ANODIZATION GROWTH AND INTEGRATION OF TITANIUM DIOXIDE
NANOTUBES IN DYE SENSITIZED SOLAR CELLS

A Thesis
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Dedications

To my parents Hendro Susilo, MD and Heliana Hananta. My brother Irfan Susilo and his wife Yenny Veronica. My nephew and niece, Ethan and Alice.
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To my thesis advisor Prof. Kenneth Lau, I’m very grateful for his mentorship and patience during my research years. His dedication and insight to answer research problems has always inspired me to continually challenge and improve myself in learning how to think independently. I’ve grown to be a more mature and stronger individual because of his advice.

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Titanium dioxide nanotube (TNT) arrays have been successfully grown by anodization in a glycerol electrolyte. A growth rate of 1.4 μm/h has been achieved, which is more than double that typically observed with tubes grown in glycerol. By adjusting anodization parameters, such as increasing anodization temperature (45 °C) with a small addition of water (5 vol%) and a high fluoride salt concentration (0.67 M), we found an optimized balance between field assisted oxide growth and chemical dissolution that allowed for the increase in growth rate. Nanotubes of 2.2 μm in length with 48.7 nm inner diameter have been obtained for 2 h of anodization time with uniform pore opening from top to bottom and relatively smooth outer walls. The TNT arrays have been integrated as photoanodes in dye sensitized solar cells and current-voltage measurements performed on these DSSCs showed that significant improvement in cell performance is expected with optimization of nanotube properties and solar cell fabrication techniques.
CHAPTER 1: INTRODUCTION

1.1 Why Solar Energy?

The growing demand for clean energy in combination with the depletion of fossil fuel resources and climate change issues such as global warming have prompted an urgent need for environmentally sustainable energy sources. Renewable energy can be obtained from sustainable resources: hydroelectric from tides and ocean currents, geothermal, wind, and solar energy striking the earth.\(^1\) Solar energy from the sun holds the most promise as an alternative energy source because the supply is essentially unlimited and free. The sun provides about 100,000 terawatts (TW) to the earth, which is about 10,000 times greater than the world’s present rate of energy consumption at 13 TW.\(^2\)

Photovoltaic (PV) cells have been used to harness this vast resource and are predicted to play a key role in sustainable energy systems.\(^1\) Grätzel proposed that covering 0.1% of the earth with PV panels of 10% efficiency would satisfy current global energy demand.\(^3\) A PV system is unique compared to other technologies because it converts sunlight directly to electricity, eliminating the need for bulky mechanical generator systems. PV panels can be installed quickly and cut into any size needed. Furthermore, the direct impact on the environment is minimal since it creates no by-products. PV production has expanded dramatically every year, increasing by an average of 48% annually since 2002, making it the world’s fastest growing renewable technology.\(^4\)

Although solar technology is an ideal candidate to fulfill the global energy demand, it still presents challenging problems for successful implementation. Two key issues in PV systems are the high cost of production and low efficiency. The first generation of solar
cells is dominated by solid-state junction cells based on silicon. The conversion efficiency achieved with this system can go beyond 30% depending on the silicon type (e.g. multicrystalline Si, multijunction concentrators). However, silicon cells are expensive to make and the manufacturing process is not environmentally friendly. Second generation of thin film PVs made from CuInSe (copper indium selenide) and CdTe (cadmium telluride) can bring the price down significantly but the efficiency is still significantly below the silicon based cells at around 7-11%. Scarcity of indium, tellurium and toxicity of cadmium makes sustainable large-scale production doubtful. Therefore, tremendous research effort is focused on next generation solar cells that are highly efficient while maintaining low production cost and more environmentally friendly manufacturing.

Grätzel’s group introduced dye sensitized solar cells (DSSC) in 1991 which is based on an interpenetrating network of semiconductor oxide nanoparticles, typically TiO₂, as a potential way to make PVs more cheaply and effectively. A fundamental difference of DSSCs compared with conventional silicon systems is that light absorption (i.e. the photosensitizer dye) is separated from charge carrier transport (the semiconductor). The highest efficiency of DSSC based on a liquid electrolyte is comparable to that of amorphous silicon at ca. 11% under AM 1.5 (1000 W/m²), making it an attractive solution for low cost manufacturing due to lower cost and availability of semiconductor material compared to silicon based material.

However, one major problem with DSSCs is the back injection of photo-generated electrons from the semiconductor to the dye (i.e. charge recombination). This is in part due to electron transport being slowed by the randomly interconnected TiO₂
nanoparticles.[5] TiO₂ structural modification has been proposed as one alternative to tackle this problem. Both modification of the liquid electrolyte and semiconductor morphology are needed to provide a more complete interfacial contact in the TiO₂/dye/electrolyte system to enhance electron transport leading to an overall improvement of DSSC efficiency.

The thesis is divided into four main chapters. Chapter 1 provides the reader with the background and motivation on titanium dioxide nanotube (TNT) synthesis by anodization as well as TNT-based DSSCs. Chapter 2 is devoted to the results from TNT anodization. Chapter 3 contains the results from TNT-based DSSCs. Chapter 4 provides conclusions from the work along with recommendations for future studies.

1.2 Anodization of TNT

Anodic oxidation has been a common method of choice to grow ordered nanostructures. This technique is simple, cheap, and provides a high degree of control over the dimensions of the nanostructures. For example, it has been known for many years that anodizing aluminum sheets in acidic electrolytes can produce porous oxide layers of several μm in thickness. Work by Masuda and Fukuda in 1995[6] showed that a high degree of ordered pore arrays could be grown under optimized anodization parameters.

By controlling anodization parameters of Ti (e.g. applied potential, concentration, temperature, aqueous and non-aqueous electrolyte), different titanium oxide structures such as a compact oxide, a disordered porous layer or a self-organized nanotube structure
can be produced. Interestingly, in the presence of fluoride in the electrolyte, a tubular titania layer forms instead of just a compact oxide layer (see Figure 1.1).

![Diagram of oxide layers](image)

**Figure 1.1.** Different types of oxide layers can be grown depending on the anodization conditions (e.g. potential, electrolyte, temperature).[^1]

### 1.3 TNT Application to DSSC

Since DSSCs (Grätzel solar cells) were introduced in 1991, they have reached record efficiencies of 11%. TiO$_2$ nanoparticles are used as the photoanode, and consists of a mesoporous film of 25 nm diameter nanoparticles deposited on top of a transparent conducting oxide with the mesoporous TiO$_2$ film thickness usually ranging from 10-12 μm. A monolayer of ruthenium complex dye is adsorbed onto these nanoparticles forming the photosensitized anode. The mesoporous electrode is then filled with a liquid electrolyte containing an I/I$^3$ redox couple. Placing a platinized transparent conducting oxide as the counterelectrode on top completes the cell assembly. Studies on electron transport have shown that in nanoparticle films such as TiO$_2$ transport of charge carriers
is on the order of seconds. Therefore, the probability for a recombination reaction to occur before charge carriers are collected is significantly high. This is believed to be the limiting mechanism in DSSCs based on nanoparticles. Detailed studies on the kinetics and dynamics of nanoparticulate DSSCs by intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS) have shown that charge transport proceeds by a random walk through a trapping/detrapping diffusion mechanism of the electrons in the porous matrix.\textsuperscript{[8]} To reduce this effect, oriented 1D nanostructures are emerging as a promising replacement of random nanoparticle networks for faster electron transport.

\textbf{1.3.1 Nanoparticle based DSSC}

A schematic diagram of the DSSC is shown in Figure 1.2. The semiconductor of choice is anatase TiO\textsubscript{2}, but alternative wide band gap oxides are also being investigated, such as ZnO, SnO\textsubscript{2}, and Nb\textsubscript{2}O\textsubscript{5}.\textsuperscript{[9-13]} Titanium dioxide is relatively cheap, widely available, non-toxic, and have been widely used in healthcare products due to its biocompatibility.\textsuperscript{[14]}

The TiO\textsubscript{2} layer is composed of nanometer sized particles that are interconnected through sintering. The surface is sensitized with a ruthenium complex dye that absorbs light in the visible solar spectrum range. Photo-excitation of the dye leads to electron injection into the conduction band of TiO\textsubscript{2}. The oxidized dye is then restored to its original state by electron donation from the redox couple in the electrolyte. The electrolyte used is usually an iodide/triiodide redox couple dissolved in a liquid organic solvent. Regeneration of iodide ion into triiodide happens at the platinum counter electrode. Finally, the electrical circuit is completed through electron migration in the external circuit.
1.3.2 TNT based DSSC

The aligned structure of nanotube arrays has the potential to be applied as an alternative electrode configuration in DSSCs. One of the limiting factors of using the mesoporous network is slow electron transport because of the mesoporous TiO$_2$ film. The structural disorder at the contact between nanoparticles enhance scattering of free electrons that reduces electron mobility.$^{[15]}$ Introducing ordered nanoscale architectures in the form of nanorods, nanowires, and nanotubes have the potential to improve electron transport. The vertically aligned nanostructure is expected to create a more direct pathway for electron transport. In addition, the more open structure gives a better contact with the dye and electrolyte that can further improve ion diffusion (charge transport) at the semiconductor-electrolyte interface.
1.4 References


CHAPTER 2: TNT ANODIZATION

2.1 Motivation

Preparation of nanostructures from transition metal oxides has seen considerable attention with TiO$_2$ gaining much scientific interest because it demonstrates broad functional properties that can be applied to many different areas. Various morphologies of titania nanorods, nanowires, and nanotubes have been synthesized by techniques such as surfactant template-based,$^{[1]}$ hydrothermal,$^{[2]}$ and sol-gel methods.$^{[3-4]}$ These nanostructures have been applied to various areas such as water photoelectrolysis$^{[5]}$ and dye sensitized solar cells.$^{[6-8]}$ However, to maximize the use of these nanostructures in many devices, it is desirable to orient the nanostructures on substrates in a single (vertical) direction as well as to form a dense ordered array.$^{[9]}$ Anodic oxidation has been one common method of choice to synthesize titania nanotubes. The technique is relatively simple while still provides a high degree of control of nanotube dimensions. By controlling anodization parameters (e.g. applied potential, concentration, temperature, aqueous vs. non-aqueous electrolyte) different titanium oxide structures such as a compact oxide, a disordered porous layer or a self-organized nanotube structure can be produced. Interestingly, in the presence of fluoride in the electrolyte, tubular titania layer forms instead of just a compact oxide layer.$^{[10]}$

The first generation of TiO$_2$ nanotube (TNT) arrays was grown in aqueous hydrofluoric acid (HF) electrolytes. Zwilling and coworkers$^{[11]}$ reported the porous surface of titania films electrochemically being formed in fluorinated electrolyte by anodization. The challenge with the aqueous based electrolyte is that the nanotube layer is limited to 500-600 nm due to rapid chemical etching by HF, which dissolves most of the growing oxide
preventing long tube formation. The rapid titania dissolution by HF is reduced by substitution with a less aggressive solution containing fluoride salts such as ammonium fluoride (NH₄F) and sodium fluoride (NaF). Further, by going to a non-aqueous based electrolyte, formation of self-organized TiO₂ nanotubes with tube lengths greater than 2 μm can be achieved. Recent generations of nanotubes have been grown in nearly water-free electrolytes typically in ethylene glycol or glycerol resulting in the growth of smooth tubes. Tubes up to 220 μm in length have been synthesized using ethylene glycol with NH₄F and have been applied in water photoelectrolysis and dye sensitized solar cells (DSSC). The growth of tubes in this electrolyte is quite fast, taking 17 h to grow 220 μm or about 13 μm/h. However, tubes synthesized in ethylene glycol have a high degree of variation in average pore diameter along their lengths. Scanning electron microscopy (SEM) taken at the top, middle and bottom parts of the nanotubes confirmed pore narrowing, about 5 times smaller going from top to the bottom. On the other hand, tubes synthesized with glycerol show uniform pore diameter from top to bottom while still retaining smooth outer walls.

Although smooth and longer tubes have been grown and pore opening is more uniform compared to ethylene glycol, it takes a significant amount of time to reach micron scale thickness with glycerol. Tubes with 7 μm length take at least 13 h of anodization or 0.5 μm/h so growth rate is an order of magnitude slower compared to ethylene glycol. This step might complicate the fabrication process when used in different applications. Therefore, we want to enhance the growth rate of tubes grown with glycerol by modifying the different parameters governing kinetics of tube growth.
2.2 Experimental

For anodization, commercial titanium foils (15x15x0.25 mm, Alfa Aesar, purity 99.5%) was used as the working electrode and a platinum sheet (0.127 mm, Alfa Aesar, purity 99.99%) served as the counter electrode. The titanium foil was mechanically polished with colloidal silica (OP-S suspension, Struers) to reach a mirror-like quality and cleaned by sonicating in deionized water and acetone for 5 min each. A copper wire for electrical connection was attached to the backside of the foil using a combination of adhesive tape and glue (Loctite ultra gel) that was allowed to dry overnight under nitrogen. A final layer of acrylic based nail polish was applied to ensure complete backside insulation. The titanium foil was anodized in an electrolyte of glycerol (BDH, 98% purity) containing ammonium fluoride (JT Baker, 99.1%) and deionized water. The electrolyte mixture was stirred for 5 min at 350 rpm and put in a constant temperature bath prior to anodization. The distance between the two electrodes was fixed at 25 mm. A constant voltage was directly applied using a DC power supply (Agilent 3612A) for anodization and current-transient data was recorded at a rate of 1 mA/s using a multimeter (Fluke 289) connected to a computer station. The as-anodized sample was rinsed thoroughly with deionized water and dry ethanol, and then dried under a nitrogen stream. Additionally, the sample was soaked in dilute HF (0.1 vol%) for 90 s, rinsed again with water and dry ethanol, and dried with nitrogen. Thermal annealing was performed on some as-anodized samples at 400°C for 3 h using a hot plate to convert the amorphous oxide tubes to the crystalline anatase phase. Surface morphology, structure, and dimensions of TiO₂ nanotubes were characterized and measured with scanning electron microscopy (Zeiss Supra 50VP FESEM). X-Ray Powder Diffractometer (Siemens D500) set at 0.04°/step and scanning
time of 1 s/step was used to get diffraction peaks from Ti foil, as-anodized and annealed samples.

2.3 Results and Discussion

We are able to accomplish faster tube growth by increasing anodization temperature (45°C) with a small addition of deionized water (5 vol%). The growth rate is roughly doubled to 1.4 μm/h and tube qualities are retained (i.e. uniform pore diameter from top to bottom, relatively smooth outer tube wall). To the best of our knowledge, there have not been reports on tubes anodized in glycerol with growth rates exceeding that from Macak’s group while maintaining similar tube attributes.

According to Schmuki and coworkers,[17] the formation of TNTs is believed to be the result of a competition between field assisted anodic oxidation (Equation 1) and chemical dissolution of the forming oxide (Equation 2). As shown, Equation 1 describes the formation of oxide under an applied electric field while Equation 2 refers to the chemical dissolution of oxide promoted by the presence of fluoride ions in the electrolyte to form a fluoro-complexes (TiF$_6^{2-}$).

\[
\text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4\text{e}^- \quad (1)
\]

\[
\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow \text{TiF}_6^{2-} + 2\text{H}_2\text{O} \quad (2)
\]

At the beginning of anodization, a dense oxide layer forms on the surface of the titanium according to Equation 1. Ti metal species is oxidized under an applied potential and migrates to react with O$^{2-}$ ions from H$_2$O, forming the initial oxide layer. Further oxide
layer thickening is controlled by field aided ion transport ($O^{2-}$ from $H_2O$ in the electrolyte and $Ti^{4+}$ ions from the underlying Ti metal).

Since the formed oxide layer is highly resistive to the flow of charges, this reduces the electric field strength and leads to a decrease in current. At the same time, chemical etching of the oxide layer by fluoride ions (Equation 2) leads to the formation of a porous oxide layer, which finally results in tubular formation through constant chemical dissolution of the field assisted growing oxide layer. Fluoride ions are capable of forming the water-soluble $TiF_6^{2-}$ complex according to Equation 2. This complex formation leads to the dissolution of formed $TiO_2$. Over time, the porous oxide layer grows deeper through continuous chemical etching, eventually forming separate tubular structures. By carefully tuning the anodization parameters that control the field-assisted oxidation and chemical etching reactions, we hypothesize that tube growth rate can be optimized.

![Figure 2.1](image)

**Figure 2.1.** Current transient profile during anodization at 45°C with 0.67 M $NH_4F$ and 5 vol% $H_2O$ in glycerol (inset shows the first 100 s of the profile).

A typical current transient profile shown in Figure 2.1 can be divided into three stages. In the first stage, there is a sharp decrease in current within the first 5 seconds that can be
attributed to the formation of an initial compact oxide layer of TiO$_2$. In the second stage which lasts for about 30 s, chemical dissolution of the TiO$_2$ oxide layer by the presence of fluoride in the electrolyte starts to form nanopores in the growing oxide layer and with pore growth happening through inward dissolution there is a slight increase in current. In the third stage, there is a competition between formation and dissolution of TiO$_2$ that reaches a dynamic equilibrium and gradually resulting in a steady state current.

To find the optimized anodization parameters, we performed a series of experiments studying the effect of (i) water content, (ii) temperature, and (iii) fluoride concentration on nanotube growth rate in the glycerol electrolyte system.

**Figure 2.2.** SEM images (top view) of as-anodized samples grown in glycerol for 1 h at 25 °C, 0.67 M NH$_4$F and various water content: (a) 3 vol%, (b) 5 vol%, (c) 25 vol%, and (d) 50 vol% H$_2$O. Scale bar = 200 nm.
Water content. Figure 2.2 shows the effect of water content on anodization. Tubes are formed at all water content studied ranging from 3 to 50 vol%. At 3 vol%, the tubes seem to be the least uniform compared to those grown at higher water content. There appears to be a hazy top layer consisting of irregular thin wisps of tube fragments that we attribute to incomplete etching of compact oxide. By going up to 5 vol%, the hazy top layer appears to be minimal and tube openings are more clearly seen while going to even higher 25 and 50 vol%, tube tops look completely clean. Tube internal diameters are as follows: 3 vol% (d=31.85 nm), 5 vol% (d=47.8 nm), 25 vol% (d=78.8 nm) and 50 vol% (d=84.78 nm). Tube internal diameter is observed to increase by more than twofold going from low to high water content. However, doubling the water content to 50 vol% resulted in a nanotube morphology similar to that at 25 vol%. Upon closer inspection of the tubes from the high water content runs at higher magnification and of their cross-sectional side views (data not shown), the tube walls appear to be highly rippled and uneven. Ripple formation can be correlated to current fluctuations and instabilities during anodization. Lower water content results in smaller fluctuations because diffusion of charges is slow and therefore less ripples are present compared to anodization at higher water content. In aqueous solution, ripples are present throughout the whole tube length. This could also explain why the tube openings in the 25 and 50 vol% runs appear to be less circular compared to lower water content runs given the anodization instabilities. Water is believed to have dual roles in TNT anodization. It is needed to promote oxide growth of the nanotubes (Equation 1). At the same time, H⁺ ions produced from Equation 1 will diffuse towards the bottom of the nanotube pores under an electric field. Accumulation of H⁺ ions at the pore bottom decreases pH at this location (local acidification) and attracts
F\(^-\) ions, which are responsible for chemical dissolution of the oxide layer (Equation 2). With greater water content, the increase in fluoride concentration will significantly accelerate chemical etching and oxide dissolution resulting in bigger pore openings as observed with the higher water content runs. We also observe that the addition of more water actually resulted in shorter tube lengths for the same anodization time i.e. lower growth rate (see Table 2.1) due to accelerated chemical dissolution. Thus, there exists an optimum window for the amount of water where the rate of chemical dissolution can be kept in check while still maintaining relatively fast field assisted oxide growth. We therefore selected 5 vol% for the remainder of the studies because it yielded the fastest growth rate while still maintaining relatively round pore opening and clean tops.

**Figure 2.3.** SEM images (top view) of as-anodized samples grown in glycerol for 1 h at 5 vol% H\(_2\)O, 0.67 M NH\(_4\)F and various anodization temperatures: (a) 25 °C, (b) 45 °C, and (c) 65 °C. Scale bar = 200 nm.

**Temperature.** Based on Figure 2.3, the anodization temperature has an appreciable impact on tube morphology. Going from 25 to 45 °C, there seems to be slightly more heterogeneity in tube height resulting in some tubes being longer than others. This effect becomes very prominent at 65 °C to the point where long tubes have formed bundles
resulting in significant top surface heterogeneity. The higher temperature has the effect of decreasing electrolyte viscosity according to the Stokes-Einstein equation. Therefore the diffusion of ions to the pore bottom is increased, which in turns leads to greater local acidification and higher chemical dissolution rate (Equation 2). Tube length increases by more than twofold going from 0.6 to 1.4 μm when temperature was increased from 25 to 45 ° (see Table 2.1). At the higher temperature of 65 °C, tube length was not measurable as the tubes were extremely fragile and getting a clean SEM cross section was practically impossible. From what can be observed from SEM side views, there remains a fractured layer which appears to be shorter than that at 45 °C. It is highly likely that the growing oxide layer experienced severe etching at 65 °C so that even for the same anodization time, tubes become mechanically unstable and break off instead of forming the anticipated longer tubes. Thus, the optimum growth condition was reached around 45 °C.

**Figure 2.4.** SEM images (top view) of as-anodized samples grown in glycerol for 2 h at 5 vol% H₂O, 45 °C and NH₄F concentration of (a) 0.47 M, and (b) 0.67 M. Scale bar = 200 nm.
**Fluoride concentration.** As shown in Figure 2.4, the effect of increasing the concentration of NH₄F from 0.47 to 0.67 M yielded tubes with a cleaner opening as a result of greater chemical dissolution. This is consistent with the disappearance of the hazy top layer with increased water content for the same reason. The tube length is slightly longer by 0.1 μm at the lower concentration of 0.47 M (see Table 2.1). However, it is difficult to judge completely the effect of fluoride concentration on tube length due to the narrow window of concentration data. Exploring the concentration range at higher temperature will give a better picture of the overall effect of fluoride concentration on tube dimensions. However, even with a slight decrease in concentration less chemical etching is observed giving a thicker oxide layer growth and longer tubes.

**Growth rate.** Table 2.1 summarizes the various anodization growth conditions and the resulting nanotube lengths. Tube length decreased by 0.2 μm going from low to high water content, and the tubes formed at these anodization conditions were less than 1 μm in general for an anodization time of 1 h. Longer tubes observed at low water content supports the hypothesis of accelerated chemical dissolution with the addition of water. For the same anodization time of 1 h, tube length more than doubled when temperature was increased from 25 to 45 °C but decreased with further temperature increase due to tube instability. Optimized growth rate seems to be achieved at higher temperature and fluoride concentration but with low water content. Further increasing anodization to 2 h at 45 °C and 5 vol% H₂O resulted in close to double the length compared to the 1 h growth. Temperature seems to have the dominant effect on enhancing growth rate (1.4 μm/h) as compared to the effect of water content and salt concentration.
Table 2.1. Tube length measurements based on various anodization conditions.

<table>
<thead>
<tr>
<th>Water content (vol%)</th>
<th>Nanotube length (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C, 0.67 M NH₄F, 1 h</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.6</td>
</tr>
<tr>
<td>5</td>
<td>0.6</td>
</tr>
<tr>
<td>25</td>
<td>0.45</td>
</tr>
<tr>
<td>50</td>
<td>0.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Nanotube length (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 vol% H₂O, 0.67 M NH₄F, 1 h</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.6</td>
</tr>
<tr>
<td>45</td>
<td>1.4</td>
</tr>
<tr>
<td>65</td>
<td>Not measureable</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NH₄F concentration (M)</th>
<th>Nanotube length (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 vol% H₂O, 45 °C, 2 h</td>
<td></td>
</tr>
<tr>
<td>0.47</td>
<td>2.2</td>
</tr>
<tr>
<td>0.67</td>
<td>2.1</td>
</tr>
</tbody>
</table>

By increasing the aspect ratio of the tubes, we begin to observe the issue of tube bundling because of incomplete etching of the top layer resulting in very thin tubes that started to collapse. There have been reports of different strategies to remove this top layer. A two-step anodization in which the anodized tubes from the first step were removed to create the tube bottom template for the second step resulted in the formation of well aligned nanotubes without bundling.[18] Other groups have added an electropolishing step of the titanium foil in combination with the two-step anodization to create an extremely smooth
initial surface for better electric field distribution, which helped to align the nanotubes and prevented bundling.\textsuperscript{[19]}

These different strategies are very laborious involving multiple steps, which might add complexity to the overall fabrication process. Following the work of other groups,\textsuperscript{[20]} dilute HF etching can be used as a simpler strategy to clean off the thin layer on top. By controlling HF concentration and soak time, etching will selectively dissolve the top layer. Thus, we tested the dilute HF clean on the 3 vol\% H\textsubscript{2}O run which showed the hazy top layer. An etching time of 90 s removed about 0.2 μm thickness of the layer. Sonication was also tested as a way to remove the top layer but in contrast tube length was cut by 50\% or more. In addition, significant sample liftoff was observed when sonicating for an extended period of time.

\textbf{Figure 2.5.} SEM images (top view) of as-anodized samples grown in glycerol for 2 h at 3 vol\% H\textsubscript{2}O, 45 °C and 0.67 M NH\textsubscript{4}F (a) prior to HF etching, and (b) post-etching in HF (0.1 vol\%) for 90 s. Scale bar = 200 nm.
Factors like crystal structure and the stability of the anodized titania nanotubes at high temperatures have to be considered for different applications. In photovoltaics, the crystal structure plays an important role in charge separation and transport, affect the overall performance of the device. When TiO$_2$ nanotubes layers are produced by anodization, the as-anodized samples are typically amorphous.

![XRD spectra for tubes grown in glycerol for 2 h at 45 °C, 5 vol% H$_2$O and 0.67 M NH$_4$F before and after annealing at 400 °C in air for 3 h (A=Anatase, T=Ti substrate).](image)

**Figure 2.6.** XRD spectra for tubes grown in glycerol for 2 h at 45 °C, 5 vol% H$_2$O and 0.67 M NH$_4$F before and after annealing at 400 °C in air for 3 h (A=Anatase, T=Ti substrate).

An amorphous structure implies the presence of a high number of defects, which can act as traps and recombination centers for electrons and holes. The anatase crystal phase of TiO$_2$ is preferred because it has a higher charge carrier mobility compare to the rutile
phase. Thermal annealing at a temperature between 300-500 °C allows the amorphous TiO$_2$ to convert to anatase. Recently, Frank’s group [21] has shown that TNTs grown by anodization were stable up to 600 °C while higher temperatures resulted in significant wall perforation and the formation of nanoparticles. They found that the conversion from the amorphous to anatase phase begins at 400 °C with significant rutile formation observed only at higher temperatures.

Thus, we looked at our samples before and after annealing at 400 °C, as shown in Figure 2.6. The XRD spectra show that the as-anodized sample only contained peaks for titanium metal that matched that of the titanium substrate prior to anodization, indicating that the tubes were grown in the amorphous state. When the tubes were heated to 400 °C, a strong peak of anatase (101) at 25.3° can be observed. In addition, there is a peak for anatase (200) that appeared at around 48°. There is a small new peak at 38.48° for the annealed sample which also correspond to titanium substrate. Intensity of titanium substrate increase a little comparing titanium substrate, as-anodized and annealed sample. It might be the positioning of the sample was not consistent so that we get different peak intensity. Change in crystallinity phase might also affect the diffraction peaks. Based on the XRD result we can conclude that the annealing at this temperature is appropriate to transform the tubes from the amorphous state to anatase.
2.4 References


CHAPTER 3: TNT BASED DSSC

3.1 Motivation

Introducing ordered nanoscale electrode architecture in the form of nanorods, nanowires, and nanotubes to replace nanoparticles have the potential to improve electron transport. These nanostructures offer direct electrical pathway for the electrons and could increase electron transport rate, which in turn may improve DSSC performance. The vertically aligned nanostructure is expected to create a more direct pathway for electron transport. In addition, the more open structure gives a better contact with the dye and electrolyte that can further improve charge transport at the semiconductor-electrolyte interface. A nanotubular layer is expected to have a much lower degree of distorted crystal structures at grain boundaries, defects that reduce electron mobility. Further studies and investigations are required in particular to study the impact of nanotubes on cell performance and electron transport properties. However before investigating this step, it is also essential to optimize the preparation of nanotube based DSSCs. Obviously, tube length and diameter play an important role in the efficiency of DSSCs (see Figure 3.1c). As mentioned in Chapter 2, many variations in tube dimensions (diameter, length) can be achieved by tuning anodization parameters\textsuperscript{[2-4]} and it is particularly useful for the DSSC application because of this flexibility.

There are two ways to utilize these nanotube arrays in DSSCs (see Figure 3.1a and b): (1) backside illumination, which refers to illumination from the platinized counter electrode, which is less than optimal for light to electrical energy conversion because the platinized counter electrode partially reflects light, while iodine in the electrolyte absorbs photons in the near UV region; (2) front-side illumination, where light is illuminated from the
transparent active TiO$_2$ electrode, which requires the nanotube arrays to be grown on a transparent substrate, and therefore an initial layer of titanium needs to be deposited prior to anodization.

![Figure 3.1](image)

**Figure 3.1.** (a) Schematic of the DSSC based on TiO$_2$ nanotubes, (b) the electron pathways in nanoparticulate vs. oriented nanostructure electrodes, and (c) I-V curves of nanotube and nanoparticle DSSCs as a function of layer thickness.\[^1\]

Several efforts have been pursued to deposit Ti on transparent conducting glass. Grimes and coworkers\[^5\] have been able to fabricate nanotubes on top of FTO glass by using rf sputtering to deposit the initial titanium layer. The titanium film of 500 nm thickness was rf-sputtered onto FTO glass that was held at 500 °C prior to growing the nanotubes by anodization. The resulting tubes were 360 nm in length with 46 nm pore diameter.
Although the electrode was only 360 nm thick, under AM 1.5 solar illumination, the generated photocurrent was 7.87 mA/cm² and a photocurrent efficiency of 2.9% was obtained. However, poor adhesion of sputtered Ti to glass remains a problem and this layer was observed to be detached during anodization. Park and coworkers[6] uses titanium isopropoxide to help with attachment to the glass substrate. The resulting cells have very small area in the range of 0.03-0.15 cm² because structure was destroyed during annealing. Lei and coworkers[7] used ultrasonication to detach the anodized TNT, then using a combination of polyethylene glycol and TiO₂ sol containing Ti(OBu)₄ to attach the TNT to glass substrate. The efficiency reached 8.07% for 20 µm long tubes and can be an attractive fabrication process for front side illuminated solar cells.

Voltage decay measurement indicates that the highly ordered nanotube arrays have more superior electron lifetime in comparison to nanoparticulate systems.[5] Possible higher efficiency DSSCs for nanotube based system can be achieved by increasing the length of the nanotube arrays to several micrometers because it appears that the amount of the adsorbed dye might be a limiting factor.

However, nanotubes grown directly on transparent conductive glass is rather problematic. The relatively slow metal deposition method limits the ability to get a thick enough layer of Ti onto FTO. Also, thicker metal films peeled off as soon as an anodization voltage was applied, indicating that the adhesion between the sputtered metal and FTO can be quite poor. Thus, we have opted to utilize titanium foil as the electrode for anodization and backside illumination in DSSCs.
3.2 Experimental

Anodization was performed in glycerol electrolyte at temperature 45 °C with the addition of 5 vol% deionized water and 0.67 M NH₄F for 2 h. The resulting tube length was 2.1 µm and pore diameter was 47.8 nm. After anodization, a lift-off of the TNT foil edges was done using adhesive tape to remove the tubes at the edges and provide a space for device sealing. The as-anodized sample was then annealed at 400 °C for 3 h to convert the tubes from the amorphous to anatase phase. To introduce the photosensitizer dye, the TNT foil was sealed with Surlyn (25 µm thick, Solaronix) on the edges and an FTO glass (15 Ω/cm², Hartford Glass) on top that has a hole drilled to allow vacuum infiltration of the ruthenium dye of cis-bis(isothiocyanato)bis(2,2’-bipyridyl-4,4’-dicarboxylato)ruthenium(II) (N3, Solaronix) in a dry ethanol solution at a concentration of 3x10⁻⁴ M. The cell was then soaked in the dye for 24 h. The top FTO glass and Surlyn spacer were then removed and any excess dye was washed out. A new platinized FTO glass acting as the counter electrode was then placed on top and again with a small hole drilled for electrolyte infiltration. Platinization was done by spin coating 0.05 M solution of H₂PtCl₆ in 2-propanol on the FTO glass followed by heating at 450 °C for 20 min. A second Surlyn spacer (60 µm thick, Solaronix) was used to seal the TNT foil edges and prevent shorting of the two electrodes. An electrolyte of 0.5 M lithium iodide (LiI)/0.05 M iodine (I₂) was introduced through vacuum infiltration. The hole was then sealed. Current-voltage measurements of the liquid electrolyte DSSC were made with a Gamry Reference 600 potentiostat under AM 1.5 (100 mW/cm²) backside illumination through the platinized FTO glass. The sample was treated by soaking in HF for 90 s after anodization.
3.3 Results and Discussion

The open circuit voltage ($V_{oc}$), short circuit current ($J_{sc}$) and fill factor ($FF$) of the cell are 0.24 V, 0.71 mA/cm$^2$ and 0.4, respectively, yielding a power conversion efficiency of 6.51x10$^{-3}$ %. The fill factor $FF = (V_{mp}xJ_{mp})/(V_{oc}xJ_{sc})$, is defined as the ratio of the actual maximum power ($V_{mp}xJ_{mp}$) to the theoretical achievable power based on the open circuit voltage and short circuit current. Solar cell efficiency is then the percentage power converted from absorbed light to electrical energy, given by $[(V_{oc}xJ_{sc}xFF)/P]x100\%$, where $V_{oc}$ is the open circuit voltage, $J_{sc}$ is the short circuit current density, $FF$ is the fill factor and $P$ is the incident light irradiance under standard conditions (100 mW/cm$^2$). Measurement was done on the anodized TNT with an average tube length of 2.2 μm and an internal diameter of 47.8 nm.

![Figure 3.2](image)

**Figure 3.2.** Current-voltage trace of anodized TNT (HF etched) based DSSC in a liquid electrolyte under standard illumination conditions.
The low photocurrent and photovoltage values, which resulted in low device efficiency, can be attributed partially to the lack of optimization of the fabrication process of TNT solar cells. The challenge with TNT solar cell fabrication lies in the sealing step. The sample foil could not be kept entirely planar due to difficulties with detaching the foil off the epoxy mold after the polishing step. There is the possibility that some of the nanotubes fractured in the middle region where the light will be absorbed as a result of bending, leading to lower photocurrent values. Backside illumination through the platinum counter electrode side was used because the titanium foil was not transparent but some of the light will be absorbed or reflected. The platinum thickness was estimated to be on the order of hundreds of nanometers so the thickness has not been optimized yet for backside illumination.

The use of adhesive tape for edge lift-off might not be completely effective in removing tubes from the foil edges causing problems with sealing. It was observed that electrolyte was leaking out underneath the Surlyn spacer, and with the loss of redox species the injected electrons from the excited state of the dye can undergo recombination with the oxidized dye instead of the iodine redox couple. Another possibility is that the N3 dye solution used was several few months old and has been reused more than once for soaking so the dye itself might be low in activity. Being able to achieve consistency in the fabrication process will be required for future device performance testing.
3.4 References


CHAPTER 4: CONCLUSION

Several conclusions can be drawn based on results presented in this thesis. It was observed that current transient data can be used as a useful qualitative tool to monitor the growth phases of TNT in non-aqueous electrolytes. We found that nanotube growth rate in glycerol increased by at least two times to $1.4 \, \mu m/h$, which is to our knowledge the fastest so far in any glycerol anodization study. Further results from SEM showed that good nanotube quality with uniform pore diameter from top to bottom and relatively smooth outer tube walls are achieved.

Water is needed to accelerate both oxide growth and chemical dissolution of the oxide. However, there is an optimum amount, which provides an effective balance between these two chemical reactions. A lower amount of water between 3-5 vol% gave the best results with tube lengths in the micron scale while shorter tubes are observed with 25 vol%. Doubling the amount of water to 50 vol% did not produce any significant change in tube morphology and dimensions. Increasing temperature increased chemical dissolution rate due to a decrease in viscosity which allowed faster ion diffusion. However, the effect of fluoride salt concentration was inconclusive. Post anodization HF etching showed promise in reduce bundling and incomplete etching of top layer. XRD showed that annealed TNT at 400 °C for 3 h converted the amorphous phase to anatase phase. Finally, TNT based DSSCs could be fabricated but I-V measurements indicated high recombination and low photocurrent values. The fabrication steps therefore need to be further improved.
Based on the results, we can make improvements and adjustments for future studies. The exact amount of water present in the electrolyte or salt needs to be quantified because it can change with time, which may lead to a large error in the actual amount of water present during anodization. Post anodization etching of the top layer can be improved by varying the HF concentration and soaking time. To improve the fabrication steps in TNT based DSSC, there are several strategies that can be employed. Titanium foil can be further flattened using a mechanical press after the polishing step. Bending of the titanium foil can be further minimized by attaching the foil to a rigid substrate such as a glass slide. Other ways are to use an acrylic instead of an epoxy based mold during polishing so that a simple wash with acetone allows the polished foil to be detached without any large mechanical force. Having a flat foil will improve the problem with sealing the DSSC. In addition, masking the edges of the foil during anodization rather than lifting off grown tubes at the edges after anodization can ensure the edges are clean and spacer adhesion to the metal substrate is optimal. Finally, a study of dye loading into the nanotube layers can be useful, and together with surface area measurements, the data can be correlated with overall solar cell performance. Therefore, we expect that tube morphology and dimensions can be tuned to achieve enhanced DSSC efficiency.
APPENDIX A

1. Titanium Foil Grinding and Polishing

Note: Grinding and polishing conditions are obtained based on 3 samples/load. Conditions should be adjusted based on the number of samples.

1. Cut titanium foil sheet (Alfa Aesar, 250 μm thickness 99.5% purity) with scissors into 1.5x1.5 cm pieces.

2. Flatten the pieces by pressing it between 2 metal pieces (steel block) and apply pressure with mallet for a few times. Pay attention that the edges are reasonably flat (this step can also be done using a mechanical press).

3. Glue one flat piece to epoxy mold (Leco, epoxy resin and curing agent kit, follow instructions on the back of the containers) with super glue (Loctite liquid control) and press down with hands for 10-20 s to ensure proper attachment to the mold. Wait for 1 min for glue to cure. Some of the glue will cover the metal foil but this can be removed later during grinding.

4. Raise the metal sample holder to about 1 mm by placing 6 dimes under the holder near each sample opening.

5. Load the sample molds on the appropriate holder opening (can fit 6 samples), the side with titanium foil piece should be facing down. Tighten the screws on the side of each sample using appropriate allen key.

6. Push down the backside of the mold so it is not moving during screw tightening, the sample holder should not be moving too much when tightening as well.

7. Check that each sample mold is protruding at the same level and plane of about 1
mm and tightly secured. This step is crucial so redo steps 5-7 until this can be achieved.

8. If less than 6 samples are used, balance the sample placement to prevent sample holder from wobbling during grinding/polishing. Blank molds can also be used as dummy samples to provide balance.

9. Turn on the machine head (switch on the back) and base (switch on the right side). There is also a main power source box located on the wall that is sometimes turned off. Switch it on by pressing down handle to “ON” position then do step 11. If the box is locked please contact Dr. Barsoum’s lab for access.

10. Unlock the lever on the right hand side of the machine head by pushing it up, the head should raise up allowing the sample holder to be placed.

11. Fix the sample holder located on the grinding/polishing machine head (Struers Rotopol-22). Press the black button that will open the clamp so the sample holder can be inserted. There are 3 pins inside the head which will match the opening on the sample holder, this can be used to guide the holder placement on the grinding/polishing head (meanwhile keep pressing black button).

12. Release black button to allow clamping of sample holder. Try to rotate sample holder to check if it is locked.

13. Lock the head by pushing down the side lever gently so the head will lower down. There will be a warning if the lever is pushed down too fast and the head will not be in a locked position, simply unlock the lever and do it again.

14. Fill a squeeze bottle with tap water from the sink next to machine and wet the grinding wheel to make the grinding paper adhere better.
15. Remove the frames (outer and inner) of the grinding wheel and place grinding paper (Struers, silicon carbide paper 320 grit size) on top of wetted grinding wheel then put the frames back.

16. Wet the grinding paper with tap water.

17. Set the speed to 300 rpm located on the base part.

18. There are several settings on the machine head for force, time (in increment of 30 min), and wheel direction (shown by two arrows going in opposite/same direction). Opposite direction means the sample and polishing/grinding wheel will spin in opposite direction and vice versa. Set force = 60 N, time = 2 min, direction = clockwise.

19. Start the base first by pushing green button and the polishing wheel should start spinning. Start the head by also pushing green button. The head with the attached sample holder will spin and lower down until it touches the grinding paper. Watch that the sample holder is not wobbling or making a loud noise, if this happens it means the samples are not placed on the same plane and has to be taken out and repeat steps 5-7 then put it back on the machine again.

20. Water from a squeeze bottle should be immediately be splashed throughout the whole grinding time (water should be aimed at the moving sample holder).

21. When grinding time is completed, the head will stop spinning and be slightly raised away from grinding wheel. Turn off the wheel by pressing red stop button and then turn off head by doing the same thing.

22. Release sample holder by pressing down on black button and then inspect the samples. At this point, all the oxide should have been removed from foil. The foil
should look shinier with very fine and uniform scratches.

23. Wash samples with water to remove any debris.

24. Lock the sample holder to prepare it for the polishing process.

25. Put the polishing pad (Struers, MD-Chem) on the polishing wheel. The polishing wheel is magnetic and pad has a magnetic backing (also a way to distinguish between the grinding and polishing wheels).

26. Wet polishing pad with colloidal silica suspension (Struers OP-S solution). Set polishing wheel speed = 150 rpm, direction = clockwise. Set head part force = 60 N, time = 5 min, direction = clockwise.

27. Pour enough suspension every 30 s aimed at the center region of the pad. Do visual checks to make sure the pad is wet at all times (white color from suspension). Note: At this point the suspension volume for each addition is not well controlled so replacement with a syringe will give more precise volume control and better aim at the center region where the samples are located.

28. When polishing is completed, take out the sample holder and wash with water. Inspect the polished foils. At this time the fine scratches should not be visible and the metal should be shinier and a blurry reflection should be visible.

29. Set time = 3 min for the second polish and increase force = 100 N. After this second polishing step, sample should achieve a mirror like quality and reflection should be clear and recognizable. Total polishing time should not exceed 8-10 min to get this polish quality.

30. Wash sample with tap water and air dry. A white color residue from the polishing suspension might appear on the sample after drying and will be removed later by
multiple washing steps.

31. Unscrew samples from holder and store in a container for further processing. Be very careful not to touch the polished surface as it might introduce defects.

32. Dispose the grinding paper. Take out the polishing wheel frame, polishing wheel (removable), polishing pad and put them under the sink to wash with excess water. Check with air drying to see if there is any remaining polishing suspension, wipe with napkins if necessary. Do the same with the sample holder. Lastly, use a water hose to wash the drainage area (under the polishing wheel) and wipe it clean with napkins.

33. Put everything back. Wipe other parts of machine clean where white color is visible.

34. Switch off machine by turning off the base and head power. Leave the main power source at ON position.

2. Post Polishing Cleaning

1. Detach polished sample from molds using a razor blade. To minimize bending of the sample, start by razoring from one edge and then turning the sample while razoring deeper along the edges.

2. Gently lift the sample with tweezers holding the edge only, wash the sample at least 3 times to remove residual polishing suspension (keep replacing deionized water until it is no longer cloudy).

3. Sonicate the sample in deionized water for 5 min.
4. Replace deionized water with acetone and sonicate for 5 min (to remove residual glue on foil back).

5. Dry both sides of foils under a dry nitrogen stream.

6. Take an insulated copper wire about 5 cm and remove about 0.5 cm of the insulation from both ends.

7. Turn the foil so the non-polished side is facing up, put a new glass slide under the polished side to minimize scratches.

8. Cut a piece of tape (3M scotch tape) of about 0.75x1 cm and attach firmly one end of the wire onto the non-polished side of the foil. Ensure that the tape completely encloses the exposed wire. The tape piece should be smaller than the foil size.

9. Remove any trapped air bubbles by pressing down on the tape using a plastic razor blade.

10. Add glue (Loctite super gel) onto any visible opening around the tape and wire interface to completely seal the exposed wire.

11. Put polished foil with glued wire into a glass container. Flow in nitrogen for about 10 seconds and immediately cap the container.

12. Let the glue dry overnight under nitrogen atmosphere.

13. Finally, paint a layer of nail polish (acrylic based, generic brand) and let it dry for about 15-20 min to add an additional layer (1-2 mm thick) of protection and electrical insulation.
3. Anodization

1. Fill a water bath (Buchi B-491) to about ¾ full and set the temperature to 45 °C. Temperature reading is displayed on the LCD screen of the water bath.

2. Another thermocouple is placed in the water bath as a comparison with the reading on the LCD display. Temperature offset is usually not more than 1 °C.

3. Take out ammonium fluoride (JT Baker) from the dry box. Note: Ammonium fluoride salt should be stored under dry atmosphere because it is hygroscopic. Minimize the exposure time of salt to the surrounding air. Moisture will cause salt to form big clumps.

4. Put plastic weighing boat on digital measuring scale (Mettler Toledo) and tare (zero) the reading.

5. Using a plastic spatula, weigh in 1.74 g of ammonium fluoride salt corresponding to 0.67 M (avoid putting in clumps/big chunks).

6. Put a magnetic stirrer into 100 mL glass beaker (Kimble Chase, no pouring spout beaker). Beaker should be washed with water and nitrogen dried before anodization experiment.

7. Transfer the ammonium fluoride salt from the plastic boat to the beaker.

8. Pipet 3.5 mL deionized water and add it to the salt inside the glass beaker. The bulk of the salt should dissolve immediately.

9. Using a stir plate at 350 rpm, stir for about 1 min or until most salt dissolved and no large particles are visible.

10. Add 70 mL of glycerol slowly while keeping stirrer on. Use a plastic spatula to manually help the stirring process with glycerol. Stir for 10 s.
11. Cover beaker top with rubber stopper (VWR).

12. Put the beaker with the assembled electrolyte into the heated water bath and wait for 15 min to ensure the electrolyte equilibrates to the bath temperature. To make sure the water level in the water bath is just below the mouth of beaker, use a glass petri dish as a stand to raise the beaker to the appropriate height.

13. Without any connections, turn on the potentiostat and check that the voltage is set at 20 V by turning the voltage knob (Agilent 3612A). Turn it off after the voltage is set at the correct value.

14. Clip sample at one end of the exposed wire to one side of a pen-like probe. The other end of the probe connects to the multimeter terminal (choose miliampere channel) to allow current reading. Connect another cable from the ground terminal of the multimeter to the potentiostat terminal (positive).

15. Clip the counter-electrode (Platinum sheet, 127 μm) directly to the probe without using copper wire and connect to the potentiostat terminal (negative).

16. After both electrodes are properly placed then immersed them into electrolyte. Electrode distance is 3 cm, separated by 2 clips planted on rubber stopper to keep distance fixed.

17. Connect the USB terminal on the multimeter to the computer for data logging. Turn on the multimeter (Fluke 289A) and open Flukeview software on the connected computer.

18. Choose the “logging” function and change the time interval to 1 s (15 min is the default setting).
19. Click “start” and immediately turn on the potentiostat. Another window will pop up that will show real time data recording. There should be bubbles forming on the counter electrode side (hydrogen formation).

20. Let it run for 2 h. Turn off the potentiostat and click “stop” button on the Flukeview software. Choose “save as” function and name the file. The file is stored under default database, however you can also define new database from the “file” pulldown menu. The saved file will be in csv format which can be open in excel by choosing “export” from “file” pulldown menu. Current should fluctuate once the potentiostat is turned on, if it reading zero check that all the connection in circuit is not broken.

21. Immediately take out the sample and rinse multiple times with deionized water.

22. Continue rinsing with ethanol multiple times.

23. Dry sample under a nitrogen stream.

24. Take out wire and glue using razor blade while holding the wire in vertical position, be careful not to bend the sample.

25. Discard the electrolyte and excess salt during weight measurement into the appropriately labeled waste containers.

26. Wash beaker and stirrer with tap water and dry under a nitrogen stream.

27. If done, dump the water from the water bath into the lab sink and wipe it clean and dry.
4. HF Etching

1. Dilute the stock HF reagent (JT Baker, HF dip 50:1) to 0.1 vol% with deionized water (9 parts water, 1 part HF) into a glass beaker. Important: Please read and understand the safety procedures in the MSDS before handling HF, wear lab coat, gloves, and work under a chemical hood. Use a calcium gluconate cream as a first aid response to minor HF exposure or contact to the body.

2. Hold the foil using tweezers and then immerse the TNT foil fully in HF for 90 s (release tweezers).

3. Take out and wash with deionized water multiple times.

4. Wash with ethanol multiple times and dry under a nitrogen stream.

5. Discard HF into an appropriately labeled waste container for HF.
APPENDIX B

1. Solar Cell Fabrication

1. Clear the edges of TNT foil using a tape lift-off, each edge should be about 0.3 mm, leaving an active area close to 1x1 cm.

2. Put sample on a hot plate and turn on temperature to 100 °C, wait 10 min.

3. Increase temperature to 200 °C wait 10 min.

4. Increase temperature to 300 °C wait 10 min.

5. Increase temperature to 420 °C and leave it for 3 h (there is a temperature offset of about 20 °C, so actual temperature should be closer to 400 °C).

6. Turn off hot plate, cool down for 20 min,

7. Drill a small hole through two separate pieces of FTO glass (15 Ω/cm², Hartford Glass). Size of the glass is 1”x1.25”.

8. Clean the pieces of FTO glass by sonicating in soapy water, acetone and dry ethanol sequentially for 10 min each.

9. Use a Surlyn spacer (25 μm thickness, Solaronix) to sandwich and seal TNT foil and one of the drilled and cleaned FTO glass by heating to 120 °C. The spacer is cut using a razor and should be placed on the foil edges that has been cleared with tape earlier.

10. Perform vacuum drying by placing a suction line connected to a pump onto the drilled hole. Turn on pump and wait about 5 min.

11. Using a syringe containing about 1 mL ruthenium dye of cis-bis(isothiocyanato)-bis(2,2’-bipyridyl-4,4’-dicarboxylato)ruthenium(II) (N3, Solaronix, Switzerland)
in a dry ethanol solution at a concentration of $3 \times 10^{-4}$ M, inject the ruthenium dye by sticking the needle into the suction line, and then turn off pump so that the dye can infiltrate the TNTs. A pink color of the dye should be visible in the active region only.

12. Take off the Surlyn spacer using a razor blade, then soak TNT foil in dye solution for 24 h.

13. Spin coat a 0.05 M solution of H$_2$PtCl$_6$ in 2-propanol onto the other drilled and cleaned FTO glass. Pipet 50 μL solution at 2500 rpm for 1 min.

14. Heat platinized FTO glass at 450 °C for 20 min and then cool down.

15. Wash soaked TNT foil (after 24 h) with ethanol to remove any excess dye.

16. Put another Surlyn layer between TNT foil and platinized FTO glass and heat to 120 °C for sealing.

17. Introduce a liquid electrolyte of 0.5 M lithium iodide (LiI)/0.05 M iodine (I$_2$) through the drilled hole on the FTO glass through a similar process as with the dye. Liquid electrolyte should completely fill the active area (yellowish color).

18. Hole can be sealed using Surlyn, heat to 120 °C and cool down to room temperature.

2. Solar Cell I-V Characterization

1. Turn on main power supply (watch “power mode” lit up).

2. Turn “lamp on” switch on the main power supply.

3. To calibrate light source, uncap Si photodiode and put under light illuminator for 3 min.
4. Cool down Si photodiode for 1 min until power meter reading does not fluctuate. Put Si photodiode cap back on.

5. Zero the optical power meter (Newport 1916-C).

6. Clip a black gasket with a 0.26 cm$^2$ hole on top of the photodiode and center it to the light source.

7. Change the lens focal point using the condenser knob as necessary.

8. Record the light intensity value on the optical power meter.

9. Clip a black gasket with a 0.26 cm$^2$ hole on top of the platinized FTO glass to perform backside illumination.

10. Connect the working electrode and counter electrode to the solar cell. Refer to the terminal color chart pad located near the equipment.

11. Place cell under light illuminator.

12. Open Gamry Framework software, choose “Experiment” then “Physical Electrochemistry” (Option B) then “Linear Sweep Voltammetry” (Option 6).

13. Name the sample.

14. Choose range for voltage sweep and scan rate. Press start.

15. When scan is finished, choose “F2-skip” option.

16. Turn off lamp by pushing “lamp off” button.

17. Wait 15-20 min before turning off power supply.

18. Turn off power supply.

19. Choose “Echem Analyst” program to open file. Choose “all files” from pull down menu next to file name and pick the saved file.

20. To open file with Excel instead, right click file and choose “open”.