactivity towards each other, precursors react aggressively forming the required chemical species on the used substrate.\textsuperscript{17} An inert gas is pulsed into the reaction chamber between pulses to clear away any residues. This process continues until the required thickness is attained. Figure 2-7 shows an illustration of the ALD process. The key parameter is for the reaction to reach saturation in each step, ensuring constant thicknesses between subsequent cycles/steps. Ever since the late 1980’s, ALD has been extensively used in the Integrated Circuit (IC) industry.\textsuperscript{17} Recently it has found extensive use in the field of Dye-sensitised Solar Cells,\textsuperscript{18,20} as well as for the photodecomposition of water,\textsuperscript{16} to passivate surface states,\textsuperscript{21} enhance charge carrier separation,\textsuperscript{22} increase light trapping,\textsuperscript{23} and facilitate water oxidation kinetics.\textsuperscript{24} The aim of using ALD technology in this thesis is the deposition of very thin layers of ZrN onto ZrO\textsubscript{2} in order to modify the photocatalytic effect of ZrO\textsubscript{2} in solar water splitting.

Figure 2-7: Schematic explaining the steps involved in depositing one cycle of material in ALD.\textsuperscript{25}
References


Chapter 3

Literature Review

3.1 Fabrication of ZrO$_2$ NT Arrays

Being of catalytic importance, a substantial part of synthesis literature has been concerned with fabrication procedures of different nanostructures of ZrO$_2$ over recent years. ZrO$_2$ nanotubes (NTs), nanowires, nanobelts, nanorods, nanoflowers, nanobars, nanodiscs, and nanoparticles have been fabricated, in most cases via hydrothermal and sol gel techniques. Regarding NTs in particular, deposition techniques such as ALD were also used for their synthesis. Problems arising with all previous techniques, such as the need for templating, as well as the sometimes-costly precursors, drove research endeavors towards finding a more cost-effective, and more facile technique for ZrO$_2$ NT synthesis.

In this sense, anodic oxidation (anodization) emerges as one of the simplest techniques for the synthesis of nanotubular arrays of valve metals in general, and of ZrO$_2$ in particular. In brief, a foil of the base metal of the desired metal oxide NT arrays is inserted, as the anode, in an electrolytic cell with Pt as the cathode. The electrolyte contains an etchant that, upon the application of a potential difference between the electrodes, travels to the anode and, due to surface irregularities, starts etching a nanotubular structure. The presence of Oxygen ions in the electrolyte assists in the formation of metal oxide NTs. Many process variables affect the final structure of the NT arrays; the most important ones are applied potential, electrolyte composition, etchant concentration, and anodization duration. The effects of manipulating those particular process variables in anodization will be reviewed.
herein. Also, the mechanisms reported in the literature on the formation of the NT layer will also be reviewed.

3.1.1 Anodization Variables

Table 3-1 shows the summary of a few of the most prominent studies on the synthesis of ZrO$_2$ NT arrays via anodic oxidation. Anodization electrolytes are mainly composed of an etchant (chloride, sulphate, fluoride…etc) dissolved in an inorganic aqueous solution or an organic one. Many groups studied the effect of changing the solvent of the electrolyte. Tsuchiya et al.$^{14,15}$ studied the effect of adding an acid as the solvent. It was observed that with sulphuric acid as the solvent, the length of the NTs changed with time. Removing the acid from the aqueous etchant solution diminished this dependence. Furthermore, using different acids as solvents (i.e. changing electrolyte pH),$^{16}$ the authors found an inverse relationship between the pH and the etching rate.

Another study lead by the same group$^{17}$ revealed that local alterations in pH occurring at the advancing NT base can hinder ion diffusion inside the electrolyte leading to the formation of irregularly-shaped NTs. Decreased pH was also reported to cause a reduction in NT diameter.$^{13}$ In another study conducted by Zhao et al.,$^{18}$ organic solvents were used to determine their deviations from inorganic ones. NT arrays with much larger aspect ratios (~3000) were attained. The authors concluded that the enhanced etching rates in fluoride-containing organic electrolytes, as compared to their inorganic counterparts, were the driving force behind the high aspect ratios. Fitzner et al.$^{13}$ reported similar results, where much longer NTs were attained with organic electrolytes. However, studying the etching rates in both types of solvents, they reported a much lower etching rate in organic electrolytes (logarithmic vs linear relation); this effect was attributed to the increased viscosity of
the organic electrolyte. Figure 3-1 illustrates the results of their study showing the change of NT array thickness with time in both types of electrolytes. It is worth noting that, in the study conducted by Zhao et al., the applied potential was 50 V, and anodization was done for 24 hrs only. On the other hand, the study of Fitzner et al. was conducted with wide ranges of applied potentials and anodization durations.

Another effect of switching between organic and inorganic electrolytes is the crystallinity of the resulting NT arrays. Many reports in the literature support the crystallinity of ZrO$_2$ NTs as-anodized in inorganic electrolytes.\textsuperscript{14-17,19} There exists, however, some reports in the literature where such NTs are found to be amorphous as-anodized.\textsuperscript{20,21} In contrast, most reports in the literature support that NT arrays as-anodized in organic electrolytes are amorphous,\textsuperscript{22-24} again with some studies reporting crystallinity.\textsuperscript{25}

![Figure 3-1: The effect of switching between organic and inorganic electrolytes on the rate of etching NT arrays in Zr foils.\textsuperscript{13}](image-url)
Table 3-1: A summary of experimental conditions and results of some of the most important literature on the anodization of Zirconium.

<table>
<thead>
<tr>
<th>References</th>
<th>Voltage (V)</th>
<th>Time</th>
<th>Etchant Composition (^*)</th>
<th>Best Reported Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>20</td>
<td>5 hrs</td>
<td>0.5-5wt% HCl + 3.5wt% H(_2)O @GE/FA (1:1)</td>
<td>@2wt% HCl: L=33(\mu)m, D=250-300nm</td>
</tr>
<tr>
<td>27</td>
<td>50</td>
<td>-</td>
<td>1wt% NH(_4)F @GE/FA</td>
<td>-</td>
</tr>
<tr>
<td>24</td>
<td>50</td>
<td>3 hrs</td>
<td>1wt% NH(_4)F + 1wt% H(_2)O @GE/FA (1:1)</td>
<td>L=8(\mu)m, D=125nm, WT=30nm</td>
</tr>
<tr>
<td>18</td>
<td>50</td>
<td>24 hrs</td>
<td>1wt% NH(_4)F + 2wt% H(_2)O @GE/FA (1:1)</td>
<td>L=190(\mu)m, D=66nm, WT=32nm</td>
</tr>
<tr>
<td>22</td>
<td>50</td>
<td>24 hrs</td>
<td>1wt% NH(_4)F + 1wt% H(_2)O @GE/FA (1:1)</td>
<td>L=100(\mu)m, D=300-350nm</td>
</tr>
<tr>
<td>20</td>
<td>5, 10, 20</td>
<td>1 min-1 hr</td>
<td>0.5wt% HF</td>
<td>@20V-20min: L&lt;1(\mu)m, D=20nm, WT=5nm</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>1-10 min</td>
<td>0.5wt% HF</td>
<td>L&lt;1(\mu)m, D=20nm, WT=5nm</td>
</tr>
<tr>
<td>15</td>
<td>20</td>
<td>1-5 hrs</td>
<td>E1: 0.2wt% NaF @1M H(_2)SO(_4) E2: 0.2wt% NaF only</td>
<td>E1: L=10-40(\mu)m @1-5hrs, D=50nm E2: L=1(\mu)m @5hrs, D=70nm</td>
</tr>
<tr>
<td>17</td>
<td>20</td>
<td>1 hr</td>
<td>E1: 0.2wt% NaF @1M H(_2)SO(_4) E2: 0.4wt% NH(_4)F @1M (NH(_4))(_2)SO(_4)</td>
<td>L=15(\mu)m, D=50nm</td>
</tr>
<tr>
<td>16</td>
<td>20</td>
<td>1 hr</td>
<td>0.4wt% NH(_4)F @1M (NH(_4))(_2)SO(_4)</td>
<td>L=17(\mu)m, D=50nm</td>
</tr>
<tr>
<td>19</td>
<td>10, 20, 30, 50</td>
<td>3 hrs</td>
<td>0.5wt% NH(_4)F @1M (NH(_4))(_2)SO(_4) (pH-6)</td>
<td>@10V: L=12(\mu)m, D=40nm</td>
</tr>
<tr>
<td>28</td>
<td>15, 20, 25, 30</td>
<td>1, 2, 4, 8, 12, 24 hrs</td>
<td>0.35M NH(_4)F + 5vol% H(_2)O @GE</td>
<td>L=4-13(\mu)m, D=45-50nm</td>
</tr>
<tr>
<td>21</td>
<td>10, 15, 20, 25</td>
<td>Varying</td>
<td>0.75M NH(_4)F @1M (NH(_4))(_2)SO(_4)</td>
<td>L=4-13(\mu)m, D=20-70nm</td>
</tr>
<tr>
<td>29</td>
<td>20, 26, 32, 44, 50</td>
<td>2, 5, 10, 20 min</td>
<td>0.35M NH(_4)F + 5vol% H(_2)O @GE</td>
<td>L=1.79-3.80(\mu)m, D=35-80nm</td>
</tr>
<tr>
<td>23</td>
<td>15, 20, 25, 30</td>
<td>10, 20, 30, 40, 50, 60 min</td>
<td>5wt% NH(_4)F + 5vol% H(_2)O @GE</td>
<td>L=1-5(\mu)m, D=15-50nm</td>
</tr>
<tr>
<td>30</td>
<td>15, 20, 25, 30</td>
<td>10, 30, 40, 50, 60 min</td>
<td>0.35M NH(_4)F + 5vol% H(_2)O + 0.05M (NH(_4))(_2)HPO(_4) @GE</td>
<td>L=2-12(\mu)m, D=35-75nm</td>
</tr>
<tr>
<td>31</td>
<td>80</td>
<td>1, 5, 10, 20, 30 min</td>
<td>0.1, 0.5, 0.7, 1.1mol/L NH(_4)F + 5vol% H(_2)O @GE</td>
<td>L=4-10(\mu)m, D=90-130nm</td>
</tr>
<tr>
<td>12</td>
<td>20, 50</td>
<td>1 hr</td>
<td>0.01-5wt% NH(_4)F @1M NaSO(_4) (pH-3)</td>
<td>L=6(\mu)m, D=40-50nm, WT&lt;10nm</td>
</tr>
<tr>
<td>25</td>
<td>10, 30, 40</td>
<td>1 hr</td>
<td>0.07wt% NH(_4)F @GE</td>
<td>L=1-2(\mu)m, D=30nm, WT=10nm</td>
</tr>
<tr>
<td>32</td>
<td>40</td>
<td>Varying</td>
<td>0.35M NH(_4)F + 0, 1, 5vol% H(_2)O @GE</td>
<td>L=690-710nm, D=22-40nm, WT=35-38nm</td>
</tr>
<tr>
<td>33</td>
<td>5, 7, 10, 15, 20, 25</td>
<td>-</td>
<td>0.15M NH(_4)F @1M (NH(_4))(_2)SO(_4)</td>
<td>D=10-50nm</td>
</tr>
<tr>
<td>34</td>
<td>20</td>
<td>3 hrs</td>
<td>1wt% NH(_4)F + 3wt% H(_2)O @GE/FA (1:1)</td>
<td>L=30.93(\mu)m, D=60nm</td>
</tr>
<tr>
<td>35</td>
<td>20, 50, 60</td>
<td>1, 3, 18, 24 hrs</td>
<td>E1: 1wt% NH(_4)F + 3wt% H(_2)O @GE/FA (1:1) E2: 1wt% NH(_4)F + 1wt% H(_2)O @GE/FA (1:1)</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60</td>
<td>30 min-24 hrs</td>
<td>0.1 M HF + 0-50vol% GE @0.5 M Na(_2)SO(_4) (pH=2.5)</td>
<td>L=2-44(\mu)m, D=15-55nm, WT=16nm</td>
</tr>
<tr>
<td>36</td>
<td>20</td>
<td>30 s-2 hrs</td>
<td>0.15M NH(_4)F @1M (NH(_4))(_2)SO(_4)</td>
<td>-</td>
</tr>
</tbody>
</table>

*GE = Glycerol, FA = Formamide
Since the etchant is part of the anodizing electrolyte, its study is also of importance towards understanding how process parameters affect the final NT structure. In this sense, Guo et al.\textsuperscript{26} used HCl as the etchant instead of the more orthodox fluoride etchant. An optimum concentration of 2wt% HCl produced NTs with straight walls (Figure 3-2a). Note that the NTs had large diameters (250-300 nm) for samples anodized for only 5 hours as compared to those samples anodized in fluoride-based electrolytes. Lee and Smyrl\textsuperscript{20} directed their studies towards one of the most popular etchants in the anodization of Ti foils: HF. Although the resulting NTs had a very small average wall thickness (~5 nm), which is good for solar water splitting (see Chapter 2), the NTs were wavy and irregular (Figure 3-2b), which would increase the surface defect states. In the studies mentioned above by Tischiya \textit{et al.},\textsuperscript{16,17} NaF and NH\textsubscript{4}F were used as etchants in the anodization of Zr foils. It was reported that NH\textsubscript{4}F results in much more regular and straight NTs (Figure 3-2 panels c and d), when compared to NaF, H\textsubscript{2}SO\textsubscript{4}, and HF. The authors attributed this to the buffering effect of NH\textsubscript{4}F, which diminishes the effects of the local pH alterations mentioned above. This, in turn, would produce straighter NTs.

Figure 3-2: ZrO\textsubscript{2} NTs synthesized in electrolytes with etchant being (a) HCl,\textsuperscript{26} (b) HF,\textsuperscript{20} (c) NaF,\textsuperscript{16} and (d) NH\textsubscript{4}F.\textsuperscript{17}
Many reports then followed on the use of NH$_4$F as the etchant.\textsuperscript{30,32,37} Ying \textit{et al.}\textsuperscript{31} changed the concentration of NH$_4$F and studied the resulting structures. They observed a primary increase in the diameters and lengths of the NTs up until 0.7 mol/L in concentration, where a decrease was observed in the length of the NTs, mainly attributed to the increase in oxide dissolution rate (etching of the NTs themselves). Also, above this concentration, NTs failed to form. This latter observation was connected with a disrupted equilibrium between the etching rate and the rate of electrochemical oxidation. It is also worth mentioning that Ying \textit{et al.} reported on the increase in crystallinity of the as-anodized samples with increasing NH$_4$F concentrations. Similar results were reported by Ismail \textit{et al.},\textsuperscript{12} where crystallinity increased with fluoride concentrations. However, in this latter study, length only decreased with increasing concentrations of NH$_4$F.

Another important part of the electrolyte is the water content. This importance emerges from the fact that, during anodization, water is the main source of oxygen ions in the NTs.\textsuperscript{38} Most significantly, Muratore \textit{et al.}\textsuperscript{32} studied the effects of changing water content on the resulting NT structure. A decreasing wall thickness, and an increasing NT diameter were observed with increasing the water concentrations in the anodization electrolyte. The authors also observed an enhancement in the tubular structure with increasing water contents. In addition, observing a fluoride-rich bottom (barrier) layer, the thickness of this layer appeared to decrease with increasing water content,\textsuperscript{39} which should lead to longer NTs.\textsuperscript{12}

One of the most important variables controlling the structure of the final NT arrays in anodization is the applied potential.\textsuperscript{33} Many groups reported on the effect of applied potential on the structures and shapes of ZrO$_2$ NT arrays. Zhao \textit{et al.}\textsuperscript{19} studied the effect of increasing the applied potential on the quality of the final oxide array,
when anodizing Zr foils in inorganic, poorly acidic electrolytes with a fluoride etchant. NT arrays were attained at 10, 20 and 30 V, whilst no apparent nanotubular structure formed under 50 V. Looking onto the mechanism of formation where the fluoride ions are responsible for etching the oxide layer, and the hydroxide ions in the electrolyte are responsible for keeping the structure of the NTs intact and crack-free, the authors concluded that increasing the applied voltage would accelerate both ions in the electrolyte towards the advancing NT bases, as well as push the dissolution and oxidation reactions forward. However, with fluoride ions being much faster than hydroxide ions, they become replenished much faster at the NT base and are always in abundance, whilst the slower hydroxide ions get exhausted at the NT bases faster than they can be replenished. Thus, the insufficient presence of oxidizing ions, and the abundance of the etching ions would induce cracking in the oxide layer, decreasing regularity of the tubular structure, and destroying the arrays if the potential was too high. Zhao et al. also reported that this localized decrease in hydroxide ion concentration, and the high potential-induced localized increase in temperature at the NT bases promote the growth of the monoclinic phase. Thus, NTs become crystalline as-anodized in the case of increasing potentials in inorganic aqueous electrolytes. A similar result was reported by Ismail et al.25

Wang et al. also studied the effects of increasing the applied voltage on the length and diameter of the resulting ZrO₂ NTs. Their studies showed that, for anodization periods less than 1 hr, there seemed to be a linear relation between voltage and the lengths and diameters of the resulting NTs.23,29 On the other hand, with anodization durations exceeding 1 hr, that relation deviates from linearity.28 In another study, Ismail et al.12 reported on obtaining the same NT length when Zr foils were anodized in aqueous acidic electrolytes at 20 and 50 V. The authors explained
this observation by the penetration of the accelerated F ions through the NT bases, thus disrupting NT growth, and resulting in the thickening of the oxide layer beneath the NTs instead of the NT array increasing in thickness. This phenomenon of increasing bottom-layer thickness at high voltages was also reported by Muratore and coworkers.\textsuperscript{38} Ismail et al.\textsuperscript{12} also reported that the polarization of the Zr-O bonds in the NTs at high voltages may lead to the destruction of the nanotubular layer. In addition, when working with organic electrolytes,\textsuperscript{25} the authors observed a decrease in NT array thickness with increasing applied potentials, which contradicts the results of Wang et al.\textsuperscript{23} The reported thickening of the bottom-layer maybe the reason behind their observations. However, in agreement with Wang’s observations, the authors observed an increase in diameter with applied voltage. This increase was attributed to the vigorous lateral etching of the fluoride ions at high voltages. In this sense, and in contrast with the relation between NT length and applied voltage, there seems to be no contradictions in the literature on the fact that NT diameter increases with voltage,\textsuperscript{31,37} however, whether the relation between diameter and voltage is linear or otherwise is still an issue of debate.

Another important variable affecting the final structure of the NTs is the anodization duration. Studies in the literature report that the length of ZrO\textsubscript{2} NTs increases with anodization time,\textsuperscript{13,15,20,23,29,30} which may be directly related to the observation that the fluoride barrier layer thickness decreases with increasing anodization durations.\textsuperscript{13,35,36,38} In addition, numerous studies conducting Zr foil anodization in organic electrolytes for less than 1 hr report on a linear dependence;\textsuperscript{23,29,30} on the other hand, some studies using organic electrolytes at longer anodization durations report on a non-linear dependence.\textsuperscript{13,28} Switching to inorganic electrolytes is known to produce opposite results, such that a linear relationship between anodization
time and NT length\textsuperscript{13,15,36} is attained at durations longer than roughly 30 minutes, while for shorter anodization durations, the relationship deviates from linearity.\textsuperscript{36} Zhang \textit{et al.}\textsuperscript{36} presented a relationship between NT array thickness ($T$) and time ($t$):

$$T = At^{0.25} \quad [4.1]$$

such that $A$ is a constant that depended on the rate of etching.\textsuperscript{36} In this sense, although Lee and Smyrl reported a linear relationship at short anodization durations (1-10 min),\textsuperscript{10} the trendline used showed a clear deviation from experimental results, one that can be decreased if a polynomial trendline was used instead. Note that studies showed that 30 microns was the maximum attainable length in inorganic electrolytes.\textsuperscript{13} It is also worth noting that Tischiya \textit{et al.}\textsuperscript{15} had reported an independence of NT length on anodization duration in aqueous NaF electrolytes (without the addition of any other chemicals).

Regarding NT diameters, most studies report on their independence on anodization durations in all electrolytes, and for all anodization durations.\textsuperscript{13,23,28-30,36} However, Ying \textit{et al.}\textsuperscript{31} did report a direct dependence for periods less than 30 minutes. Zhang \textit{et al.}\textsuperscript{36} also reported the increase in NT diameter with anodization durations at the very first minutes of the process. After that, NT diameters remained constant.

\textit{3.1.2 Anodization Mechanism}

With the presence of discrepancies within the literature on the effects of process parameters as shown in the previous section, the true mechanism behind the formation of ZrO\textsubscript{2} NT arrays is not very well understood by researchers in the field until now. However, the basic steps for the formation of the arrays gain acceptance in most studies conducted in the literature. For the purposes of this thesis, the discussion will only outline the mechanism of formation of ZrO\textsubscript{2} NT arrays in fluoride-based
electrolytes. Basically, the following key steps are known to occur during anodization of Zr foils:

1) **Metal Oxidation:** Once the foil is inserted into the electrolyte, a large anodization current is observed, which accounts for the motion of all negative ions in the electrolyte (O\(^2^-\), OH\(^-\) and F\(^-\)). This leads to the oxidation of the surface. As the oxide layer becomes thicker within the Zr foil, the electric field across that layer decreases, thus causing a reduction in the anodization current,\(^{18}\) i.e.

\[
Zr + 4OH^- \rightarrow Zr(OH)\_4 \quad [3.2]
\]

\[
Zr(OH)\_4 \rightarrow H\_2O \rightarrow ZrO\_2 \quad [3.3]
\]

2) **Barrier Layer Formation:** many reports in the literature discuss the formation of an oxide barrier layer,\(^{11}\) which is natural given the fast oxidation kinetics of valve metals. However, there are studies in the literature reporting on the observation of a fluoride-rich, oxygen-deficient bottom layer of the nanotubes.\(^{35,36,39}\) These observations advocate for the formation of a ZrF\(_4\) barrier layer below the oxide barrier layer, which is attributed to the F\(^-\) ions being faster than O\(^2^-\).

3) **Pore Nucleation:** Field-assisted dissolution of the oxide layer, which results from the potential-induced weakening of the Zr-O bonds,\(^{25}\) promotes the formation of pits on the surface of the oxide layer, i.e.

\[
ZrO\_2 + 2H^+ \rightarrow ZrO^{2+} + H\_2O \quad [3.4]
\]

Also, acceleration of F ions towards the oxide layer initiates chemical dissolution of the layer, increasing the pits and cracks on the surface.\(^{19,25}\) The electric field across those pits and cracks increases. This incites more and
more of the etchant ions to particularly attack those areas in the oxide layer, i.e.

\[ ZrO_2 + 6F^- + 4H^+ \rightarrow [ZrF_6]^{2+} + 2H_2O \]  \[3.5\]

4) **Oxide Layer Thickening**: the increased electric field across the nucleated pores pushes O\(^2^-\) and OH\(^-\) ions towards the bases of the pores, where they penetrate the layer and move towards the metal/oxide interface, oxidizing more metal and thickening the oxide layer.\(^{15}\)

5) **Sustained NT Growth**: with field-assisted and chemical dissolutions of the oxide layer competing with the further oxidation of the metallic foil and the advancing oxide layer front into the metal, an equilibrium is attained, and the nanotubular structure grows steadily with time.\(^{35}\)

6) **Process Termination**: some groups report on the termination of NT growth when the rate of oxide dissolution at the pore tops is equal to the rate of oxide dissolution at the NT bases.\(^{25}\) Others discuss the increased penetration of F\(^-\) ions at the NT bases, which thickens the fluoride-rich barrier layer,\(^{12}\) and thus decreases the electric field across it, which in turn would greatly decrease the rate of oxide dissolution at the NT bases and terminate the growth process.

### 3.2 Zirconium Oxynitrides for Photocatalysis

Being a wide band gap semiconductor, ZrO\(_2\) lacks appeal towards visible-light photocatalysis studies, and its use in water splitting research is thus scarce.\(^{40,41}\) Furthermore, a small number of studies focus on the modification of ZrO\(_2\) electrodes for various applications,\(^{42-44}\) with most of the fuel production literature focusing on thermochemical water splitting (not solar-based).\(^{45-47}\) In addition, its use in composite electrodes is usually intended for its thermal and passivation properties.\(^{48,49}\) On the
other hand, Zirconium oxynitrides have been used in photocatalysis more often throughout the literature. In this section, the properties of Zirconium oxynitrides, relative to other metal oxynitrides, as well as their use in photocatalysis will be reviewed.

Transition metal oxynitrides have been widely studied recently due to their enhanced optical properties, as compared to their wide-band gap oxide counterparts. Such an enhancement is believed to originate from the raising of the VBM of the metal oxide as a result of the incorporation of N 2p orbitals over the O 2p VBM of the oxide. Different synthesis routes are used to obtain such Oxygen-Nitrogen mixed phases. The most direct of which is the deposition of metal nitride in the presence of water vapor or Oxygen. Other synthesis routes include the gas-nitridation of metal oxides using Ammonia or Nitrogen gases, as well as hydrothermal techniques. Indeed, Titanium, Tantalum, Tungsten, Niobium, and Zirconium oxynitrides were used for the photocatalytic decomposition of water. Although all of the mentioned oxynitrides exhibited visible-light absorption, major problems still face the oxynitrides field, namely: stability, and low photoconversion efficiencies. The latter problem originates from the large number of defect states that comes about during the synthesis of metal oxynitrides, or the required bias potential due to unfavorable band edge positions. The former problem originates from the chemical instability of many oxynitride phases, as well as the photo-oxidation of oxynitrides during the water splitting reactions.

For Zirconium Oxynitrides (herein dubbed as ZrON), numerous studies focused on the synthesis of different oxynitride phases by controlling the Oxygen:Nitrogen ratios inside the material. Bazhanov et al. studied the different structures of ZrON using Density Functional Theory (DFT). According to their study,
ZrON created through deposition or nitridation of ZrO₂ are mixtures of ZrO₂ and Zr₃N₄ not ZrN. Such ZrON phases have the cubic or hexagonal crystal systems,⁶³ and are created by the replacement of Oxygen ions in the lattice with Nitrogen ions according to the following:

$$3O_2 + 2N \rightarrow 2N_2 + O_2 + 3O$$ \hspace{1cm} \text{[3.6]}

In another study, Mohamed et al.⁶⁴ studied oxynitride films deposited by pulsed reactive DC sputtering. It was observed that, upon increasing the Nitrogen gas partial pressure, the resulting phase changed from monoclinic oxide to orthorhombic oxynitride, then to amorphous oxynitride, and finally to the cubic nitride phase. Also, a decrease in the band gap and change in color of the resulting phases was observed.⁶⁴ Tomsah⁶⁵ also studied the effect of changing the reactive gas flow during pulsed DC magnetron sputtering on the optical properties of ZrON. Again, a decrease in the band gap was observed upon the incorporation of a little amount of Nitrogen into the oxide lattice. Following a more classical approach, Lerch⁵⁵ studied the nitridation process of ZrO₂ under high temperature (1900°C). He found that the reaction could only proceed in the presence of an Oxygen getter as follows:

$$\text{ZrO}_2 + \frac{2x}{3}N_2 \rightarrow \text{ZrO}_{2-2x}N_{4x/3} + xO_2$$

Regarding the application of ZrON in photocatalysis, it is indeed a fact that, from all the metal oxynitrides mentioned above, ZrON is one of the least studied for solar water splitting. With some studies being on ZrON as catalysts for the decomposition of Ammonia, or for the Oxygen Reduction Reaction (ORR) in fuel cells, only one study in the field of solar water splitting appears in a number of reviews on oxynitrides.⁵⁰,⁶⁶ Conducted by Mishima et al., this study⁶¹ pioneered the
work on ZrON electrodes for water splitting. First, a theoretical background was presented on the VBM and CBM nature of ZrON as compared to their oxide counterparts. It was observed that the VBM of the oxide phase in raised upon the addition of Nitrogen atoms in the lattice due to the introduction of the N 2p orbitals on top of the O 2p orbitals, which constituted the VBM in the oxide phase. In addition, the position of the CBM changed slightly upon the addition of Nitrogen. This was attributed to the different crystal structures of both materials. After that, NH₃ nitridation of ZrO₂ powder was taken out. UV-Vis spectra showed an enhancement in the absorption with the absorption edge pushed to 500nm. Furthermore, the Oxygen evolution in AgNO₃ aqueous solution was tested under illumination. Using only 0.05g of catalyst, an evolution rate of 2.3 μmol/hr was attained. Evolution persisted until 500nm as shown in Figure 3-3. This evolution rate was attributed to high mobility of photogenerated holes in the VB, which occurred as result of the N 2p orbitals being very close to the O 2p orbitals such that the latter are considered as part of the VBM, and not shallow defect states that act as recombination centers.

![Figure 3-3: The rates of Hydrogen and Oxygen gas evolution over Pt-ZrON and ZrON catalysts, respectively, versus the wavelength of the incident light. Absorbance is also presented.](image)

43
References


38. Muratore, F.; Baron-Wiecheć, A.; Gholinia, A.; Hashimoto, T.; Skeldon, P.; Thompson, G. Comparison of nanotube formation on zirconium in


Chapter 4
Materials & Experimental Procedures*

4.1 Photoanode Fabrication

4.1.1 Synthesis of ZrO₂ NT Arrays

Pure zirconium foils (Alfa Aesar, 99.8% purity) were ultrasonically cleaned in acetone/ethanol and distilled water, respectively. Anodization, shown schematically in Figure 4-1, was done in a two-electrode cell with the zirconium foil as the working electrode and Platinum foil as the counter electrode, in glycerol-based electrolytes containing variable amounts of formamide, H₂O, and NH₄F. The anodized area was fixed at 10x10 mm. The distance between the electrodes was fixed at 20 mm, and experiments were taken out at room temperature. Anodization current was tracked on 5 min intervals. Anodization was performed using an Agilent E3612A DC power supply. As-anodized specimens were annealed in a LINDBURG Programmable Furnace model N41/M 29667 at 500°C for 4 hrs, as well as in a Thermo-scientific LINDBURG/BLUE M TF55030C tube furnace at 400 and 350°C for 4hrs, with up/down rates of 1°C/min.

Figure 4-1: A schematic showing the anodization setup and the method of formation of NT arrays.

* Parts of this chapter were published in the following paper: Amer, A. W.; Mohamed, S. M.; Hafez, A. M.; AlQaradawi, S. Y.; Aljaber, A. S.; Allam, N. K. Self-assembled zirconia nanotube arrays: fabrication mechanism, energy consideration and optical activity. RSC Adv. 2014, 4, 36336-36343.
4.1.2 Fabrication of ZrN/ZrO$_2$ Composite Photoelectrodes

ZrO$_2$ NT arrays as-annealed in 350°C were used for the subsequent deposition of the ZrN ALD layers. ALD of ZrN films with different numbers of cycles (1-600) was implemented in a Cambridge Fiji F202 Plasma ALD System. The precursor used for Zirconium was Tetrakis(dimethylamido)zirconium, while pulses of Ammonia gas were used for \textit{in-situ} nitridation. All depositions were taken out at 200°C in vacuum at a rate of about 0.5 Å/cycle.

4.2 Morphological, Crystalline Structure, and Chemical States Analysis

The morphology of the as-anodized samples was studied using a LEO Supra 55 Field Emission Scanning Electron Microscope (FESEM). The crystalline structure of as-anodized and annealed samples was studied using a PANalytical X'Pert PRO XRD diffractometer. The chemical states of samples with different cycles were determined using a Thermo-scientific K-Alpha X-ray Photoelectron Spectrometer (XPS) having an Aluminium anode. At least 3 analysis positions were surveyed for each sample with a sampling area of 400 μm$^2$.

4.3 Optical and Photoelectrochemical Characterization

The optical properties of the as-anodized/annealed foils were measured using a designed (homemade) setup that was installed into a Newport QE-PV-SI QE/IPCE instrument. Finite Difference Time Domain simulations were implemented on a computer-written code. The source used was a Gaussian pulse source having a central frequency of 1498.96229 THz, and a pulse width of 2997.92 THz. For detection, two observation planes were positioned at the top and the bottom of the nanotubes to
measure the transmittance and the absorbance, respectively. A lorentzian model was used for simulating the permittivity–frequency plot, along with minor curve-fitting in order to match the simulation model with the experimental results done on ZrO$_2$ nanotubes.

For all composite samples, UV and visible optical properties were investigated using Deuterium and Tungsten lamps in a Shimadzu UV-3101PC UV-Vis-NIR Spectrophotometer. $J$-$V$ and OCP-$t$ data were recorded using a CHI Model 700D Series Electrochemical Workstation. 1 Sun illumination was provided by a Xenon lamp using an AM 1.5G filter. For $J$-$V$ plots, the voltage was ramped at a rate of 10 mV/s from -1 to 1 V vs Ag/AgCl and reported as is. Electrochemical Impedance Spectra (EIS) were measured at different applied potentials versus a Standard Calomel Electrode (SCE) using a BioLogic SP-200 Potentiostat. Z-fit was used to fit the spectra to equivalent circuits. Mott Schottky plots were modified and presented versus the Normal Hydrogen Electrode.
Chapter 5
Fabrication of ZrO$_2$ Nanotube Arrays*

As discussed in chapter 3, although the synthesis of ZrO$_2$ NTs via anodic oxidation is a widely-used technique, the mechanism by which these NTs form is poorly understood. Also, studying the effect of one process parameter is strictly dependent on the experimental conditions as shown in chapter 4, and there is a lack of comprehensive studies connecting all the conditions together. Furthermore, there are numerous discrepancies in the literature pertaining to the effects of particular anodization parameters as outlined above. Thus, there remains the task of taking out combinatorial studies of process parameters to strictly analyze the effects of each one independently, and come out with a full story in terms of what really happens during the anodization of Zr foils. This is the aim of part one of this thesis. Another aim for such a comprehensive study is to design a synthesis protocol for ZrO$_2$ NTs, which should facilitate the industrialization of such a fabrication route. For the purposes of this thesis, the application on which this comprehensive synthesis study was focused was photocatalysis.

Given the primary aim of this thesis behind synthesizing ZrO$_2$ NTs is their use in solar water splitting, a number of NT specifications were set as targets before engaging in this study:

- High-aspect ratio NTs were needed to ensure efficient light trapping and large active surface area.

* Parts of this chapter were published in the following paper: Amer, A. W.; Mohamed, S. M.; Hafez, A. M.; AlQaradawi, S. Y.; Aljaber, A. S.; Allam, N. K. Self-assembled zirconia nanotube arrays: fabrication mechanism, energy consideration and optical activity. RSC Adv. 2014, 4, 36336-36343.
- Minimal defects in the structure were a must, such that only vertically-oriented, regularly-shaped NTs were considered as positive results for this
- As mentioned in Chapter 2, keeping the wall thickness of the NTs below the diffusion length of the minority carriers should increase the probability of them reaching the electrolyte and being involved in the water splitting reaction. Thus, an important target for this study was the attainment of NT wall thicknesses as small as possible. Screening of the results would be done according to this criterion.

According to the targets set in this thesis, and synthesizing the results of previous research on obtaining high-aspect ratio, regularly-shaped ZrO₂ NTs, organics were chosen as the solvents of the electrolytes in this study. Also, NH₄F was used as the etchant throughout the study for its buffering effect leading to well-structured NT arrays.¹ The effects of mixing different organic solvents were studied. In addition, different fluoride/oxide content combinations in the electrolytes were prepared. Anodization potential and duration were also studied. Then, according to the results obtained about the role of all these variables in the attainment of ZrO₂ NTs, the Point Defect Model was used for the first time in literature to explain the mechanism by which every process parameter affects the final tube shape and size.

### 5.1 Effect of Solvent Composition

As outlined in the preceding chapter, organic electrolytes composed of different mixtures of Glycerol (GE) and Formamide (FA) were used to study the effect of solvent composition on the competing processes of chemical etching and oxidation. Zr foils were anodized in glycerol-based electrolytes containing different FA contents, while keeping the NH₄F and H₂O concentrations at 1wt% and 4wt%,
respectively. Figure 5-1 shows the ZrO$_2$ nanotube arrays obtained in electrolytes containing FA up to 40%. Note the changing morphology of the nanotubes from hexagonal in pure glycerol electrolyte (Figure 5-1a), to circular nanotubes as FA content was increased to 10% and 20% (Figure 5-1 panels b and c), and back again to hexagonal shape at 30% (Figure 6-1d). Notably, pure GE electrolytes resulted in NTs that were neither uniform, nor were they vertically-oriented, with cracks between islands of NTs appearing in the FESEM micrograph (Figure 5-1a). With 10 and 30% FA in the electrolytes, NTs were uniform but not regularly-shaped (highly-ordered with uniform structures). Note that the debris covering the top of the nanotubes grown in electrolytes with 10 and 30% FA probably consisted of detached nanotubes that may have fallen off the substrate during post-anodization ultrasonic cleaning. Increasing the amount of FA to 40%, a 2μm-thick layer of debris covered the NT arrays (Figure 5-1e), which was probably due to corrosion of the top ends of the nanotubes as a result of the high F$^-$ ion mobility. Further evidence proving the latter came at 50% FA, where the very fast reaction kinetics cut the Zr foil into two pieces at the electrolyte/air interface within the first 30 minutes of the process. In contrast, the NTs grown in electrolytes containing 20% FA and 80% GE were highly-ordered, vertically-oriented, uniform NT arrays. Thus this particular solvent composition was used throughout the rest of the studies in this thesis.

Figure 5-1f shows the variations of the lengths, diameters, and wall thicknesses of the nanotube arrays fabricated in electrolytes containing different FA contents. Zr foils anodized in pure GE electrolytes resulted in the shortest NTs, which can be directly related to the high viscosity of pure GE, which impedes ion movement. Increasing the FA content in the electrolyte to 10% caused a 40-50% increase in length. Raising the amount of FA added to 20% and 30% resulted in NTs
more than double and quadruple the length at 10%, respectively. This sharp increase was followed by a plateau until 40% FA.

Figure 5-1: FESEM images of as-grown ZrO\(_2\) nanotube arrays via anodic oxidation for 3hrs @50V in glycerol electrolytes containing 4wt% H\(_2\)O and 1wt%NH\(_4\)F, along with (a) 0% FA, (b) 10% FA, (c) 20% FA, (d) 30% FA, and (e) 40% FA. Panel (f) shows the variation of the ZrO\(_2\) NT dimensions with FA content.

Nanotube diameter, on the other hand, showed a much earlier plateau (near 10%), such that adding FA to the GE electrolytes resulted in NTs with more than double the diameter. However, changing FA content had little effects on NT diameter. Examining the NT wall thickness, although the average wall thicknesses seemed to increase with increasing FA content in the electrolytes, all changes observed were
within the distribution of the measured results, which leads to the conclusion of minor change in NT wall thickness with FA content, generally towards thicker walls. Table 5-1 presents the average values of NT lengths, diameters, and wall thicknesses obtained from FESEM image analysis software.

Table 5-1: ZrO$_2$ NT lengths, diameters, and wall thicknesses with varying FA contents in electrolytes.

<table>
<thead>
<tr>
<th>Percent FA</th>
<th>Tube Diameter (nm)</th>
<th>Wall Thickness (nm)</th>
<th>Tube Length (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>30</td>
<td>5</td>
<td>6.4</td>
</tr>
<tr>
<td>10%</td>
<td>74</td>
<td>7.8</td>
<td>10</td>
</tr>
<tr>
<td>20%</td>
<td>82</td>
<td>11.5</td>
<td>24.8</td>
</tr>
<tr>
<td>30%</td>
<td>80</td>
<td>14</td>
<td>48</td>
</tr>
<tr>
<td>40%</td>
<td>-</td>
<td>-</td>
<td>48</td>
</tr>
</tbody>
</table>

### 5.2 Effect of Etchant and Water Contents

In order to study the effect of different combinations of F$^-$ and O$^{2-}$ ion contents, Zr foils were anodized in glycerol-based electrolytes containing 20% FA and different F$^-$ contents (0.5, 1, and 2 wt%), as well as different water contents (2, 3, and 4 wt%). Figure 5-2 shows the FESEM images of the as-grown NT arrays under the various F$^-$ and O$^{2-}$ ion contents. Generally, except for ZrO$_2$ NTs grown in electrolytes with 1wt% NH$_4$F and 2wt% water, 2wt% NH$_4$F and 2wt% water, and 1wt% NH$_4$F and 4wt% water, all combinations resulted in mixed hexagonal-circular NT arrays. The latter combination resulted in circular NTs as shown in Figure 5-2c, while the former two combinations resulted in NTs with hexagonal cross sections (Figure 5-2 panels d and f). Only those three combinations showed long-range order throughout the substrates. It is important to note the presence of amorphous debris exclusively on the arrays anodized in all electrolytes containing 0.5wt% NH$_4$F (Figure 5-2 panels a, b and c).
Figure 5-2: FESEM images of as-grown ZrO$_2$ nanotube arrays via anodic oxidation for 3hrs @50V in glycerol electrolytes containing 20% FA, along with (a) 0.5wt% NH$_4$F and 2wt% H$_2$O, (b) 0.5wt% NH$_4$F and 3wt% H$_2$O, (c) 0.5wt% NH$_4$F and 4wt% H$_2$O, (d) 1wt% NH$_4$F and 2wt% H$_2$O, (e) 1wt% NH$_4$F and 3wt% H$_2$O, (f) 2wt% NH$_4$F and 2wt% H$_2$O, (g) 2wt% NH$_4$F and 3wt% H$_2$O, and (h) 2wt% NH$_4$F and 4wt% H$_2$O.
Table 5-2 presents the variation in the average NT lengths and wall thicknesses with changing fluoride and water concentrations in the electrolytes. As shown, increasing fluoride content in the electrolytes leads to a decrease in the average NT length, as well as a decrease in the wall thicknesses. On the other hand, with more water added to the electrolyte, NT length and wall thickness increased. Thus, although the longest NTs were attained with the lowest NH₄F and highest H₂O contents, which is beneficial for light trapping as aforementioned, those NTs had the thickest walls, which is not favorable for charge dynamics. Figure 5-3 shows the change in diameter with changing fluoride and water contents. In contrast with NT lengths and wall thicknesses, NT diameters increased with increasing both species in the electrolyte.

Table 5-2: Average ZrO₂ NT (length-wall thickness) with varying NH₄F and H₂O weight contents in the anodization electrolytes.

<table>
<thead>
<tr>
<th></th>
<th>0.5wt% NH₄F</th>
<th>1wt% NH₄F</th>
<th>2 wt% NH₄F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Length (μm)</td>
<td>Diameter (nm)</td>
<td>Length (μm)</td>
</tr>
<tr>
<td>2wt% H₂O</td>
<td>20.4</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>3wt% H₂O</td>
<td>30</td>
<td>12</td>
<td>23</td>
</tr>
<tr>
<td>4wt% H₂O</td>
<td>35</td>
<td>14</td>
<td>24.8</td>
</tr>
</tbody>
</table>

Figure 5-3: The variation in average NT diameter with changing NH₄F and H₂O contents in the anodization bath.
5.3 Effect of Anodization Duration

Anodization time was also varied for samples anodized in glycerol-based electrolytes containing 20% FA, with constant 4wt% H₂O and 1wt% NH₄F contents. Figure 5-4 panels a-f show FESEM images of the fabricated NTs after 1, 2, 4, 5, 6, and 16 hrs of anodization. Note that circular NTs were obtained for all anodization durations. Note also the presence of detached NT/debris on the surfaces of the foils anodized for 2 hours (Figure 5-4b). NT growth rates shifted from 16 μm/h for anodization time of 1 hr to 8.5 μm/h for anodization time of 2hrs. This dramatic shift in the growth rate can be related to NT detachment during the anodization process, where new NT arrays replace the detached ones, resulting in shorter NTs than expected. The NT growth rate of 8.3μm/h remained almost constant for the remaining anodization times (up to 16 h). Figure 5-4g shows the effect of increasing anodization time on the dimensions of the resulted ZrO₂ nanotubes. The effect of anodization time on NT length is fairly linear, which was expected at the relatively slow etching rate in the 20% FA electrolyte. In addition, increasing anodization time had an effect on NT diameter similar to that of increasing FA content in the electrolyte, such that more ions would reach the anode at the longer time span (or at higher FA contents in the electrolyte). A plateau was reached near 4 hrs, which can be related to an equilibrium attained between chemical etching and anodic oxidation at the top of the array. In contrast to increasing FA content, however, the average wall thickness decreased as anodization time increased, indicating a lower oxide layer growth rate as compared to the rate of chemical etching. This can be explained in terms of the naturally-added O²⁻ ions as FA content increased in the electrolyte.² This increase may be the reason behind the slowly increasing wall thickness (i.e. the increasing oxide layer on the walls) as the FA content increased. The absence of excess O²⁻ at 20% FA content
would favor the rate of chemical etching as anodization period increases, especially with the decrease in O\(^2-\) ions as anodization proceeds. Thus, wall thickness would be expected to decrease.

Figure 5-4: FESEM images of as-grown ZrO\(_2\) nanotube arrays via anodic oxidation @50V in glycerol electrolytes containing 20% FA, 4wt% H\(_2\)O and 1wt%NH\(_4\)F, for a duration of (a) 1, (b) 2, (c) 4, (d) 5, (e) 6, and (f) 16 hrs. Panel (g) illustrates the change in NT length, diameter and wall thickness with increasing anodization duration.
5.4 Effect of Anodization Potential

ZrO₂ NT arrays were also synthesized using different applied anodization voltages (10, 30, and 50 V) while keeping all other anodization parameters intact. Figure 5-5 shows the structures grown at 10 and 30 V. While no NT structures were observed at 10V, increasing the voltage resulted in the formation of NT arrays with larger tube diameters of 25 and 82 ± 1 nm for 30 and 50 V, respectively. The nanotubes synthesized at 30 and 50V had a nearly-identical wall thickness of 10.5 ± 1 nm, confirming the independence of NT wall thickness on applied potential. The tube length, however, showed an increase until an applied potential of 30V reaching a length of 40 ± 0.2 μm, in agreement with Wang and Luo. This increase in length was followed by a shallow decrease to 24 ± 0.2 μm as the applied voltage increased to 50V, in agreement with Ismail et al. It should be noted that the most ordered NTs were attained at 50 V in GE-based electrolytes (Figure 5-1c).

Figure 5-5: FESEM images of ZrO₂ NTs anodized for 3 hrs in GE-based electrolytes containing 20% FA, 1wt% NH₄F and 4wt%H₂O at (a) 10, and (b) 30 V.
5.5 Point Defect Model on Anodization of Zr Metal

Based upon the attained results, the Point Defect Model with its three different versions was used, for the first time, to unravel the effects of changing process parameters in the anodization of Zr metal to produce ZrO$_2$ NT arrays. In addition, results from the previous sections, as well as results from other studies (see Chapter 3) were used to develop the anodization model. According to the second and third generations of the Point Defect Model (PDM II-III), high oxidation state metals, such as Zr, form a bi-layer passive film, composed of a barrier layer, as well as an outer layer where film/electrolyte interactions occur. The growth of both layers depends on the constant generation and annihilation of cation interstitials and anion vacancies. Macdonald et al. studied the impedance characteristics of Zr metal immersed in aqueous de-aerated solutions, and concluded the formation of an oxide outer layer, on top of a defective oxide barrier layer. In a later study, Macdonald and Engelhardt studied the bi-layer passive film forming on Zr in hydride-rich solutions, and concluded the formation of a hydride instead of an oxide barrier layer, owing to the faster diffusion kinetics of hydrogen as compared to oxygen. With the same argument, Wang et al., using fluoride solutions, predicted the formation of a barrier layer composed of ZrF$_4$ given the fast kinetics of Fluorine ions in the solution as compared to Oxygen ions. Also, Muratore et al. observed the formation of a fluoride-rich, oxygen-deficient barrier layer at the back layer of the NTs. Their group also observed the decrease in the thickness of that barrier layer with increasing anodization durations, as well as water contents. On the other hand, increasing anodization potential seemed to decrease the thickness of the fluoride barrier layer, in close agreement with the model proposed by Ismail et al. Given all these observations in the literature, as well as the fact that F$^-$ ions are almost twice as fast as
O\(^{2-}\) ions,\(^{12}\) it is reasonable to advocate for the formation of a fluoride barrier layer when Zr metal is immersed in fluoride-rich electrolytes. Based on this hypothesis and PDM, the following model was developed.

Upon immersion of the Zr foil into the electrolyte, a defective fluoride layer starts to build up into the metal surface as a result of the constant generation of fluoride vacancies at the foil/electrolyte interface, i.e.,

\[
Zr \rightarrow ZrF_2 + 2V_F^\ast + 2e^- \quad [5.1]
\]

\[
V_F^\ast + NH_4F \rightarrow F_2 + NH_4^+(aq) \quad [5.2]
\]

On the other hand, field-assisted dissolution of the barrier layer occurs causing the decrease in the barrier layer thickness (i.e. de-passivation),\(^2,5\) i.e.,

\[
ZrF_2 + 4F^- + 2H^+ \rightarrow H_2ZrF_6 \quad [5.3]
\]

such that the formation of fluorozirconic acid (H\(_2\)ZrF\(_6\)) is the most probable route for Zr metal in fluoride-containing aqueous solutions.\(^{13,14}\) The net thickness of the steady state fluoride barrier layer depends on the fluoride concentration, voltage, pH, and the standard rate constants of the passivation/de-passivation reactions.\(^6\) Furthermore, as anodization time proceeds, the concentration of free fluoride ions in the electrolyte decreases, thus steady state is disturbed, which may lead to a decrease in the barrier layer thickness as observed in the literature.\(^{11}\) Meanwhile, cation interstitials, ejected from the foil’s surface, diffuse through the barrier layer towards the barrier layer/electrolyte interface. They then get hydrated/oxidized via the anions in the electrolyte, forming oxides (outer layer),\(^5\) i.e.,

\[
Zr \rightarrow Zr^{IV} + 2e^- \quad [5.4]
\]

\[
Zr^{IV} + H_2O \rightarrow 2H^+ + ZrO^{2+} \quad [5.5]
\]

\[
ZrO^{2+} + H_2O \rightarrow 2H^+ + ZrO_2 \quad [5.6]
\]
In addition, field-assisted dissolution (reaction 5.7) and chemical etching (reaction 5.8) create pits on top of the metastable outer layer, i.e.,

\[
\text{ZrO}_2 + 2H^+ \rightarrow \text{ZrO}^{2+} + H_2O \quad [5.7]
\]

\[
\text{ZrO}_2 + 6F^+ + 4H^+ \rightarrow [\text{ZrF}_6]^{2+} + 2H_2O \quad [5.8]
\]

Figure 5-6a schematically depicts our proposed model. The thickness of the outer layer can surpass that of the barrier layer by 4 orders of magnitude, which is typical for anodization of valve metals.\(^5\) Field-assisted dissolution of the outer layer results in surface irregularities, where fluoride ions then locally decrease the thickness of the layer through pitting action on the rough surface\(^1\) causing an increase in the electric current across it. This triggers more oxide precipitation at the areas where outer layer thickness is.\(^3\) The latter also occurs on the inner walls of the pores,\(^1\) resulting in the formation of well-defined nanotube structures.

Figure 5-6: (a) Schematic illustrating the anodization of Zr foils in fluoride-rich electrolytes. (b) EDX spectra of the bottoms of detached nano-tubes showing a F– ion at% almost double that of Zr.

Thus, the abundance of F– and O\(^2\) ions is crucial for the formation of ZrO\(_2\) nanotubes with high structural integrity. When 0.5wt% NH\(_4\)F was used in the anodization electrolyte, F– ion content was too low to form well-defined nanotubes,
especially at low water contents, and a poorly-structured layer of amorphous debris covered the nanotube arrays (Figure 5-2 panels a, b, and c). On the other hand, when the F ion content was too high, increased F ion diffusion towards the metal/barrier layer interface lead to the detachment of the outer nanotubular layer, as previously observed with Tantalum,\textsuperscript{12,17} leading to a decreased NT length. Indeed, EDX analysis of the bottoms of the detached nanotube arrays (Figure 5-6b) showed a non-stoichiometric layer of ZrF\textsubscript{2}. Increasing FA content caused the acceleration of both F\textsuperscript{−} and O\textsuperscript{2−} ions, thus shifting the reactions equilibria forward, and increasing the rate of NT formation.

With respect to increasing the voltage, PDM-II\textsuperscript{6} predicted the dependence of the steady state barrier layer thickness ($L_{SS}$) on the applied voltage, i.e.,

\[
L_{SS} \propto \frac{1}{\varepsilon} \left[1 - \alpha - \frac{\alpha_{d}}{\alpha_{p}}\right] V
\]

such that $\varepsilon$ is the electric field strength, $\alpha$ is the polarizability of the barrier layer/outer layer interface, $\alpha_{p}$ and $\alpha_{d}$ are the transfer coefficients of the passivation and de-passivation reactions. Equation 5.9 entails the increase in the fluoride barrier layer thickness as the applied voltage increases. As a result, increasing the applied potential would render the impedance of the barrier layer no longer negligible with respect to that of the outer layer. This may hinder the diffusion of cation interstitials throughout the barrier layer, thus decreasing the kinetics of nanotube formation into the outer layer, and resulting in little-to-no changes in NT lengths for higher applied potentials, as observed by Ismail et al.\textsuperscript{3} Furthermore, at high-enough anodization potentials (50 V in this study), the fluoride defective barrier layer thickness would substantially increase and cause an effect similar to increased F\textsuperscript{−} ion concentration in the
electrolyte, where the NTs would become detached, and new NT would form. Thus, the resulting length would be shorter than expected.

5.6 Thermodynamic Analysis of Anodization of Zr Foils

In order to formulate a market-reliable synthesis protocol for ZrO$_2$ nanotubes, the total energy used for their synthesis should be calculated. Thus, the energy required for the individual processes occurring inside the electrolyte during the synthesis process was calculated. The anodization process can be divided into two major processes: (1) the chemical synthesis and dissolution of the oxide layer, and (2) the physical diffusion of ions near the electrolyte/anode interface. The chemical process represented by the formation of the bi-layer passive film at the anode, as well as the evolution of H$_2$ at the cathode can be combined in an overall reaction as follows:

$$2Zr_{(s)} + 2H_2O_{(l)} + 2NH_4^+_{(aq)} \rightarrow ZrO_{2(s)} + ZrF_2_{(s)} + 1NH_4^+_{(aq)} + 2H_2(g) \quad [5.10]$$

Following Li’s model,$^{18}$ the minimum work ($W$) associated with chemical synthesis can be described as:

$$W = (H_R - TS_R) - (H_P - TS_P) \quad [5.11]$$

This gives roughly 498.533 kJ/mol$^{19}$ for anodization of Zr foils. This represents the amount of energy needed for the overall reaction to occur when reversible reactions are ignored. On the other hand, the dissolution of the barrier and outer layers is described by reactions 3 and 8, respectively. Considering the two reactions as different routes for the formation of the $[ZrF_6]^{2-}$ complex, the total energy of formation for both reactions is 395.616 kJ/mol.$^{19,20}$
The electrical energy required for the physical diffusion of ions near the electrolyte/anode interface under applied potential $V$ for time $t$ can be given by:\textsuperscript{18}

$$E = V \times A \times I \times t$$ \hspace{1cm} [5.12]

$$I = \frac{nPFDC_0}{L + Px_0}$$ \hspace{1cm} [5.13]

where $A$ is the electrode surface area, $P$ is the porosity of the nanotube array, $F$ is Faraday’s constant, $D$ is the diffusion coefficient of ions inside the electrolyte, and $C_0$ is the concentration of $F^-$ ions inside the bulk electrolyte away from the diffusion layer. $L$ and $x_0$ are the array thickness and diffusion layer thickness, respectively. Finally, $n$ is the number of exchanged electrons in the overall process. The porosity of the nanotube samples was calculated for nanotubes with circular cross section to be 44.9%. Following Li’s approach,\textsuperscript{18} the diffusion coefficient for $F^-$ ions inside the electrolyte was taken to be $10^{-5}$ cm$^2$/sec, and $x_0$ was set to be 10.5 μm. With the nanotube length of 24 μm, and $C_0$ of $3.4 \times 10^4$ mol/cm$^3$, the energy required for the physical diffusion of $F^-$ ions near the anode surface is about 110,799.436 kJ/mol.

Thus, the total energy required for the synthesis of ZrO$_2$ nanotubes via anodization of Zr foils is estimated as 111,693.6 kJ/mol, with the physical diffusion of ions inside the electrolyte being the most energy-consuming step in the anodization process.

### 5.7 Annealing of ZrO$_2$ NT Arrays

Because amorphous NT arrays have lots of defect states (especially at their surface), annealing was an important step towards being able to use the NT arrays as photoelectrodes for water splitting. Thus, ZrO$_2$ NTs anodized at 50 V for 3 hrs in GE electrolytes having 20% FA, 1wt% NH$_4$F, and 4wt% H$_2$O were annealed at 500°C in
air. Most of the NT arrays shattered during/after annealing. However, FESEM imaging of the resulting layers were still possible. Figure 5-7a shows one FESEM image of the annealed sample. As shown, the long-range order of the NT arrays was completely disturbed, leaving the NTs bent and destroyed. Figure 5-7b shows the XRD spectra of as-anodized and as-annealed NT arrays. The as-anodized nanotubes were amorphous, with some peaks appearing at 35°, 37°, 48°, and 64° characteristic of the (002), (101), (102), and (003) facets of hexagonal Zr metal. These peaks possibly originated from the substrate. In addition, a trace broad peak lies in the region between 28° and 32°. After annealing at 500°C, this broad peak was de-convoluted showing three distinct peaks at 28°, 30°, and 31°, which correspond to the (111) facet in the monoclinic oxide phase (28° and 31°) and the (111) facet in the tetragonal oxide phase (30°) (27,28). Smaller peaks appeared near 50°, which correspond to the (220) and (022) facets in the monoclinic oxide phase, as well as the (112) facet in the tetragonal oxide phase. Thus, XRD patterns confirm the formation of ZrO2 nanotubes with mixed tetragonal and monoclinic phases. Generally, it is well known that bulk ZrO2 crystals exhibit a monoclinic structure at room temperature, and don’t exhibit the tetragonal structure before 1200°C. However, a so-called size effect occurs when decreasing the size of ZrO2 crystals, where the tetragonal or even the high-temperature cubic phases arise at room temperature. Thus, the appearance of a tetragonal phase in the synthesized NT arrays is plausible. In addition, this tetragonal phase is known to disappear as the annealing temperature increases, and given the different volumes, during the tetragonal-monoclinic transformation, a 4% expansion in the unit cell occurs. This might be the reason behind the damaged NTs as shown in Figure 5-7a.
To solve the problem of NT arrays being damaged during annealing, the temperature was decreased to 450 and 400°C. Both annealing temperatures still damaged the samples, where the NT arrays detached from the Zr substrate, then shattered before they can be recovered from the furnaces. Thus, the temperature was further decreased to 350°C. Doing so, about 7 out of every 10 samples came out intact. Figure 5-8a shows FESEM images of samples as-annealed at 350°C for 4 hours. The long-range order and the thin NT walls were recovered after annealing.

Note that the sample in the image was anodized in electrolytes containing 2wt% NH₄F and 2wt% H₂O, thus the hexagonal cross section. Figure 5-8b shows the XRD spectra of that sample. As shown, a similar mixed structure was attained at these annealing conditions, but with decreased crystallinity (lower CPS for each peak). This maybe the reason why NT arrays survived this annealing temperature more, where the higher temperatures further catalyzed the tetragonal-monoclinic transformation, resulting in an increased grain expansion, and thus the destruction of the NT arrays. Given the intact arrays, as well as the preserved nanotubular structure and order, the temperature of 350°C was used for annealing throughout the thesis.
5.8 Optical Analysis of ZrO₂ NT Arrays

As discussed in chapter 3, the use of Zirconia in solar water splitting is mainly limited by its wide band gap. The ZrO₂ NTs synthesized in this work, however, were expected to have a band gap that was different from the well-known 5.0 eV for Zirconia due to their high purity, as well as their nano dimensions. Realizing the band gap of the pristine NTs as an important step to validate the upcoming modification step, rigorous optical analysis was taken out on the ZrO₂ NTs before setting forth towards modification with ZrN. To investigate the optical characteristics of as-annealed ZrO₂ NTs, Finite Difference Time Domain (FDTD) calculations were performed, along with experimental characterization for transmittance and absorption of the nanotubes. FDTD is a well-known computational technique that allows the investigation of the optical properties of the nanotubes through observing the propagation of electromagnetic waves throughout the lattice. Along the simulation process, the values for the fields throughout each computational grid are updated, rendering FDTD a very useful tool for the optimization of material optical properties.
Figure 5-9 panels a and b illustrate the model used in the FDTD analysis. Following the work of Ong et al.,\textsuperscript{24} normal incidence of the electromagnetic waves in the negative Z direction was assumed. The model was built for highly-oriented ZrO\textsubscript{2} NTs having circular cross-section with an average length of 18 mm, an outer diameter of 64 nm, and a wall thickness of 12 nm. The cell used was surrounded by a matching layer to absorb any reflected electromagnetic waves outside the NTs at all frequencies and angles of incidence.

ZrO\textsubscript{2}, being a dispersive material, necessitates the accurate calculation of the material's permittivity in order to be able to investigate the optical properties of the NTs. For this purpose, density functional theory (DFT) calculations were first performed, using the exchange–correlation functional of Perdew–Burke–Ernzerhof (PBE), to obtain the dielectric function for pure zirconia. Figure 5-9c shows the real (\(\varepsilon'\)) and imaginary (\(\varepsilon''\)) parts of the dielectric function together with the operating frequency i.e.,

\[
\varepsilon' = n^2 - k^2 \quad \text{[5.14]}
\]
\[
\varepsilon'' = 2nk \quad \text{[5.15]}
\]

Figure 5-9 panels d and e show the strong agreement of the measured transmittance and absorbance with the simulated results. Note that the absorbance (A) was measured according to the following relation:

\[
A = \left| \log \left( \frac{p_t}{p_i} \right) \right| \quad \text{[5.16]}
\]

such that \(p_t\) and \(p_i\) are the transmitted and incident fields, respectively. Due to the small reflection from the nanotube tops in comparison with the transmitted field, this reflection can be neglected.\textsuperscript{24}
Figure 5-9: (a) Schematic showing the model built for the FDTD calculations, (b) a plot showing the incident, reflected, and transmitted electromagnetic fields in the time domain. (c) Dependence of the relative permittivity of ZrO$_2$ on the frequency of the incident field. (d and e) A comparison between the measured and simulated transmittance and absorbance, respectively, for NTs having a length of 18 mm, a diameter of 64 nm, and a wall thickness of 12 nm. (f and g) Simulated data for transmittance and absorbance of nanotubes having different lengths. (h) Simulated data for transmittance of nanotubes having different wall thicknesses.
Figure 5-9f shows a decrease in the transmittance of the incident field for longer NTs, in agreement with other reports in the literature.\textsuperscript{25,26} This is attributed to the increase of the absorption on the incident field with increasing NT length, as shown in Figure 5-9g. Also shown is the fact that incident fields with energy larger than 3.5 eV are totally absorbed by the NTs. Such an observation can be used to get a rough estimate of the ZrO\textsubscript{2} NTs’ band gap.

Because the wall thickness of the nanotubes is very crucial when designing photoactive systems, the effect of increasing wall thickness on the optical properties of the NTs was studied using the proposed FDTD model. Figure 5-9h shows the change in transmittance of the nanotubes as the wall thickness of the nanotubes get thicker, while keeping the outer diameter and the tube length fixed. As shown, the transmittance decreases with increasing the wall thickness of the nanotubes, due to the decrease in the volume of the air column inside the nanotubes, thus increasing the effective index of refraction.\textsuperscript{24} Also, there seems to be a shift in the transmittance edge with increasing wall thickness towards higher energies. This may indicate a decrease in the band gap with decreasing NT wall thickness, which is beneficial to the study at hand. In the following chapter, Tauc analysis is used to experimentally measure the band gap of the NTs with the smallest wall thickness.

5.9 Conclusions

In this part of the thesis, the conditions of synthesizing ZrO\textsubscript{2} NT arrays \textit{via} anodic oxidation were studied. As a summary, increasing formamide and water contents in the electrolyte, as well as anodization time and voltage till 30 V, resulted in an increase in the NT lengths and diameters, which was attributed to the increased reaction kinetics. Although increasing F ion concentration led to increased NT
diameters, it resulted in a decrease in the length. Similar results were obtained with increasing the anodization potential above 30 V. NTs synthesized in O$_2$-rich electrolytes exhibited thicker tube walls as compared to those synthesized in electrolytes with lower formamide concentrations. The optimum process conditions were determined as follows: for highly-ordered ZrO$_2$ NTs with circular morphology, Zr foils were anodized for 3 h at 50 V in a glycerol-based electrolyte containing 20% FA, 1 wt% NH$_4$F, and 4 wt% H$_2$O. To obtain NTs with hexagonal morphology, etchant and water contents were 2 wt%. A model for the anodization of Zr foils was proposed based on the Point Defect Model such that a fluoride barrier layer grows into the metal, on top of which an oxide outer layer precipitates. The effect of nanotube dimensions on their optical properties was studied using FDTD. A good agreement between theoretical and the experimental results allowed for the accurate prediction of the optical properties. Unlike absorption, transmittance of the nanotubes was shown to decrease with nanotube length and wall thickness.

Given the results mentioned above, as well as the target mentioned at the beginning of this chapter, a certain set of anodization conditions were picked to develop the ZrO$_2$/ZrN composite electrodes for solar water splitting. These anodization conditions were chosen on the basis of obtaining the most highly-ordered ZrO$_2$ NTs having the smallest wall thickness possible, as well as reasonable lengths (too long NTs would increase impedance of electronic motion thus decreasing the current; too short NTs would decrease light trapping). Also, optical analysis was conducted to prove that the pristine NTs had no visible-light activity, thus rendering the upcoming modification step dire. That being said, the following GE-based electrolyte bath was chosen to proceed with the modification step of this study: 20% FA, 2wt% NH$_4$F, and 2wt% H$_2$O; the anodization potential was kept at 50 V to obtain
highly-ordered NT arrays, and the anodization duration was kept at 3 hrs to get a wall thickness that was thin enough, without achieving very long NTs.
References


Chapter 6

ZrN/ZrO₂ Composite Photoanodes*

From the brief review presented in Chapter 3, it is clear that the use of ZrON in water splitting is very promising. Also, studies on the nature of the catalysis effects of ZrON in water splitting are very lacking. In addition, the use of ZrON in nanotubular form is indeed absent in the literature although this would further enhance their abilities as water splitting catalysts. In this sense, equipped with optimized, highly-ordered ZrO₂ NT arrays having small wall thicknesses, the ground was set for delving into the second part of this thesis: the development of ZrO₂/ZrN composite photoelectrodes for solar water splitting. Again, with focus directed towards the application intended of such photoelectrodes, the targets of this part of the thesis were set as follows:

- Achieving visible-light absorption with the composite photoelectrodes was set as the first key performance indicator. The portion of the visible light spectrum being absorbed was not the main criterion; pushing the absorption edge of the ZrO₂ NTs into the visible spectrum was the main aim.
- Upon reaching the first target, the second target was the enhancement of photoelectrochemical characteristics, which was measured by comparing photocurrents, as well as charge carrier dynamics.

ZrO₂ NT arrays anodized in GE electrolytes containing 20 vol% FA, 2 wt% NH₄F, and 2 wt% H₂O, then annealed at 350°C for 4 hours were used as the base substrates to deposit different thicknesses of ZrN via Atomic Layer Deposition

* Parts of this chapter were submitted as a paper.
(ALD). As aforementioned, the composite electrodes were designed so that the ZrN would oxidize on top of the ZrO$_2$ NTs leading to the development of a ZrON layer at the surface of the NTs. As the deposited layer gets thicker, spontaneous oxidation would become harder, and an extra Oxygen annealing step would be needed to develop the required structures. This, combined with the fact that the thicker the deposition was, the more the defect states would be, dictated that ALD be used, instead of regular deposition techniques, to develop very thin ZrN layers on top of the NT arrays.

6.1 Morphological and Structural Analysis

As mentioned in Chapter 5, the instrument used for ALD had a deposition rate of about 0.5 Å/cycle. Thus, for a small number of ALD cycles (<40), it would have been difficult to detect an increase in thickness using FESEM. To accommodate this situation, the characterization plan depended mainly on XPS spectra to detect the presence of a nitride phase, as well as FESEM imaging to detect agglomerations on the surface as primary proof of the presence of a layer covering the NTs, or any detectable change in wall thickness. Generally, as mentioned in Chapter 2, ALD is used for the deposition of homogeneous and conformal coatings.\textsuperscript{1-3} However, it is also well-known that disturbances (e.g. agglomerations) during the deposition of the first few cycles may affect further cycles.\textsuperscript{4,5} To examine the nature of the ZrN coating atop the ZrO$_2$ NTs for homogeneity of deposition, FESEM was used (Figure 6-1). Firstly, no change in wall thickness could be detected within the distribution of data in all samples. Also, when deposition cycles were increased till 10 (Figure 6-1b), relatively large (500 nm) particles were detected on the surface, with most of the ZrO$_2$ bare but for a very thin translucent layer covering some NTs as shown in the inset of Figure 6-
1b. Upon the deposition of 20 cycles (Figure 6-1c), the surface became covered with more particles, which were approximately double in size. Samples having 48 cycles (Figure 6-1d) of ZrN also showed agglomerations all over the surface. This inhomogeneity in deposition persisted up to 200 ALD cycles, where a porous fiberous layer covered the tops of the NTs, still exposing some of the NTs surfaces as shown in Figure 6-1e. Thus, from the results of FESEM imaging, it was predicted that the top surface layer would have mixed phases of oxide and oxynitride, and that both phases would have a role in the photocatalytic properties of the composite electrodes.

![Figure 6-1: FESEM images of ZrO$_2$ samples having (a) 5, (b) 10, (c) 20, (d) 48, and (e) 200 ALD cycles of ZrN.](image-url)
Figure 6-2 shows XPS core spectra for samples having 10, 48, 95, and 142 cycles of ALD. As shown in Figure 6-2a, NT samples having 10 and 20 cycles of ALD had ZrN layers that were too thin to show an independent peak in the N 1s spectra. Because of the same reason, samples having 48 cycles of ALD showed a very wide peak as shown in Figure 6-2a, which is reasonable given the penetration depth of XPS was 2-5 nm minimum, which means that XPS cannot detect thinner phases, and 48 ALD cycles are about 2.5 nm. This peak became more pronounced as the number of cycles increased to 95 (~5 nm) and 142 (~7.5 nm), proving the presence of a nitride compound on the surface. De-convoluting the nitride peak in the spectra of the latter sample, there exists three separate peaks: one centered near 396 eV, one at about 397.3 eV, and the third one centered at just below 400 eV. The first peak has been previously characterized as the effects of the (ZrO)-N$_3^-$ bond in the oxynitride phase.$^{6,7}$ The second peak centered at 397.3 eV was previously attributed by numerous authors to the nitride phase (or the Zr-N bond).$^{6,7}$ Some authors attributed another peak near that one to the ZrO$_x$N$_y$ phase too.$^{7,8}$ The remaining peak present in Figure 6-2a, and centered near 400 eV is well-known to be either adsorbed Nitrogen, or general contamination.$^6$ Thus, from the primary analysis of the N 1s spectra, the presence of an oxynitride phase seemed plausible.

As mentioned above, the aim of depositing a ZrN layer on top of the ZrO$_2$ was to obtain an oxynitride phase at the surface. Thus, Zr 3d core spectra were used to detect the nature of Zr compounds present on the surface. Figure 6-2b shows these spectra for all the samples including the bare ZrO$_2$ NTs. Indeed, it is well accepted that the spin orbit doublet peaks for Zr 3d$_{5/2}$ and Zr 3d$_{3/2}$ orbitals in the oxide phase fall within the ranges of 181.9-184.0eV$^{8,9}$ and 184.5-186.6eV,$^9$ respectively.
Figure 6-2: XPS (a) N 1s, (b) Zr 3d, and (c) O 1s core spectra of bare ZrO$_2$ NTs samples, and NT samples with 10, 48, 95, and 142 ALD cycles of ZrN.
Once a very small thickness of ZrN was deposited on top of the ZrO$_2$ NTs, broadening of both peaks was observed, which is widely known to occur due to the presence of more than one valence state of Zr.$^{10,11}$ In addition, both peaks shifted towards higher binding energies. This maybe due to the alteration of the electron clouds of the Zr ions on the surface of the NTs as a result of the presence of two different species attracting their valence electrons: Nitrogen and Oxygen ions. This would make the core electrons in the Zr$^{4+}$ ions more attached to their nuclei, and thus have an increased binding energy.

Upon increasing the number of ALD cycles to 48, peak broadening became more pronounced, and a further shift to higher binding energies appeared indicating more attraction of Zr valence electrons away from their nuclei. Note also the appearance of a third peak towards the low binding energies side of the spectra. This extra peak meant that XPS was detecting a new phase. The presence of this phase at lower binding energies can be attributed to the fact that increasing Nitrogen ions in the lattice would push Oxygen ions outside (i.e. Nitrogen replacing Oxygen in the lattice). Knowing that Nitrogen has lower electron negativity than Oxygen,$^{12}$ this should increase the attraction force of Zr to electrons in the ZrN top layer,$^{6}$ when compared to the underlying nanotubes, which would decrease the binding energy of the core electrons of the surface Zr atoms towards their nuclei since the latter now have to attract more electrons overall. This should push the 3d peaks to lower binding energies.$^{12,13}$ However, this effect did not seem to be pronounced in this sample, especially with the 3 peaks still lying within the oxide range. This maybe a result of the very small thickness of the 48 cycle ALD layer (~2.5nm) and the inconformity of the layer as seen from FESEM; both factors should result in mixed spectra showing
pronounced effects from the nanotube layer, as well as less pronounced ones from the under-developed ZrN layer.

Examining the spectra from samples with 95 ALD cycles, the expected shift of the Zr 3d_{5/2} spectra to lower binding energies upon addition of more Nitrogen into the ZrO_{2} lattice is observed, where the peak is situated just before 182 eV, which is commonly attributed to an oxynitride phase.\(^6\) The sample with 142 cycles shows a further shift to lower binding energy in the Zr 3d_{3/2} level. All these results confirm the presence of an oxynitride phase on top of the NTs.

In order to further confirm the presence of an oxynitride phase, O 1s spectra were also examined as shown in Figure 6-2c. Again, a shift to higher binding energies was observed upon the deposition of the very thin layers of 10 and 48 ALD cycles. This is attributed to the attraction of some of the Zr atoms’ electrons towards Nitrogen instead of Oxygen. This would decrease the amounts of electrons bound to the Oxygen nuclei, and thus shift the peaks to higher binding energies. Note also that the broad 10 cycles peak de-convoluted into two peaks in the 48 cycles sample. Upon increasing the amount of Nitrogen atoms on the surface, the possibility of Nitrogen replacing Oxygen in the lattice increases. This would cause the latter to attract the valence electrons of the former in the lattice, and thus a decrease in the binding energy of the core electrons in the Oxygen would be expected. Thus, an oxynitride phase should appear at binding energies that are lower than those of the oxide phase. This is exactly the case in the spectra of the samples with 95 and 142 ALD cycles of ZrN, as shown in Figure 6-2c.

To confirm the presented analysis of the XPS core spectra, atomic percentages were calculated from the core spectra, and Table 6-1 shows the phases that were present on each sample. As presented, all samples showed oxynitride phases.
Furthermore, the samples with 10 and 48 ALD cycles of ZrN had Oxygen-rich non-stoichiometric phases. On the other hand, the sample with 142 cycles had a more Nitrogen-rich non-stoichiometric oxynitride phase. The NT samples having 95 ALD cycles of ZrN on top had a phase that was very near the stoichiometric oxygen-rich oxynitride phase of \( \text{ZrO}_{2.2x}\text{N}_{4x/3} \) with \( x \sim 0.35 \).\(^{14}\)

As aforementioned, oxynitride phases have band gaps that are much lower than those of their oxide counterparts.\(^{15}\) This is expected due to the VB raising effect that Nitrogen has on oxide compounds. Indeed, this phenomenon has been predicted theoretically for Zirconium oxides and oxynitrides before.\(^{16}\) Experimentally, this phenomenon can be detected by studying the nature of the VB using XPS VB spectra. Figure 6-3 shows XPS VB spectra for the bare ZrO\(_2\) NTs, NTs having 10, 48, 95, and 142 ALD cycles of ZrN, and a Zr foil having 600 ALD cycles of ZrN to resemble a nitride-rich layer. As shown, all samples had mixed orbitals between Oxygen and Nitrogen, with the sample having 142 ALD cycles showing the closest behavior to the 600 cycles sample. Note also that upon the deposition of 10 cycles of ZrN, N 2s orbitals appeared above the O 2s orbitals, which pushed the VB edge of the system upwards on a potential scale versus NHE. This would in turn decrease the band gap, as would be shown in the following section.

Table 6-1: The chemical states, Zr 3d, O 1s, and N 1s peak binding energies (+/- 0.05 eV) of bare NTs and NTs having 10, 48, 95, and 142 ALD cycles, as extracted from XPS data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical State</th>
<th>Binding Energies</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>VBM</td>
</tr>
<tr>
<td>Bare NTs</td>
<td>ZrO(_2)</td>
<td>5.8</td>
</tr>
<tr>
<td>10 Cycles</td>
<td>-</td>
<td>3.0</td>
</tr>
<tr>
<td>48 Cycles</td>
<td>Zr(<em>{2.7})O(</em>{10.8})N</td>
<td>2.8</td>
</tr>
<tr>
<td>95 Cycles</td>
<td>Zr(<em>{3.2})N(</em>{4.1})</td>
<td>2.2</td>
</tr>
<tr>
<td>142 Cycles</td>
<td>ZrO(_{1.7})N</td>
<td>2.1</td>
</tr>
</tbody>
</table>
In order to confirm the narrowing of the band gap, UV-Vis spectra and Tauc plots were used. Figure 6-4 shows the UV-Vis spectra of the bare NTs as well as the sample with 95 ALD cycles of ZrN. As shown in Figure 6-4a, the absorption edge of the bare NTs lied in the UV region just before the visible range. Upon the deposition of 20 cycles of ZrN, the absorption edge was pushed towards lower photon energy, which made the sample capable of visible light absorption. As the number of deposition cycles increased, the absorption edge moved further to encompass more photon energies form the visible-light region. Thus, the primary target of this study was attained: the composite electrode was proven capable of visible-light absorption. Figure 6-4 panels b and c show the Tauc analysis for the samples surveyed in the UV-Vis spectra; only the direct allowed band gaps were studied for relevance. Extracting the relation between the number of cycles and the band gaps, a plot was generated to predict the band gap corresponding to any number of cycles. This plot is shown in
Figure 6-4e. Bare NTs proved to have a band gap of about 3.8, which was very close to the value simulated for the circular ZrO$_2$ NTs fabricated in this study.$^{17}$ Also, as expected, being an Oxygen-rich oxynitride layer, the sample with 20 ALD cycles showed a small shift in the band gap to about 3.1 eV. After that, the relationship between the band gap and the number of cycles seemed to develop linearly up till the last sample studied. The band gap of the sample with 95 cycles was extracted as 2.4 eV.

Figure 6-4: UV-Vis spectra of ZrO$_2$ NTs having 0 and 95 ALD cycles of ZrN. (b and c) Tauc plots for the same samples, respectively. (d) An empirical relationship between the band gap of the samples and the number of ALD cycles as extracted from Tauc analysis.
6.3 Photoelectrochemical Characterization

With the band gap decrease confirmed, the following step in this study was the photoelectrochemical characterization, which would allow for the determination of the band edge alignment between the different samples, as well as allow for the comparison between the fabricated composite electrodes and other electrodes in the literature. Figure 6-5 shows the photocurrent density measured versus applied potential (vs Ag/AgCl₂). The plots show an enhancement of one order of magnitude upon the deposition of 10 cycles of ZrN. A further enhancement was observed in the sample with 48 cycles. Also, note the ‘composite effect’ arising in this particular sample, with a sudden change in the photocurrent appearing twice: near 0 V vs Ag/AgCl₂ and near 0.6 V too. This may be explained by appreciating the effects of agglomeration in the ALD layer, where parts of the NTs were still exposed to, and interacting independently with the light. The sample with 95 cycles of ZrN showed the highest photocurrent density, with the ‘composite effect’ fading due to the thick (~5 nm) layer of ZrON, although still noticed. The sample having 142 cycles of ALD showed a decrease in the photocurrent density. This may be attributed to the complete coverage of the NTs surface (see Figure 6-1), which would limit their interaction with the electrolyte, as well as the incident light, making their contribution to the water splitting process minimal, losing all the benefits of the 1-D structures. Another possible reason for the deterioration may be increased defect states with increasing ALD layer thickness, or simply the enhanced recombination probability due to the increase in the electron pathway.¹⁸
Figure 6-5: (a) Photocurrent density-voltage curves for bare ZrO$_2$ NTs, and ZrO2 NTs having different ALD cycles of ZrN. (b) A plot showing the change in the OCP with increasing number of ALD cycles.

Figure 6-5b shows a shift in the Open Circuit Potential ($V_{oc}$) to a more negative value as the number of ZrN ALD cycles increased from 0 up till 95 cycles. The $V_{oc}$ then shifted to a more positive value. The primary shift to negative values indicates a cathodic shift in the Fermi energy of the electrodes, which may be a direct result of the increase in the amount of photogenerated charge carriers with increasing ALD cycles up till 95. The anodic shift observed in the sample with 142 cycles of
ZrN is again attributed to the increased defect/surface states, which charges the surface of the semiconductor leading to Fermi level-pinning\textsuperscript{19,20} i.e. the Fermi level becomes more or less constant.

Analyzing the results, the observed increase in photocurrent density could be attributed to the capability of the composite photoelectrodes to absorb visible light, thus generating more photoelectrons to take part in the reaction. This was one sure reason. Another possible reason for the enhancement could have been the enhanced kinetics of the water oxidation reaction on the surface of the oxynitride layer as compared to the oxide layer. That is, a decreased hole transport barrier existed at the surface of the oxynitride layer as compared to that of the oxide NTs surface, and a decreased overpotential was needed for the water reduction reaction to occur at the cathode. Although the enhanced photocurrent and the cathodic shift in the $V_{OC}$ indicated the former and the latter, respectively, Further analysis was needed to confirm this enhancement in charge carrier dynamics.

Accordingly, Electrochemical Impedance Spectroscopy (EIS) was performed to confirm these conclusions, and prove the contribution of enhanced water splitting kinetics to the enhancement in photocurrent. Figure 6-6a shows the illuminated Nyquist plots near zero applied bias for the bare electrode, and the sample having 95 ALD cycles. Initial examination of the plots leads to two observations: 1) the imaginary part of the impedance for the bare NTs is about double that of the ALD sample at almost every frequency. 2) At the high-frequency range in both samples, a small semicircle arises from the interface between the Pt counter electrode and the electrolyte. 3) There exist two major semi-circles for the ALD sample: a medium-frequency and a low-frequency semicircle; the low frequency one can be further
deconvoluted into two semicircles. For the bare sample, only one major semicircle is observed, which also can be de-convoluted into two semicircles using Z-fit software.

Figure 6-6: (a) Illuminated Nyquest plots for the Bare NTs and the NTs with 95 ALD cycles. (b) and (c) Simplified circuit elements for both samples respectively.

Considering the conditions of the EIS measurements, each semi-circle in both plots can be attributed to a certain interface in the photo-electrochemical cell. For the bare electrode, the low-frequency semicircle can be attributed to the trapping reactions occurring in surface states at the NT/electrolyte interface ($R_{SS-NT}$ & $C_{SS-NT}$). The medium-frequency semicircle is attributed to bulk recombination reactions occurring in the bare NTs ($R_{Bulk-Bare}$ & $C_{Bulk-Bare}$). For the composite sample, the low-frequency semicircle was de-convoluted to accommodate two different semicircles.
representing the surface state reactions at the ALD layer/electrolyte interface \( (R_{SS-ALD} \& C_{SS-ALD}) \), as well as the charge transfer across the interface between the oxide NTs and the oxynitride layer \( (R_{Int} \& C_{Int}) \). Again, the medium-frequency semicircle is attributed to the bulk resistance of the NTs in the composite electrode \( (R_{Bulk-Bare} \& C_{Bulk-Bare}) \). In both spectra, given the very low interface resistance and high surface area of the Pt counter electrode, high-frequency effects can be neglected. Also, for simplicity, the ALD layer is assumed to completely cover the NTs surface.

Figure 6-6 panels b and c illustrate the simplified circuits to which the bare and the composite samples were fitted. Table 6-2 presents the values of the circuit elements as extracted from Z-fit software. The bare electrode shows a high resistance at the interface \( (R_{SS,NT}) \) indicative of low conduction from the NTs to the electrolyte, probably due to the presence of hole trap states at the interface or due to the relatively small number of charge carriers in the bare NTs. The latter reason is also evidenced from the low interface capacitance \( (C_{SS,NT}) \). In contrast to this behaviour, a lower interface resistance is observed for the composite electrode \( (R_{SS-ALD}) \), which is directly attributed to the increased number of charge carriers given the superior optical properties of the oxynitride layer. However, the interface capacitance in the oxynitride \( (C_{SS-ALD}) \) is three orders of magnitude higher than that of the bare samples. This, although indicative of the increased charge carriers, may also highlight the abundance of surface states that trap photo-generated carriers, thus increasing the capacitance at the interface.
Table 6-2: Values of resistances (in $\Omega$) and capacitances (in $\mu$F) in the suggested circuits as extracted from impedance spectra for both bare NTs and NTs with 95 ALD cycles of ZrN.

<table>
<thead>
<tr>
<th>Circuit Elements</th>
<th>Extracted Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{Sol}$</td>
<td>12</td>
</tr>
<tr>
<td>$R_{Bulk-Bare}$</td>
<td>1500</td>
</tr>
<tr>
<td>$C_{Bulk-Bare}$</td>
<td>3.9</td>
</tr>
<tr>
<td>$R_{SS-NT}$</td>
<td>4500</td>
</tr>
<tr>
<td>$C_{SS-NT}$</td>
<td>4.5</td>
</tr>
<tr>
<td>$R_{Bulk-Comp}$</td>
<td>1212</td>
</tr>
<tr>
<td>$C_{Bulk-Comp}$</td>
<td>2.6</td>
</tr>
<tr>
<td>$R_{Int}$</td>
<td>1700</td>
</tr>
<tr>
<td>$C_{Int}$</td>
<td>118.4</td>
</tr>
<tr>
<td>$R_{SS-ALD}$</td>
<td>2700</td>
</tr>
<tr>
<td>$C_{SS-ALD}$</td>
<td>593.3</td>
</tr>
</tbody>
</table>

Thus, EIS studies indicate the abundance of surface states in the composite sample as compared to the bare NTs. This, although expected to deteriorate the photocurrent, seemed to be overcome by the much greater numbers of photo-generated charge carriers in the ALD layer. Another reason may be long-lived charge carriers, where the fast electron-hole recombination reactions are quenched due to electron trapping, giving enough time for slower charge transfer reactions across the electrode and into the electrolyte to occur uninterrupted.\(^\text{37}\) To confirm this, the results of EIS were used to estimate photo-electron lifetimes for both electrodes, i.e.

$$\tau_e = R_{SS}C_{SS} \quad \quad [7-1]$$

Estimating the electron lifetimes at zero applied bias gives about 20 and 1000 ms for the bare and composite electrodes, respectively. Thus, carriers photo-generated
at the composite electrode/electrolyte interface remain excited for a longer timespan when compared to those of the bare oxide NTs. In turn, photo-generated holes at the bulk of the composite electrode would have more time to travel to the interface and initiate water oxidation reaction. This strengthens the hypothesis of a catalytic effect of the oxynitride ALD layer. All in all, although the observation of increased surface states gives some credit to the surface states hypothesis stated above for the sample with the 142 cycles, further investigation is due to study the growth of this surface states-capacitance element with the number of ALD cycles. This may lead to the critical number of cycles at which the deterioration of the photocurrent due to the increased number of surface states occur. This is left for future work on this topic. Finally, examining the bulk recombination resistance and capacitance in the NTs, there seems to be a small shift towards lower capacitance and resistance in the composite electrode. This may originate from the diffusion of Nitrogen species across the interface into the NTs, as evidenced form XPS depth profiling (not presented here), thus deepening the oxynitride front further into the electrode.

As mentioned in Chapter 2, EIS is a useful technique for determining $V_{FB}$ and the donor density inside semiconducting electrodes. This is done through the Mott-Schottky (MS) analysis, which relates the space charge capacitance, as extracted from EIS, to the applied potential through the following relation:

$$\frac{1}{C^2_{SC}} = \left( \frac{2}{eN_D \varepsilon \varepsilon_0} \right) \left( \left| V_{applied} - V_{FB} \right| - \frac{kT}{e} \right)$$  \hspace{1cm} [7.2]

In general, the validity of MS analysis depends on a number of factors that, if not taken into consideration, could affect the extracted results direly. Firstly, MS analysis assumes a very large Helmholtz capacitance (see Chapter 2), and thus negligible impedance due to the Helmholtz layer. However, for some electrodes and
solutions, this may not be the case.\textsuperscript{21} Failing to incorporate the Helmholtz capacitance in these cases would result in shifted values of $V_{FB}$ being extracted from the MS analysis. Another reason behind shifts in $V_{FB}$ is the presence of surface states and the contribution of a surface states capacitance as a result.\textsuperscript{22} This should decrease the space charge layer due to trapping of photogenerated carriers, and may even cause Fermi level pinning.\textsuperscript{19} Another reason is the presence of a dielectric barrier layer, which appears in anodic oxide films, like the ones in this study. This layer would add a contribution of another dielectric capacitance.\textsuperscript{23}

Secondly, MS analysis assumes significant band bending occurring inside the electrode, and builds upon that.\textsuperscript{24} This may not be the case in nanostructured electrodes such as the ones used in this study.\textsuperscript{25} Also, the inter-nanotube separations must be large enough compared to the width of the space charge layer, which also may not be the case in the studied electrodes. Finally, MS analysis assumes a uniform distribution of charge carriers throughout the material under investigation,\textsuperscript{22} which is not the case in our composite electrode.

That being said, MS analysis seems un-plausible for the case of the nanostructured composite electrodes studied herein. However, it does remain as one of the most accurate electrochemical techniques in determining the $V_{FB}$ of semiconducting electrodes versus NHE, if the above is taken into consideration. For the mere purpose of comparing between the studied electrodes, and because the values extracted from the MS analysis were close to those in the literature, such values were not further treated for the mentioned errors, and this was left as part of future work in this topic.

Figure 6-7a shows the area-corrected MS plots for the bare NTs and NTs having 95 cycles of ALD. Values extracted from the plots are presented in Table 6-2. From an initial look at the extracted $V_{FB}$ values, a small shift from the values
mentioned in the literature is observed,\textsuperscript{26,27} which is attributed to the factors mentioned above. The bare NTs, as well as the NTs with 10 and 95 cycles showed $V_{FB}$ values of -0.17 and -0.13 V vs NHE, respectively (thus, the CBM was calculated at -0.47 and -0.43 V vs NHE, respectively).\textsuperscript{28} The 0.04 V anodic shift between the bare NTs and the NTs with ZrN ALD cycles is well-aligned with the literature considering the relatively low amount of Nitrogen in both phases.\textsuperscript{15} Furthermore, a similar shift was observed for Tantalum oxynitrides.\textsuperscript{28} Equipped with the Flat Band potentials, as well as the band gap energies from Tauc analysis, band edge alignment between the electrodes could be determined. Figure 6-7b shows the alignment of the VBM and CBM’s of the studied electrodes with respect to NHE. It can thus be concluded that the probability of charge injection occurring at the interface of the composite electrodes seems to be quite low. This explained the relatively high interface resistance ($R_{Int}$) between the oxide NTs and the ALD layer. In fact, this interface resistance, being slightly greater than the bulk NT resistance, may originate from the formation of a charge transfer barrier across the interface as the ALD layer sustains more and more band bending with increasing thickness; another possible explanation for the deterioration of the photocurrent in the sample with 142 cycles of ZrN.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure6-7b.png}
\caption{(a) Graph showing the change in charge density with respect to applied voltage for bare NTs and 95 cycles. (b) Schematic diagram illustrating the band alignment and energy levels at 95 cycles and bare NTs.}
\end{figure}
Figure 6-7: (a) Area-corrected Mott Schottky plots for the bare NTs and the NTs having 95 ALD cycles. (b) Band Alignment diagram for both samples with respect to the water splitting redox potentials.

6.4 Conclusions

In this second part of the thesis, the modification of the wide-band gap ZrO$_2$ NTs using ZrN was conducted using Atomic Layer Deposition. Examination of the composite electrodes’ chemical states revealed oxynitride layers on top of the oxide NTs. $J$-$V$ plots indicated an enhancement upon the deposition of 10 cycles of ZrN reaching a peak at 95 cycles. Further deposition diminished the photocurrent, which maybe a result of abundance of surface states, as well as an almost full coverage of the NTs surface rendering their superior properties obsolete. Tauc analysis showed a band gap of 2.4 eV for the superior sample compared to the NTs’ 3.8 eV gap. Thus, the achievement of a visible light-active electrode was confirmed. To understand the nature of the interface between the oxide and the oxynitride phases, Electrochemical Impedance Spectroscopy was conducted. Evidence for the presence of electron/hole trap states in the composite electrodes was observed from EIS data, where a decreased interface resistance and increased capacitance indicated the presence of more charge carriers at the interface between the composite electrode and the electrolyte when compared to the bare NTs sample. EIS data also showed increased photoelectron lifetimes in the composite samples, indicating enhanced water oxidation kinetics. Band-edge positions were extracted from Mott Schottky experiments, demoting the hypothesis of charge injection, and showing the straddling condition characteristic of stable photoelectrodes.
References


Chapter 7

Suggestions for Future Work

To this end, the cheap* synthesis of earth-abundant, visible light-absorbing, all Zirconium-based, nanostructured composite photoanodes for solar water splitting has been a success. Zirconium Dioxide NTs were successfully optimized to the required structure and wall thickness. Then, atomic layers of ZrN were deposited upon the NT arrays, which caused oxidation to occur, and a visible light-absorbing Oxynitride top layer to develop. The following are certain ideas for synthesis and characterization to continue on this track towards creating the ultimate Zirconium-based photoanode for solar water splitting.

7.1 Optimization of Zirconia NT Arrays for Water Splitting

Presented in Chapter 5 is the optimization of process parameters for the synthesis of circular and hexagonal Zirconia NTs via anodic oxidation. The comprehensive characterization of both type of NTs is needed to define which type provides better charge carrier dynamics. Impedance, Mott-schottky, as well as Laser Dynamics Pump-Probe experiments are respectively required to determine the interface resistance and capacitance, the flat-band potential and the donor density, and the electron lifetimes in both types of arrays. Once the superior type is determined, the optimization of NT length is also required for better charge dynamics in the water splitting photoanodes. The same experiments should be taken out to achieve the stated goal.

* When compared to other nanostructure synthesis techniques such as those used inside a cleanroom.
7.2 Optimization of ZrN Layer Thickness

In Chapter 6, ZrN thicknesses of 0.5 Å, 2.5, 5, and 7.5 nm were used to study the effect of ZrN deposition on top of the ZrO$_2$ NT arrays. The thickness of 5 nm showed superiority over the other thicknesses used in this study. Exploring other thicknesses between 5 and 7.5 nm is required to determine the inversion point in the data, that is, the actual critical thickness at which performance deviates from optimum. Also, further experimentation is needed to fundamentally understand the reasons behind the performance deterioration witnessed in the thicker depositions, namely: Impedance and Mott-Schottky experiments. Furthermore, Laser Dynamics Pump-Probe experiments should provide the deepest insight into the superiority of the composite electrodes over the bare NT arrays. At last, Incident Photon Conversion Efficiency (IPCE) experiments should be carried out to be able to compare the results in this study with results in the literature universally.
PUBLICATIONS
