The Pennsylvania State University

The Graduate School

Department of Materials Science and Engineering

# FABRICATION OF NANOSTRUCTURED COPPER OXIDE VIA

## ANODIZATION IN ORGANIC ELECTROLYTES

A Thesis in

Materials Science and Engineering

by

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### ABSTRACT

Copper oxide is a material that has attracted interest for a wide range of applications. Due to its relatively low cost, non-toxicity, and its nature as a p-type semiconductor material with narrow band gap of 1.2 eV for CuO, it has the potential for use as a photoactive material in the visible-light region. However, given its rather weak absorption profile that suffers from recombination in the bulk, reducing the photogenerated carrier diffusion distance by introducing high surface-area nanoarchitectures is one route to circumvent this problem.

Thin films of copper oxide nanoarchitectures were synthesized via anodic oxidation of copper foil in organic electrolytes with fluoride-bearing ions. Ethylene glycol (EG) and dimethyl sulfoxide (DMSO) were the solvents studied. The obtained structures were found to depend on the pH of the anodizing electrolyte, water content, temperature, voltage, and acid concentration. Nanoporous structures were formed under certain conditions in NH<sub>4</sub>F + EG electrolytes, while nanowire structures were present in HF + DSMO electrolytes. Annealing the films in O<sub>2</sub> gas achieved full conversion to CuO composition. Photocurrent measurements indicated the p-type nature of the CuO device and a photoresponse to broad-wavelength visible light.

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## Chapter 1 Introduction

#### 1.1 Emerging Energy Problem

The U.S. Energy Information Administration (E.I.A.) estimated in 2007 that global energy demand was 495 quadrillion BTU, and is expected to rise by roughly 50% to 740 quadrillion BTU by the year 2035.<sup>1</sup> Today, fossil fuels account for more than 80% of global energy consumption, and considering the majority of the world's fossil fuels are harvested outside the U.S., this puts our nation, as well as others that import their energy, in a precarious position that relies too much on external factors. Furthermore, many of the fossil fuel reserves lie in unstable regions of the world with delicate political and foreign policies. This makes the fossil fuel market extremely volatile, as evidenced by energy shortages over the past few decades and alwaysfluctuating gas prices. As the world's population and energy demand steadily increases, and natural resources become scarcer and more difficult to extract, there will only be more competition for those resources, leading to increased costs of fuel in the long run. The necessity to continue fueling our economy keeps our focus fixated on parts of the world that do not necessarily want our intervention and influence, which may lead to conflicts of interest, disputes, and ultimately in some cases, military intervention and the associated astronomical costs. Therefore it is of great importance to reduce our dependence on foreign fossil fuels, and rather focus on meeting our energy demands from within.

In addition, the consumption of fossil fuels is damaging to the sustainability of the Earth. Damage to the ozone layer, increases in particulates in the air we breathe, smog covered metropolitan centers, and the reduction of undeveloped land, are examples that all contribute to permanent damage to the Earth. As a result, climate change mitigation has been an important

topic of debate, especially over the last ten years as we begin to fully understand the consequences of our unchecked consumption. In a statement from the Tokyo Summit in 2010, the  $E_8$  chairmen issued a statement that the "smart use of electricity" is the key to a greener, safer, and more sustainable lower-carbon society on both the supply and demand side. Lower carbon-emitting technologies, and a more efficient use of electricity, will lead to decreased primary energy use and lower CO<sub>2</sub> emissions, as well as robust energy security and a better quality of life.<sup>2</sup>

### **1.2** Harvesting Solar Energy as a Sustainable Solution

Several sustainable technologies have been developed in response to the global energy challenges presented above. The emergence of the renewable energy sector in the last quarter century is a direct result of this. Sustainable methods to harvest renewable sources such as solar, wind, geothermal, and tidal have been developed with moderate success and rates of efficiency. However, renewable energy sources have always suffered from technology that is cost-prohibitive, and since our economy is based on monetary, profit-driven decisions, these technologies have only been implemented in niche markets and have yet to obtain widespread use. One of two things would need to happen for the world to adopt renewable energy as their primary energy source. Either the cost of these technologies would have to come down to be competitive with fossil fuel sources, or the efficiency of these technologies needs to increase. In either case, only then would renewable energy sources become an attractive alternative to fossil fuel sources, to both consumers and the policymakers who spearhead and initiate change.

Of these emerging technologies, it is the belief of this author that only a combination of these renewable sources can fully provide the energy needs of a given community, and that the solution will be unique to each location with different geographical features. Tidal energy would only be available to coastal communities, wind energy is only harvestable in landscapes with distinct and consistent wind profiles, etc. However, of all the current technologies offered, the harvesting of solar energy is the most viable for many parts of the world. Every part of the world receives at least some sunlight every day. In an era of dwindling fossil fuel reserves, the sun remains the most abundant source of clean energy.



Figure 1. The solar radiation spectrum (from www.nasa.gov)

Efficient harvesting of sunlight would allow humanity to tap into this vast reservoir, which is more than enough to satisfy today's energy demand. The solar constant is defined as the amount of incoming solar radiation per unit area and is measured on the outer surface of Earth's atmosphere, and its value is 1366 W/m<sup>2.3</sup> The solar constant includes all types of solar radiation, not just visible light. This polychromatic light has different numbers of photons depending on the wavelength. Refer to Figure 1 for the solar spectrum. In order for solar energy

conversion to be a viable alternative to existing technologies, the production of the technology would have to be cheap, and at the same time the net energy generation would have to be substantial. Today's production quality solar cells average around 10% efficiency, but are still too expensive to gain widespread adoption. It currently costs roughly \$4 to produce a single watt of electricity using a conventional, single-crystalline silicon solar cell (averaged over its lifetime) while it only costs about \$0.80 using fossil fuels such as oil and natural gas.<sup>3</sup> Therefore, improvement of efficiency and the reduction of cost is a high priority in both research laboratories and manufacturing.

### **1.3 Regenerative Photoelectrochemical Cells**

There are many ways to harvest solar energy, but one device that enjoys extensive research efforts is the regenerative photoelectrochemical cell, which converts light to electric power leaving no chemical charge behind. See Figure 2 for the schematic representation. This type of cell is also known as a liquid junction cell, and consists of a cathode and anode in a fixed electrolyte solution, with either or both elements being photoactive. The photoactive electrode is a semiconducting material that has a band gap of magnitude that can be overcome by incident photons. Electron-hole pairs are generated upon irradiation by photons with energies that exceed the band gap. Minority carriers are scavenged by the redox species in the electrolyte. Electron-hole pairs are separated and prevent recombination. Majority carriers travel through the semiconductor and through the external circuit to the counter electrode, where they regenerate the redox species in the electrolyte. Through this process, a photovoltage and photocurrent are generated, thus effectively converting light into electricity.

This type of device is of interest for the purpose of the present study. A wide range of metal-oxide semiconductors have physical, chemical, and band-gap properties that are desirable for stable use in a photoelectrochemical cell.



Figure 2. Schematic of regenerative photoelectrochemical cell.<sup>7</sup>

### 1.4 Characteristics of Nanostructured Metal Oxides

Nanostructured materials are defined as artificially synthesized materials that have distinct and repeatable features on a length scale less than 100nm. The motivation for synthesizing materials with such small features is that they can exhibit unique materials properties compared to their bulk counterpart, often resulting in superior device performance.<sup>4</sup> The following discussion illustrates why they are ideal for solar energy harvesting.

The performance of these devices is largely dependent on geometrical parameters of the features. For example, ordered nanotubular structures have been proven to exhibit superior performance in a range of devices. When used as hydrogen sensors, ordered titania (crystalline TiO<sub>2</sub>) nanotube arrays of 1µm length exhibit a 50,000,000% change in electrical resistivity at room temperature in response to 1000ppm hydrogen.<sup>5</sup> One reason is their extremely high surface areas compared to bulk materials. The surface area-to-volume ratio of a nanotube array

is extremely high, and increases both with increasing tube length and decreasing tube diameter. Owing to their increased surface area, nanostructured materials provide additional surface states which can effectively reduce the band gap.<sup>6</sup> Also, the directional nature of the nanostructure promotes vectorial charge transport through the nanotubular layer.<sup>7</sup> Nanostructured materials often have a greater degree of porosity as well, which can promote enhanced light scattering within the porous structure, leading to more effective photon adsorption and ultimately an increase in device efficiency when compared to a flat electrode.<sup>8</sup>

Metal oxides are a class of ceramic materials that are particularly diverse for a number of reasons. Among the most important is the fact that starting materials are abundant and cheap, and there are several low-cost fabrication methods available, without a loss in purity or increase in defects. Low cost fabrication methods are necessary in order to improve the competitiveness in the market compared to more conventional methods of energy generation. Synthesis of these materials is possible at room temperature and pressure, which greatly simplifies the process and reduces costs.

The stability of metal oxide materials in many media makes them attractive candidates for a wide range of applications. For example, the metal-oxygen bonds in  $TiO_2$  can resist breakdown in many environments, such as air, aqueous and organic media. In crystalline form, the covalent linkages result in high metal-oxide bond strengths, which are non-toxic and resist further reaction, photocorrosion, or decomposition at high temperatures.<sup>9</sup>

Many metal oxide compositions have desirable semiconducting properties as well, which are essential for potential use in a regenerative photoelectrochemical cell. In order to be useful for solar energy harvesting, the band gap of a material must be less than the energy of an incident photon. Light in the visible range carries a value between 1.6 and 3.4 eV, depending on exact wavelength. Therefore metal oxides that are equal to or below these values are of greatest importance for practical solar applications. For example, the anatase phase of titania has a band gap of 3.2 eV, which only captures a portion of the visible light energy, and is far

more efficient when illuminated with light in the UV portion of the spectrum. Great efforts have been made to narrow the band gap. Nanoporous iron (III) oxide, on the other hand, exhibits a 2.2 eV band gap, which is more suitable for conversion of visible light.<sup>10</sup> Copper (II) oxide has an even lower band gap of 1.2 eV, and has the potential to be more efficient at visible and near infrared light conversion than nanostructured metal oxides with larger band gaps.

#### 1.5 Anodic Oxidation

One widely accepted and low-cost method for synthesis of novel nanostructured materials is via anodic oxidation. This method uses an electrolytic cell where electrochemical reactions are driven within a solvent medium via an external bias. In this system, the external bias forces electrons to flow from the electrolyte to the anode, and from the cathode to the electrolyte. See Figure 3. The external bias is necessary, as the Gibb's free energy ( $\Delta G$ ) of the cell (without any bias) is positive which prevents spontaneous reactions to reach a lower energy state. The two overall electrochemical reactions and anodic current flowing from the metal to solution, while the reduction of the ion in the electrolyte results in cathodic flow from solution to the metal. In effect, the oxidation takes place at the anode, hence the term "anodic oxidation", and reduction takes place at the cathode electrode.

In a suitable electrolyte, such as one with reactive fluoride-bearing ions, the metal resists chemical etching of the surface by forming a thin passivation layer on the surface. The passivation layer is formed via ionic conduction, in which an oxide layer is generated at the metallic anode surface. The growing oxide layer reduces the flow of electrons through the cell, since the oxide has a higher resistivity value than the pure metal. Ohm's law (V = IR) defines this phenomenon, and in the case of potentiostatic anodization, the applied voltage V is fixed.



Figure 3. Electrodes in an electrolytic cell.<sup>9</sup>

Three simultaneously occurring processes result in nanostructure formation via anodic oxidation in media containing reactive anions (such as fluoride ions): the field-assisted oxidation of metal to form an oxide surface, the field-assisted dissolution of metal into electrolyte, and the chemical dissolution of metal and oxide due to etching by the anion, which is enhanced by presence of H<sup>+</sup> ions.

### 1.6 Electrochemistry in Non-Aqueous Electrolytes

When forming an anodic oxide film, pores must first be formed as nucleation sites. Pore initiation is controlled by the availability of oxygen anion carriers that can be donated to the metallic surface. Water is one polar molecule that can easily dissociate to donate free oxygen anions that contribute to pore formation. Its presence (or another suitable oxygen donator) must be present in the electrolyte. However the water must be present in amounts small enough to inhibit hydration, and instead promote oxide formation. Hence the degree of pore formation depends strictly on the electrolyte properties. Organic solvents have been used for many decades as hydration inhibitors in various anodic film growths. Anodic oxidation is strongly

dependent on the physical and chemical properties of the electrolyte, as well as the solvent structure.

#### 1.7 Research Objectives – Novel Nanostructures of Copper Oxide Materials

The exploration of anodization of several metals has led to the formation of novel nanostructured oxide materials with robust materials properties. Oxides of aluminum, titanium, iron, tantalum, and others have led to free-standing, stable, uniform nanotube and nanowire growth. These materials possess high surface areas and desirable semiconducting properties that are potentially invaluable in solar energy harvesting applications. Still, there remain many obstacles in applying these materials to applications suited for energy harvesting from the *visible light portion* of the UV spectrum. Copper oxide is a stable, non-toxic, semiconducting material with a band gap of 1.2 eV, which has the potential to capture a larger portion of the solar spectrum and contribute to higher overall conversion efficiencies. Studies of anodic oxidation of copper have been less successful in achieving novel nanostructures, and therefore it is the objective of this work to obtain novel copper oxide nanostructures suitable for use in a photoelectrochemical cell.

Chapter 2 will review the literature relevant to the evolution of the current understanding regarding the oxidation of metals via a variety of methods. It discusses the various synthesis routes and advantages and disadvantages of each, and how they relate to the synthesis method in the current work: anodic oxidation. Chapter 3 reviews the experimental details that were followed to collect data and results. Chapter 4 discusses the results on anodization of copper foil in ethylene glycol electrolyte, after a brief introduction on its anodization in aqueous electrolytes. Chapter 5 discusses the results from further studies in DMSO electrolyte. Chapter 6 summarizes this work, discusses the potential applications that might benefit from the development of this technology, and the necessary future studies to gain a more complete

understanding of the mechanisms governing the growth of the nanoarchitectures described herein.

## Chapter 2 Literature Review

#### 2.1 Nanoporous Metal Oxide Growth

Various routes to self-organized nanoporous metal oxide growth have been investigated for the past four decades, ever since the discovery of nanoporous aluminum in 1970.<sup>11,12</sup> Porous oxide growth of alumina has guided the electrochemical synthesis of other novel metal-oxide nanostructures, including those of titanium, zirconium, hafnium, niobium, tungsten, and iron. Various methods of fabricating these novel nanoporous structures have been proven, including acid-base washing,<sup>13</sup> template deposition,<sup>14</sup> sol-gel synthesis,<sup>15</sup> and hydrothermal methods.<sup>16</sup> However, the technique of anodic oxidation has been proven to allow for facile and low-cost synthesis methods for several metals. The growth of nanotubular anodic aluminum oxide (AAO) has been well studied and can be highly tuned using anodic oxidation, being developed to the stage where it is now often used as a template for the growth of other nanostructured materials.

Dekker and Middelhoek, in their pioneering studies, anodized aluminum thin films in oxalic acid, and achieved a uniform, porous oxide layer of Al<sub>2</sub>O<sub>3</sub>. They operated on the belief that the structure of these films depends heavily on the electrolyte used, and particularly on the degree to which it acts as a solvent for the oxide. In a solution containing oxalic acid, or other acids which attack the oxide, a porous layer is obtained. In contrast, anodization in an electrolyte consisting of boric acid resulted in formation of a compact uniform layer. Their results indicate that for a given anodization electrolyte, the porosity depends only on anodization voltage, and that porosity decreases with increasing voltage. They also determined that the growth of these films is determined solely by the formation of oxide at the oxide/metal interface.

As stated in Chapter 1, in an electrolyte containing fluoride-bearing ions, nanotube formation of many metals occurs as a result of three simultaneously occurring processes: (1) the field-assisted oxidation of metal to form the oxide layer, (2) the field-assisted dissolution of metal ions in the electrolyte, and (3) the chemical dissolution of metal and oxide due to etching by the fluoride ions.<sup>7</sup> The delicate balance of these reactions is achieved only when synthesis parameters such as temperature, fluoride ion concentration, water concentration, and anodization potential, occur in certain ranges. This range of successful parameters is specific and unique to each metal undergoing anodization.

O'Sullivan and Wood were the first group to suggest a basic mechanism to describe the pore formation and growth behavior in the anodization of metals such as aluminum.<sup>17</sup> Their proposal indicated that the steady-state barrier layer thickness is determined by the equilibrium between the oxide growth at the metal-oxide interface and the field-assisted dissolution of the pore bases in the metal. Pore formation commences due to the concentration of the electric field in the depressions of the oxide barrier layer. This barrier layer is never a defect-free surface, which, like all materials, naturally has surface imperfections on the nanoscale. These depressions, at which the barrier layer dissolves faster, eventually develop into the precursors of well-developed pores.

When the anodizing voltage is applied, the surface variation induces changes in volume such that sections of thicker barrier layer thickness (on the scale of tens of nanometers) act as nucleation sites, and grow in size until they merge. Thin areas of oxide are left between them, which become further depressed, and penetrate further and deeper into the metal. These areas eventually create a scalloped pore base which constitutes the basis for nanotube formation. As the current density increases, the pore diameter increases, leading to an overall smaller number of larger pores. Finally the steady state is reached, where pore diameters no longer increase, and nanotube length increases linearly with time. This situation is depicted visually in Figure 4,

along with the corresponding current density plot, and can be broken down into four distinct stages:<sup>7</sup>

- Immediately following application of anodic bias, barrier oxide layer begins to grow.
- (II) Prior to true pore formation, small variations in the outer regions of the barrier layer are formed.
- (III) Propagation of thick and thin sections of barrier layer lead to well-defined scalloped pore bases.
- (IV) Steady-state pore structure is formed by closely packed cylindrical cells, indicated by the lack of a rate of change of current density  $(\partial^2 J/\partial t^2 = 0)$ .



Figure 4. Schematic describing the evolution of porous structure during potentiostatic anodization of aluminum.<sup>7</sup>

### 2.2 Synthesis of TiO<sub>2</sub> Nanotube Arrays

After the nanoporous alumina discoveries, titania was one material that was widely investigated due to many of its useful engineering properties, such as its stability in a variety of media, non-toxicity for biomedical applications, photoresponse and resistance to photocorrosion, and desirable band gap properties.

Although many methods have been developed to fabricate novel titania nanostructures with high surface areas and aspect ratios, none of the synthesis routes could replicate the highly ordered, vertically-oriented nanotube arrays obtained via anodization in a fluorinated based electrolyte. This method allows for the self assembly of precisely controlled nanostructures that are free standing, forgoing the need for a template such as anodic aluminum oxide (AAO).

For over a decade, the anodization parameters to achieve nanotubular architectures of titania have been investigated. Parameters such as anodization potential, time, and electrolyte composition distinctly affect the nanotube morphologies. The initial report of TiO2 nanotube arrays came in 2001 when Gong et al. developed 500 nm length nanotubes that were grown in an aqueous HF-based electrolyte.<sup>18</sup> See Figure 5 for corresponding FESEM images and Figure 6 for a schematic representation, indicating that the barrier layer grows in thickness as the metal layer is etched. They used a two-electrode electrochemical cell containing 0.5 - 3.5 wt% HF with applied potential between 3 and 20 V. However, due to HF's dissociation constant of  $K_{\alpha} = 3.5 \times 10^{-4}$  [pK<sub>a</sub> = - logK<sub>a</sub> = 3.5], at pH < 3.45, a large amount of free HF exists near the anode where it is generated. This resulted in a rapid rate of oxide dissolution and short nanotubes. They were motivated to achieve longer nanotube lengths by modifying the electrolyte composition, and were successful with the incorporation of an aqueous buffer. By controlling the pH, they decreased the oxide chemical dissolution rate, resulting in enhanced tube lengths. They also found that reducing the anodization temperature to near freezing yielded a doubled tube length. Subsequent studies indicated that nanotube growth benefits from mildly reducing conditions in the electrolyte.



Figure 5. FESEM images showing top-view and cross-section of TiO<sub>2</sub> nanotube arrays fabricated in 0.5 wt% HF aqueous electrolyte at 20 V for 20 min.<sup>18</sup>



Figure 6. Schematic representation of a generic metal oxide nanoporous array structure obtained via potentiostatic anodization.<sup>10</sup>

In comparison to aqueous electrolytes, the donation of oxygen is more difficult in organic electrolytes, thus organic electrolytes are more reducing compared to a purely aqueous electrolyte.<sup>19</sup> Due to this fact, successful anodization techniques were further developed by

using non-aqueous polar organic electrolytes such as formamide (FA), N-methylformamide (NMF), dimethyl sulfoxide (DMSO), and ethylene glycol (EG), in combination with a fluoridebearing species, such as HF, NH<sub>4</sub>F, and/or KF. The inclusion of water is also an essential element for nanotube growth in organic electrolytes. Water must be present because it easily dissociates to donate free oxygen that assists in the oxide growth. However, achieving long nanotube arrays requires the water content to be less than ~5%, in which case the chemical dissolution of the oxide is minimized and optimal growth rates can be sustained.<sup>9</sup>

In 2005, Ruan et al. used a mixture of DMSO and HF to fabricate  $TiO_2$  nanotube arrays of 2.3 mm length.<sup>20</sup> They used a DMSO – 4% HF electrolyte at a potential of 20 V for 70 hrs at room temperature. In 2007, Yoriya et al. improved the length by a factor of 50, by using a DMSO – 2% HF electrolyte at 60 V for 70 hrs. For a given pore diameter and wall thickness, the internal surface area increases almost linearly with tube length. This increase in tube length resulted in a surface area per geometric area (geometric roughness factor) of ~3475.<sup>21</sup>

Mor et al. proposed a mechanism for the anodic formation of TiO<sub>2</sub> nanotubes in acidified electrolytes based on their observation of the anodization process on aqueous-based HF electrolytes.<sup>22</sup> They determined that the chemical dissolution of titania in the HF electrolyte is a key factor in the formation of nanotubes over simpler nanoporous structures. The dissolution must be high enough to penetrate pore bottoms and facilitate nanotube lengthening; however the chemical dissolution also must be low enough so that it does not etch away the nanotube walls.

They concluded that the key processes to nanotube formation use the following mechanism:<sup>7</sup>

Oxide growth at the surface of the metal due to interaction of the metal with O<sup>2-</sup> or OH<sup>-</sup> ions and migration of these anions through the oxide layer after formation of the initial oxide layer.

- (ii) Ejection of the  $Ti^{4+}$  cations from the  $Ti TiO_2$  interface and the migration of these cations through the oxide toward the oxide-electrolyte interface.
- (iii) The Ti O bond is weakened due to polarization from the applied electric field, resulting in the dissolution of metal cations.  $Ti^{4+}$  cations migrate toward solution and  $O^{2-}$  anions migrate to the metal surface.
- (iv) Chemical dissolution of Ti and TiO<sub>2</sub> in the acidic electrolyte, critical for the selforganized formation of nanotube arrays. Reduction of the oxide barrier layer keeps the electrochemical processes active.

The overall reaction for the anodization of titanium, immediately following the onset of anodization, can be represented by Equation 1:

$$Ti + 2 H_2 O \rightarrow TiO_2 + 4 H^{\dagger}$$
(1)

The oxide layer undergoes pitting due to localized dissolution of the oxide from the Fions. The barrier layer at the pottom of the pits is kept thin, increasing the electric-field intensity across the remaining barrier layer, further driving pore growth.

These processes can be represented by examining the current density during anodization, such as the schematic in Figure 4. Initially, the formation of the thin insulating barrier oxide layer is indicated by a drop in the current density, since the oxide layer inhibits conduction relative to the metal (Figure 4-I). The current flow then transitions from all-electronic to all-ionic as the barrier layer is formed. At this point the fluoride ions cause pitting on the surface, acting as pore nucleation sites (Figure 4-II). The reduced oxide layer thickness during this time indicates an increase in the current density (Figure 4-III). The current maximum corresponds to when the pore density reaches saturation. After saturation of pore density, the steady-state is reached where nanotube growth is stable (Figure 4-IV). This may be indicated by an unchanging current density, or a linearly increasing or decreasing current density, depending on the electrolyte composition. Figure 7 indicates the current-time behavior during the first 30 mins of anodization of Ti in an EG – NH<sub>4</sub>F – H<sub>2</sub>O electrolyte, while varying voltage.



Figure 7. Voltage-dependent time-current behavior during the first 30 minutes of anodization of Ti in an 0.3 wt% NH<sub>4</sub>F, 2 vol% H<sub>2</sub>O in ethylene glycol electrolyte.<sup>7</sup>

## 2.3 Anodization of Other Metals

Following from the pioneering studies of anodic growth of AAO and TiO<sub>2</sub>, similar systems since have been explored with other metals, with varying degrees of success.

#### 2.3.1 Iron Oxide

Iron (III) oxide (Fe<sub>2</sub>O<sub>3</sub>) is a widely available non-toxic material with a visible spectrum bandgap,<sup>23</sup> therefore giving the material considerable interest for achieving cost-efficient and durable photoelectrochemical cells. Many attempts have been made to fabricate ordered nanostructures of iron (III) oxide. In 2005, Duret et al. have achieved photocurrents in the mA range under AM 1.5 solar illumination. Via ultrasonic spray pyrolysis, mesoporous haematite thin films consisting of 5-10nm thick nanoleaflets were fabricated.<sup>24</sup> In 2006, Gratzel et al. fabricated silicon-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanodes,<sup>25</sup> while Ingler et al. recently reported an  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> based self-biased photoelectrochemical cell.<sup>26</sup>

However novel these studies were, none took advantage of the self-aligning methods of anodization without the use of a template. Building upon prior expertise in the fabrication of highly ordered titania nanotube arrays, Prakasam et al. reported on the synthesis of self-aligned nanoporous iron (III) oxide nanostructures via anodization. Electrochemical oxidation of an Fe foil was performed to achieve a nanoporous film. Subsequently, the amorphous film was annealed to form crystalline haematite, which is a thermodynamically stable crystallographic phase of Fe<sub>2</sub>O<sub>3</sub> that is abundant, stable, non-toxic and contains a band gap in the visible region of the UV spectrum.

In this study, glycerol was used as the electrolytic medium due to its lower diffusion coefficient working to prevent acidification at the oxide-electrolyte interface. Highly self-organized nanopores were observed in an electrolyte containing 1% HF + 0.5% ammonium fluoride ( $NH_4F$ ) + 0.2% nitric acid ( $HNO_3$ ) in glycerol at 10°C. Figure 8 shows FESEM images of this synthesis over three voltages, indicating increased porosity with increased voltage. Pore size measured approximately 50 nm at 40 V, 100 nm at 60 V, and 150 nm at 90 V. Below 25 V the formed oxide surface layer exhibited no porosity.

The system also appeared to be very sensitive to temperature. Samples anodized below 5°C did not exhibit pore formation, even after anodization for over 2 hrs. Samples anodized above 15°C gave way to a porous structure but with much lower pore density. For sample conditions that resulted in a nanoporous surface, continuing anodization for prolonged times did not result in enhanced porosity and in many cases destroyed the nanoporous structure that would have resulted from a shorter anodization time. Figures 9(b,c) show FESEM images depicting the change in nanoporosity of the surface between 30 min and 1 hr anodization times. Figure 9(a) indicates the current-time behavior of the anodization process for the glycerol-based bath, which is notably different than for example, the anodization of Ti in  $NH_4F - EG$  (which is known to produce nanotubes). The characteristic minimum in the current density profile is missing; rather the current drops to a minimum value and does not subsequently increase,

which would be characteristic of stable pore formation and nanotube growth. Hence no nanotubes are achieved under these anodization conditions.



Figure 8. FESEM images of iron anodized in 1% HF + 0.5% NH<sub>4</sub>F + 0.2% HNO<sub>3</sub> in glycerol at 10°C: (a) 40 V, (b) 60 V, (c) 90 V.<sup>10</sup>



Figure 9. (a) Current-time behavior during potentiostatic anodization of Fe foil at 10°C in nitric acid (HNO<sub>3</sub>), ammonium fluoride (NH<sub>4</sub>F), hydrofluoric acid (HF) in glycerol at 40, 60, and 90 V (b) FESEM image of the sample after 30 min anodization (c) FESEM image of sample after 1 h anodization in the same electrolyte.<sup>10</sup>

Prakasam concluded that the anodization bath temperature and NH<sub>4</sub>F concentration were the two primary parameters responsible for controlling the sample morphology. It was observed that at 4°C (a temperature outside the range for porous surface at 0.5% NH<sub>4</sub>F), doubling the concentration of NH<sub>4</sub>F to 1% increased the rate of oxidation and field assisted dissolution, enabling well-defined pores. Furthermore, the effects of temperature (for the same acid concentration) indicate that the field-assisted dissolution is a thermally assisted process, in agreement with anodic growth of alumina.

#### 2.3.2 Tantalum Oxide

Tantalum oxide is another material that has received considerable attention in the literature for its applications in use as a protective material, catalyst, capacitor, resistor, and optical device, as well as in biomedical applications.<sup>27</sup> Anodization of tantalum has been widely studied in a variety of electrolytes, but yielding nanoporous films,<sup>28</sup> nanodots,<sup>29</sup> nanodimples,<sup>30</sup> and hollow spheres.<sup>31</sup> Only recently has its ability to form nanotubes via anodization been discovered. In 2008, Allam et al. developed nanotube arrays using an electrolyte bath containing HF and H<sub>2</sub>SO<sub>4</sub>.<sup>27</sup> In volumetric ratios of 1:9 and 2:8, anodization at 10 – 20 V resulted in ordered a nanodimpled surface with 40 – 55 nm pore diameter.

The addition of 5 – 10% of either EG or DMSO to the HF –  $H_2SO_4$  bath resulted in the formation of  $Ta_2O_5$  nanotube arrays up to ~20 µm thick.<sup>27</sup> However, they found that the concentrated HF solution induced a violent electrochemical reaction, leading to the separation of the nanotube arrays from the underlying substrate in as little as 120 s.<sup>32</sup> It is believed that the interfacial stress between the oxide film and the substrate metal layer was the cause.<sup>33</sup> Therefore in subsequent experiments, 85% of the HF solution was replaced with deionized H<sub>2</sub>O, allowing the anodization reaction to be readily controlled over several hours.

Figure 10 shows FESEM images of anodization at 15 V for 30 min, and indicates that the nanotubes have an average outer diameter of 45 nm and an average length of 6  $\mu$ m.<sup>32</sup> Furthermore, the nanotube arrays were very stable and homogeneous, resulting from the addition of H<sub>2</sub>O to the electrolyte bath. Figure 11(a) indicates that the nanotube length increased with increasing applied voltage, for both EG and DMSO additives. Figure 11(b) shows the current-time behavior, illustrating the dip-rise-gradual fall profile indicative of nanotube formation, in agreement with Ti in aqueous or organic fluorine-containing solutions.



Figure 10. FESEM images of Ta<sub>2</sub>O<sub>5</sub> nanotube arrays anodized at 15 V for 30 min (a) top image (b) bottom surface (c-d) cross section views.<sup>27</sup>



Figure 11. (a) Variation of nanotube length as a function of anodization voltage for samples fabricated in the presence of EG and DMSO. (b) Anodization current-time response of Ta samples anodized in different electrolytes.<sup>27</sup>

Feng et al.<sup>32</sup> were then able to anneal the  $Ta_2O_5$  nanotube arrays in ammonia at 700°C for 10 h in order to convert to  $Ta_3N_5$  composition. Tantalum nitride has a band gap of approximately 2.07 eV, making more than 45% of the incident solar spectrum energy available for solar energy conversion. The stability of the film combined with these physical properties

make tantalum nitride an attractive candidate for applications in water splitting and solar generation of hydrogen via water photoelectrolysis.

#### 2.4 Copper Oxide Nanoarchitectures

#### 2.4.1 Copper Oxide Properties

Copper oxide exists as either copper (II) oxide, CuO, or copper (I) oxide, Cu<sub>2</sub>O. It is an attractive material to research for a number of reasons, including its diverse range of potential applications, non-toxic nature, abundance of starting material (copper), and relatively cheap processing. In either form, it exists as a non-stoichiometric p-type semiconductor, with a direct band gap of 2.17 eV for Cu<sub>2</sub>O, and 1.2 eV for CuO.<sup>34</sup> Therefore copper oxide has become a highly desirable material for use in solar energy conversion applications such as CuO and Cu<sub>2</sub>O-based solar cells. In addition, Cu<sub>2</sub>O's conduction and valence bands are located near the reduction and oxidation potentials of water, respectively, which enables Cu<sub>2</sub>O to produce hydrogen by direct water photolysis with little or no external bias.

However, the absorption profile of copper oxide in the visible range is rather weak, implying that for a flat copper oxide electrode under solar illumination, a significant fraction of charge carriers will be generated in the bulk of the oxide and lost in recombination.<sup>35</sup> This problem can be overcome by utilizing an oxide layer with porous nanoarchitecture that has been proven for other materials, such as GaP and SiC.<sup>36,37</sup> In such porous structures, all charge carriers are photogenerated within a small distance of the semiconductor – electrolyte interface, and charge carrier separation will be more efficient. In addition, multiple light scattering in a porous structure enhances the effective absorption. Due to the motivation of this research being the maximization of efficiency of visible light harvesting, the focus of this thesis has been to

utilize copper oxide with as low a band gap as possible, while retaining semiconductor properties; therefore production of CuO is of greatest interest.

CuO belongs to the monoclinic crystal system, with a crystallographic point group of  $C_{2h}$ . Its lattice parameters are given in Table 1 below, and the unit cell is depicted in Figure 12.<sup>38</sup>

Table 1. CuO monoclinic crystal lattice constants

а	4.6837 A
b	3.4226 Å
C	5.1288 Å
α	90°
β	99.54°
Y	90°



Figure 12. CuO unit cell indicating the copper atom coordinated by four oxygen atoms in approximately a square planar configuration.<sup>38</sup>

### 2.4.2 Nanostructured Copper Oxide Literature

The literature available for the synthesis of nanostructured copper oxide thin films is abundant for a variety of experimental techniques, but remains largely unsuccessful for anodic oxidation on metallic copper substrate. Since the 1970s, CuO/Cu<sub>2</sub>O has been a material of interest for photovoltaics applications and potential use as a p-type semiconductor.<sup>38</sup> However it has not been used in any major device applications. It has proven a difficult task to isolate either CuO or Cu<sub>2</sub>O; usually a mix of the two is produced.

Thermal oxidation is the most widely used method of obtaining copper oxide for the fabrication of solar cells. Resistivities of polycrystalline copper oxide lower than 100  $\Omega$ -cm have been reproducibly obtained. The procedure involves the oxidation of pure copper at an elevated temperature (> 1000°C). The length of this oxidation will determine the thickness of the oxide layer, and the oxidation step is followed by annealing the sample at 500°C and quenching in cold water.<sup>39</sup> This method is well-documented, but does not allow for the fabrication of a high surface area and high aspect ratio film, and generally results in thicker films. The high temperature processes usually limit the control of fine interfacial features of the oxide films, which significantly affect the optical and photoelectrochemical properties of the resulting oxide.<sup>40</sup>

Reactive sputtering is a process in which thin (< 1 $\mu$ m), uniform, and low resistive films can be obtained. For the interested reader, Drobny and Pulfrey have detailed an experimental study on the electrical and optical properties of reactively sputtered Cu<sub>2</sub>O films.<sup>41</sup> They conducted both dc and rf sputtering of copper in an oxygen-argon mix, and they discovered that the resistivity of the copper oxide thin film could readily be controlled by simply varying the oxygen partial pressure.

Electrodeposition has been an attractive method for producing copper oxide thin films at atmospheric temperature and pressure, simplifying the synthesis process. Using this method, amorphous films are deposited, and annealing in oxygen above certain temperatures achieves crystallinity. Cu<sub>2</sub>O films have been reported to be electrodeposited by cathodic reduction of an alkaline lactate solution on copper substrate. The properties of electrodeposited films are similar to those of thermal oxidation, however they suffer a comparatively high resistivity  $(10^4 - 10^6 \Omega - cm)$  due to a higher density of defect states.

Template assembly<sup>42,43</sup> and colloidal methods<sup>44,45</sup> have also been reported in the literature for copper oxide nanoarchitectures. However, these methods make it difficult to assemble the resulting architectures on conductive substrates, which is necessary for device integration. These methods also leave the nanomaterials prone to aggregation when the templates are etched away.

In contrast, anodization of metals including copper can be considered as an alternate route, as it is a commonly developed surface treatment process used to grow a variety of nanoarchitectures on many metals that are already being used in a range of applications. Preparation of copper oxide using this method would overcome a number of the problems outlined with the other synthesis methods. Most notably, some advantages include the possibility of working at or near room temperature, as well as having a natural and efficient metal back contact integrated into the device, without need for further modification.

In the early 1980s a few reports of anodic oxidation of copper were reported,<sup>46,47</sup> but were not considered reliable due to the presence of produced compounds other than copper oxide and copper. X-ray diffraction and photoresponse studies indicated the presence of materials with higher band gap than  $Cu_2O$  (2.17 eV) were produced, limiting their usefulness. Interest in anodic oxidation of copper then waned.

During the last decade, the interest in electrodeposited copper oxide thin films has been revived. In 2009, Patake et al. deposited porous, amorphous copper oxide thin films onto a steel substrate at room temperature using an alkaline sulfate bath for supercapacitor applications.<sup>48</sup> Copper oxide was cathodically deposited in 0.05 M copper sulfate solution. The copper sulfate solution was complexed with 0.05 M citric acid and and the pH of the bath was kept at 9 by adding 1M NaOH. They found the cyclic voltammetry curves were symmetric in nature and an increase in capacitance was correlated to an increase in the film thickness. Figure 13 gives SEM images of the resulting copper oxide thin films.


Figure 13. SEM images of copper oxide thin film (a) 1,000x magnification (b) 20,000x magnification.<sup>48</sup>

Even more recently, Wan et al. demonstrated controlled dendrite growth of Cu<sub>2</sub>O using electrodeposition.<sup>49</sup> Different dendrite morphologies were formed on F-doped tin oxide (FTO) covered glass substrates by potentiostatic deposition of cupric acetate. By varying the pH of the electrolyte, they were able to affect the lateral and vertical growth of the dendrites. However the size of these dendrites is on the order of  $2 - 5 \mu m$ , much too large to be considered nanofeatures. Furthermore, dendrites of this feature size do little to improve the surface area to an appreciable extent.

A chemical wet-etch process was utilized by Zhang et al. to prepare CuO nanobelts with high surface area and small crystal grains.<sup>50</sup> In their synthesis, 0.3 M ammonia was added to Cu(NO<sub>3</sub>)<sub>2</sub> dissolved in H<sub>2</sub>O under constant stirring. Cu(OH)<sub>2</sub> precipitates were formed, and were sealed in an autoclave at 60°C for 4 hrs to achieve CuO nanobelts. These nanobelts were mixed with carbon nanotubes in an appropriate ratio to fabricate pseudocapacitor electrodes with stable cycling performances. These electrodes showed a much higher specific capacitance compared to pure single-walled carbon nanotube films and exhibited more stable cycling performance as well. Figure 14 shows TEM and high resolution TEM images of the nanobelts fabricated.



Figure 14. (a) TEM and (b) HRTEM images of as-prepared CuO nanobelts with a diameter of 5-10nm and lengths of up to several micrometers. <sup>50</sup>

In 2007, Singh et al. achieved growth of different nanostructures (nanowires, nanothreads, nanocubes) by anodic oxidation of copper through a simple electrolysis process.<sup>51</sup> They employed water (with ionic conductivity ~6  $\mu$ S/m) as an electrolyte, with no special electrolytes, surfactants or chemicals needed, and using platinum as the counter electrode. They found that both anodization potential and time influenced the morphology of the nanostructures. Nanothreads were formed at 6 V during 15 – 30 mins anodization, while extending the anodization to 45 – 60 mins led to nanowires. Figure 15 shows TEM images of a typical sample anodized at 2, 4, 8 and 10 V, respectively.

Although the produced nanostructures enhanced surface area and aspect ratio, this technique had its drawbacks as well. The nanostructures were largely unstable on the copper substrate. The nanothreads and nanowires were only found in solution, whereas only nanocubes remained on the copper substrate. In addition, they calculated the optical band gap of their material to be between 2.61 and 2.69 eV, even larger than the known band gap of Cu<sub>2</sub>O (2.17 eV).



Figure 15. TEM micrographs of the synthesized nanostructures at (a) 2 V, (b) 4 V, (c) 8 V, (d) 10 V.<sup>51</sup>

Perhaps the closest work to the study of this thesis was reported by La et al. in 2010.<sup>52</sup> They fabricated wire-like bundled arrays of copper hydroxide prepared by the electrochemical anodization of copper foil. This report is novel in that there are no reports detailing the use of aqueous sodium hydroxide as a base for electrochemical copper anodization. Variations in NaOH concentration, reaction temperature, anodization time, and current density were used to establish the relationship between anodization conditions and resulting nanostructure films. Wire-like orthorhombic  $Cu(OH)_2$  nanobelts with an average width of 100 - 300 nm and length of  $10 \,\mu$ m were synthesized with the preferential [100] growth direction when using a bath of  $1 \,M$  NaOH at  $20^{\circ}$ C, while keeping the current density constant at 2 mA cm<sup>-2</sup>. When the concentration of NaOH was decreased to  $0.5 \,M$ , the 1-D nanobundle structure became narrower and longer without and change in composition or crystalline structure. In many cases,

the nanostructures were well-adhered to the copper foil surface, in conflict with previous attempts. However, although it appears the growth direction was preferential in certain cases, the nanowire bundles did not grow uniformly out from the copper foil, i.e. there was no perpendicular preference to create self-assembled nanostructures with long-range order. Figure 16 illustrates the randomness of the nanowire bundles obtained for various NaOH concentration baths.



Figure 16. SEM images of copper foil anodized in different NaOH concentrations: (a) 0.5 M, (b) 1.0 M, (c) 2.0 M, (d) 4.0 M. All were generated under the same current density of 2 mA cm<sup>-2</sup> and reaction time of 600 s at 20°C.<sup>52</sup>

The above synthesis has also been performed in potassium hydroxide (KOH), and taken one step further by Wu et al.<sup>53</sup> They fabricated Cu(OH)<sub>2</sub> nanoneedle and nanotube arrays in an aqueous solution of 2 - 3.5 M KOH at a constant current density of 1.5 mA cm<sup>-2</sup>. They varied

temperature between 2 and 30°C and achieved highly dense nanostructured arrays. At lower temperatures and lower KOH concentration, Cu(OH)<sub>2</sub> nanoneedle arrays were formed, while at higher temperatures and higher KOH concentrations, Cu(OH)<sub>2</sub> nanotubes and in small amounts CuO nanoparticles were formed. They subsequently subjected the Cu(OH)<sub>2</sub> nanoneedle samples to a heat treatment of 150°C for 3 hrs to complete dehydration to convert to CuO, and then again to 200°C for another 3 hrs (under nitrogen) to promote crystallization of CuO. Figure 17 shows SEM images of several samples at increasing time intervals.



Figure 17. SEM images of as-prepared  $Cu(OH)_2$  nanoneedles deposited at a constant current density of 2 mA cm<sup>-2</sup> in 2.0 M KOH solution for different deposition times (a) 300 s, (b) 500 s, insert contains magnified view; (c) 1000 s, (d) 1500 s. T = 28 ± 2°C.<sup>53</sup>

#### 2.4.3 Potential – pH Relationship

A critical parameter when considering anodic oxidation of metals is the pH of the electrolyte bath. From thermodynamic data, a relationship between pH and applied potential can generate a valuable guideline in determining the evolution of the thin film at the electrolyte –

metal interface. This relationship between pH and potential is known as a Pourbaix diagram. For example, titanium is thermodynamically reactive; however it is very corrosion resistant because of a highly stable passive film formed at all pH in oxidizing potentials.<sup>9</sup> This is shown schematically in Figure 18 for the Ti – H<sub>2</sub>O system at 25°C. Throughout most of the pH range (except at the extremes), a stable TiO<sub>2</sub> layer is thermodynamically favorable to form. This fact makes titania a robust and versatile material for use in anodization in a wide range of electrolyte compositions and conditions.



Figure 18. Pourbaix diagram of Titanium – H<sub>2</sub>O system at 25°C.<sup>9</sup>



Figure 19. Pourbaix diagram of Copper – H<sub>2</sub>O system at 25°C.<sup>54</sup>

Figure 19 shows the Pourbaix diagram for the  $Cu - H_2O$  system at room temperature. Region 1 of Figure 19 represents the acidic pH and impressed anodic potential. In this region, ionic dissolution of copper dominates, and there is no surface layer formed on the copper.<sup>54</sup> For this reason, continuous dissolution leads to severe pitting and a loss in surface planarity. Recall from Section 2.1 that pitting is a prerequisite to nanotube formation. However this process must be in balance with competing electrochemical processes so that pitting leads to systematic, ordered oxide layer growth and not just continuous corrosion of the Cu surface.

Region 2 of Figure 19 indicates the neutral and alkaline pH and impressed anodic potential. With the increased pH, the mass transfer of metal ions into solution is limited by the solubility of the metal interface.<sup>54</sup> At this point, concentrated ions accumulate at the surface, forming the passive surface layer. Thus in this pH range of approximately 5 - 13, copper is oxidized. Note that this region for copper oxide is narrower than that of titania formation.

Region 4 indicates a narrow band where a small applied potential (either anodic or cathodic) generates  $Cu_2O$  instead of CuO. This is one reason why it is difficult to obtain pure CuO or  $Cu_2O$  as a product of anodization, rather a mix of the two is often found in practice. Region 3 indicates the applied cathodic potential, where there is no oxidation activity and metallic copper is the dominating species.

It is important to reinforce that the data for these Pourbaix diagrams are normally collected in aqueous media, where it is easy to accurately monitor the pH. A great deal of work, on copper, titanium, or otherwise, including this thesis, is concerned with anodization in organic media; hence the Pourbaix diagram can only be taken as a guideline and not as an absolute.

#### 2.5 Summary

Based on these findings in the literature, it is evident that reliable and controllable anodization protocols are established for the synthesis of well-defined nanostructures from

metals such as titanium, tantalum, iron, aluminum, and others. However, anodization of copper has been largely unsuccessful, and more specifically proper anodization conditions leading to the formation of controllable copper oxide nanoarchitectures (such as nanotubes) remain unsolved to date.

It is this gap in knowledge that motivates the work in this thesis. An attempt to improve the understanding of the anodization of copper is made in subsequent chapters, with a primary focus on the variation of anodization conditions in organic electrolytes. Factors that have been shown to affect the outcome of nanostructures in other established systems include the following:

- Solvent
- Acid content
- H<sub>2</sub>O content
- pH
- Temperature
- Voltage

Therefore these are the chief parameters that have been chosen to be examined. A systematic and logical variation of these conditions, discussed in Chapters 4 and 5, will lead to an increased understanding of which of these parameters play a critical role in the formation of controllable nanoarchitectures of copper oxide via anodization.

# Chapter 3 Experimental Procedures

This chapter describes the anodization process of copper oxide thin films, as well as characterization of their properties, high temperature annealing treatment used to crystallize the films, and measurement of photoresponse.

# 3.1 Anodization of Copper Oxide

Copper oxide nanostructured materials were fabricated via potentiostatic anodization in aqueous and organic electrolytes containing fluoride (F<sup>-</sup>) and chloride (Cl<sup>-</sup>) bearing ions. Based on successes with previous studies of titanium, iron, and tantalum, work in ethylene glycol (EG) electrolytes was used. Furthermore, anodization in dimethyl sulfoxide (DMSO) was explored as well.

#### 3.1.1 Substrate Preparation

Copper foil was purchased from Sigma-Aldrich. Two different types of foils were used: 0.25 mm thick, 99.8% pure Cu foil, and 0.25 mm thick, 99.9% pure *annealed* Cu foil. Each foil was cut into rectangles of 2.0 cm x 1.0 cm, and the squares were washed with acetone, D.I.  $H_2O$ , and isopropanol (IPA) prior to anodization. In addition, the foils were washed in dilute (0.1 M) HCl for three minutes in order to remove the native oxide layer that forms due to exposure to ambient atmosphere. In some cases, mechanical polishing was performed with 0.2 µm alumina powder in order to give the copper foils a shiny smooth luster.

The working Cu electrode was subjected to potentiostatic anodization in a two-electrode electrochemical cell, where a platinum foil (2.0 cm x 3.0 cm) was used as counter-electrode.

The two electrodes were connected to a dc power supply (Agilent E612A D C) for anodization. The distance between the two electrodes was held constant at 3 cm. The working electrode was lowered into the electrolyte, with an area of 1.0 cm x 1.0 cm submerged in the electrolyte. The voltage was rapidly applied thereafter. Upon completion of anodization, the electrodes were removed from the electrolyte bath before voltage was terminated. The anodization current was monitored using a Keithley 2000 digital multimeter interfaced with a computer for data collection. After anodization, samples were rinsed in IPA and completely dried with 99.99%  $N_2$  gas.

#### 3.1.2 Electrolyte Preparation

Organic-based electrolytes were prepared using ethylene glycol (EG, 99.8%, anhydrous, Sigma-Aldrich), or dimethyl sulfoxide (DMSO, 99.9%, Sigma-Aldrich). All anodizations were performed from the same batch of solvent. Fluoride-bearing species used were hydrofluoric acid (HF) and ammonium fluoride (NH<sub>4</sub>F, 97%, Aldrich). The total volume of each electrolyte bath was fixed at 50 ml.

#### 3.1.3 Anodization Parameters

Anodization times and voltages were varied between 2 - 30 mins and 5 - 80 V. pH values between 4 - 12 were studied. Temperature was varied between 0 - 80 °C. The interelectrode spacing was kept constant at 3.0 cm.

#### 3.1.4 Thermal Annealing

The as-anodized samples were normally amorphous, thus thermal annealing was necessary to induce crystallization. The samples were leaned nearly upright on the wall of a ceramic boat, allowing at least a small space for moving gas to flow through. Oxygen gas was chosen as the ambient in order to prevent the copper oxide thin film from assuming a different composition. A ramp rate of 0.5 °C/min was chosen to prevent damage to the nanostructures,

as previous studies have demonstrated destruction at higher ramp rates. Thermal annealing at 400°C for 4 hours proved sufficient to crystallize the films, confirmed via x-ray diffraction.

#### 3.2 Microstructure Characterization

Nanostructure morphologies of the copper oxide films were investigated by use of a field-emission scanning electron microscope (FE-SEM, Leo 1530). Feature size, pore depth, film uniformity, and cross-section topology were evaluated.

# 3.3 Structural Characterization

The crystal structure of the nanostructured films were evaluated by x-ray diffraction (XRD). The crystallization of the films was investigated by a glancing-angle x-ray diffractometer (GAXRD, Scintag, Inc., Cupertino, CA/Philips X'Pert MRD PRO, Netherlands) using CuK<sub> $\alpha$ </sub> radiation. The films were scanned from 10-70 degrees 2 $\theta$ , with a step size of 0.5° and 2 s count time.

### 3.4 Photoelectrochemical Measurements

Sample photoresponse was measured electrochemically in a standard three-electrode configuration with copper oxide thin film on metal copper foil backbone as the working electrode, platinum foil as the counter electrode, and saturated Ag/AgCl as reference electrode with 1.0 M KOH solution as the electrolyte. A scanning potentiostat (CH instruments, model CHI 600B) was used to measure dark and illuminated current at a scan rate of 10 mV/s. Samples were tested under solar simulated light equivalent to AM 1.5 light at 100 mW/cm<sup>2</sup> (intensity set using NREL calibrated solar cell).

# Chapter 4 Anodization of Copper in Ethylene Glycol

#### 4.1 Preliminary Studies in Aqueous Electrolytes

Past attempts by the Grimes group to anodize copper oxide nanotubes were unsuccessful, but did lead to some preliminary conclusions (unpublished) that the current work expands upon. Anodization in aqueous KOH electrolyte yielded a heavy dependence on the pH of the electrolyte. In KOH solutions with pH < 10, no film was observed on the copper foil, instead a blue solution was formed in the electrolyte, indicating that Cu was continuously dissolved in the electrolyte. Current transient measurements confirm the continuous dissolution of Cu as the current continues to increase over the duration of the tests. At pH > 10, with 0.15 M KOH at 10 V, a precipitate collected in the electrolyte, and yielded copper oxide crosslinked needles/ribbon architecture. However no oxide layer was found on the surface of the copper foil. These results indicate that the dissolution rate of the system was too high.

Based on these observations, anodization at a lower voltage was thought to slow the dissolution rate. Anodization at 5 V eliminated formation of precipitate in the electrolyte. An aqueous electrolyte consisting of 0.15 M KOH and 0.1 M NH<sub>4</sub>F for greater than 3 minutes indicated nanostructures formed on the copper foil surface via FESEM. As indicated in Figure 20, close-packed nanospheres with 300 - 500 nm diameters were observed. Pore diameters of approximately 10 - 20 nm were found, and the structures remained intact on the surface of the copper foil after sonication for 10 s, indicating strong adherance. The surface of the copper foil can also be observed through gaps in the close-packed spheres and indicating limited stacking of the spheres. Anodization for up to 20 minutes resulted in these nanofeatures similar to those

in Figure 20; beyond this time the structures were lost and the appearance of a deep blue color in the electrolyte bath indicated dissolution of copper.

Varying concentrations in the range of 0.1 - 0.3 M for KOH and 0.05 - 0.25 M for NH<sub>4</sub>F did not lead to any enhancement of porosity or reduction in average size of nanospheres. The pH > 10 limit of the previous work was also confirmed by observing the combination of reducing [KOH] and/or increasing [NH<sub>4</sub>F]. In these cases, aggressive dissolution was evident and nanostructures did not appear on the copper foil surface. Upon raising the anodization voltage to 6 V, the nanosphere structures disappeared as well.



Figure 20. FESEM images of anodization of Cu foil in 0.15 M KOH + 0.1 M NH<sub>4</sub>F in H<sub>2</sub>O at 5 V for 5 mins. Scale bars = (a) 1μm; (b) 300 nm.



Figure 21. FESEM images of anodization of Cu foil in 0.15 M KOH + 0.1 M NH<sub>4</sub>Cl in H<sub>2</sub>O at 5 V for 5 mins. Scale bars = (a) 1μm; (b) 200 nm.

The anion was also varied in this study, to gain insight as to whether a chloride anion could enhance the porosity or create more novel nanostructures. Holding all other anodization parameters constant, in general larger nanosphere structures were achieved, with diameters averaging closer to 1 µm. However in presence of Cl<sup>-</sup> anion, the porosity of the features appear to be reduced, indicated by the clogged pores in Figure 21. Based on these findings, the chloride anion was abandoned in subsequent studies.

### 4.2 Ethylene Glycol Anodization Parameters

In contrast to aqueous electrolytes, which typically require very low anodization voltages and a narrow pH range, ethylene glycol has proven to be a robust electrolyte medium for anodization of a number of materials. As indicated by Yoriya<sup>9</sup> and Shankar<sup>7</sup>, the donation of oxygen, which is necessary for oxide formation, is more difficult in organic electrolytes. The inclusion of H<sub>2</sub>O is an essential element for nanofeatured oxide growth in organic electrolytes. Water is a good choice because it easily dissociates to donate free OH<sup>-</sup> radicals that assist in the oxide growth. However, achieving long nanotube arrays (at least in TiO<sub>2</sub>) requires the water content to be less than ~5%, in which case the chemical dissolution of the oxide is minimized and optimal growth rates can be sustained. This is one reason for the advantage of using organic electrolytes such as ethylene glycol; in aqueous electrolytes the abundance of water makes it difficult to control the dissolution.

In subsequent sections, the ethylene glycol parameter space is explored. An ethylene glycol bath with fluoride-bearing anions, based on its use for anodization of titanium, was conceived. Although different materials will require a unique electrolyte bath to form stable nanostructures, as a starting point, a bath consisting of  $0.1 \text{ M NH}_4\text{F} + 0.1 \text{ M KOH}$  was considered.

#### 4.2.1 H<sub>2</sub>O Content

To analyze the effects of water content, anodization voltage was kept constant at 30 V while varying H<sub>2</sub>O content in the ~ 5 vol % range. Figure 22 illustrates the current transient of the system with H<sub>2</sub>O content at 2, 4, and 8%. The pH of the electrolyte baths were 7 – 8 depending on exact H<sub>2</sub>O content. All three transients roughly follow the classic dip-rise pattern that indicates pitting takes place. In each case the transient takes on similar shapes, but ultimately the steady states are varied. At 2% H<sub>2</sub>O the transient levels off eventually, whereas for higher H<sub>2</sub>O contents the current continues to steadily increase. It can be seen that the highest water content, 8%, results in the largest current density as well, although it is not a linear increase in the current dictates steady-state growth of the oxide layer. Hence we would expect the 8% sample to have undergone the most pitting and have the greatest potential for novel nanoarchitectures.

Figure 23 shows the corresponding FESEM images of the anodized surface, and it can be clearly seen that this is not the case. A nanoporous structure exists for all three baths; 2% and 4% H<sub>2</sub>O have roughly the same density, however upon adding 8% H<sub>2</sub>O, the porosity greatly decreases. This result is in agreement with anodization of other well-established metal oxides as indicated in the literature review. The nanoporous features in Figures 23 (a) and (b) take on an array of loosely circular shapes when viewed from directly above. It appears to be one step past the pitting stage, attempting the beginnings of nanotube formation. However upon anodization for longer times, the structures never grew beyond the point that is shown in the figures.



Figure 22. Current transient data of electrolyte bath 0.1 M  $NH_4F$  + 0.1 M KOH in EG anodized at 30 V, with three  $H_2O$  contents: 2% (red), 4% (blue), 8% (green), by volume.



Figure 23. FESEM images of anodization of Cu foil in 0.1 M NH<sub>4</sub>F + 0.1 M KOH in EG at 30 V: (a) 2% H<sub>2</sub>O; (b) 4% H<sub>2</sub>O; (c) 8% H<sub>2</sub>O. Scale bars = 1 $\mu$ m.

#### 4.2.2 Effects of Polishing

Mechanical polishing of the copper foil was considered in order to not only remove the native oxide layer prior to anodization, but to smooth the surface as well. The motivation for mechanical polishing was to attempt to provide a more uniform surface in order for more ordered pitting to occur, which would lead to hexagonal close-packed arrays of nanotubes such as in titania nanotube formation. This step is NOT required for nanotube formation in titania, most likely due to titania's exceptional stability and resistance to corrosion in a variety of media and electrochemical environments. Copper, on the other hand does not benefit from such robust mechanical properties, thus mechanical polishing was attempted prior to anodization, to curb these shortcomings. The samples were polished with 0.2 µm alumina powder for 20 minutes prior to anodization, until the foils exhibited a shiny reflective luster.

Figure 24 indicates the current transient of the anodization of copper foil in the same conditions as in Section 4.2.1. It can be seen that there is a clear degradation of a consistent current density, and absolute values of current density are dramatically decreased as well. The fluctuations are more pronounced for the 4 and 8 % samples, while the 2% H<sub>2</sub>O sample has very little current density fluctuation and reaches steady state within 10 s. Based on these observations and in conjunction with FESEM images (not shown) that did not exhibit porosity similar to Figure 23, it was deduced that mechanical polishing prior to anodization did not prepare the copper foil surface for improved pitting. This fact is in agreement with the lack of mechanical polishing needed for anodization of other metals as well. In fact, it can be concluded that the rough surface nature of foils as-received are likely to contribute to the formation of pits. Therefore further attempts to mechanically polish the copper foils prior to anodization were abandoned in subsequent anodizations. Removal of the native oxide layer prior to anodization was performed in submersion in dilute HCl, as is detailed in Section 3.1.1.



Figure 24. Current transient data of copper foil anodized in the same conditions as in Figure 22 with the exception of mechanical polishing with 0.2  $\mu$ m alumina powder prior to anodization.

#### 4.2.3 Acid Content

In the nanoporous structures developed such as those in Figure 23, where the porosity is readily visible yet growth of thicker oxide layers is elusive, it was hypothesized that further growth beyond this stage is hindered by the strength of the fluoride-bearing ion. In other words, the anion etches the surface of the oxide layer at a rate rapid enough to inhibit steady-state growth. Due to this fact, the concentration of ammonium fluoride was systematically varied.

As a first step to confirm this belief, an anodization bath with *increased* ammonium fluoride concentration of  $[NH_4F] = 0.25$  M was used. Figure 25 shows the results of this investigation via the current transient, indicating a steady drop in current at all times. Corresponding FESEM images from the 4% H<sub>2</sub>O sample, at two magnifications, are shown in Figure 26. In comparison with Figure 23, very little surface porosity is evident. Another observation providing indication that the copper foil was being etched by fluoride-bearing ions

was the evolution of a blue-green tint of the electrolyte bath during anodization. Further confirmation was given by measuring the pH of the electrolyte bath to be ~5, which is on the fringe in the Pourbaix diagram's estimate of the range of CuO film growth (Figure 19).



Figure 25. Current transient data of electrolyte bath 0.25 M  $NH_4F$  + 0.1 M KOH in EG, anodized at 30 V with three  $H_2O$  contents: 2% (red), 4% (blue), 8% (green), by volume.



Figure 26. FESEM images of anodization of Cu foil in 0.25 M NH<sub>4</sub>F + 0.1 M KOH + 4% H<sub>2</sub>O in EG at two magnifications; scale bar = (a) 1  $\mu$ m; (b) 300 nm.

After these findings, it was evident that a lower acid concentration was necessary to minimize etching of the strong fluoride-bearing ion. Due to the availability of H<sub>2</sub>O to donate OH<sup>-</sup> radicals for growth of the oxide layer and to isolate the effects of the fluoride-bearing ion, subsequent anodizations were carried out without addition of KOH, i.e. electrolyte bath composition of NH<sub>4</sub>F + H<sub>2</sub>O in EG. Concentrations of reactants were held to [NH<sub>4</sub>F] < 0.1 M and [H<sub>2</sub>O] < 5 vol % based on observations already discussed.

Anodization of copper foil was carried out with [NH<sub>4</sub>F] = 0.02 M, 0.03 M, and 0.05 M. Current transient curves followed the same general trend as in Figure 22, albeit with lower absolute current densities due to the lower acid concentration. Figure 27 shows FESEM images of four samples at similar magnification levels, and only varying ammonium fluoride concentration. The 2% H<sub>2</sub>O concentration was chosen for all samples in accordance with Figure 23(a) showing maximum porosity. It can be seen from the images that the sample with 0.03 M NH<sub>4</sub>F has the greatest level of uniform porosity on the surface of the copper foil. There is reduced porosity in the 0.02 M and 0.1 M NH<sub>4</sub>F samples, indicating these are the upper and lower boundaries for limited porosity in this system with 2% H<sub>2</sub>O at 30 V. In the middle of Figure 27(c), a deep trench was focused on, illustrating the increased depth of the oxide layer. It is important to note that all electrolyte baths were within the theoretical pH range (5-13) of CuO film growth derived from the copper-oxygen Pourbaix diagram, which stresses that the Pourbaix diagram can only be used as a rough guide in organic electrolytes and that other anodization parameters may dictate the growth of copper oxide layers.



Figure 27. FESEM images of copper foil anodized at 30 V over various concentrations of  $NH_4F$ , in an electrolyte bath containing  $NH_4F + 2\%$   $H_2O$  in EG: (a) 0.02 M  $NH_4F$ , scale bar = 100 nm; (b) 0.03 M  $NH_4F$ , scale bar = 200 nm; (c) 0.05 M  $NH_4F$ , scale bar = 100 nm; (d) 0.1 M  $NH_4F$ , scale bar = 200 nm.

#### 4.2.4 Voltage and Temperature

In EG electrolytes, past studies specify novel nanostructures and nanotube formation in as low as 30 V and as high as 100 V.<sup>5,7,9</sup> In an H<sub>2</sub>O-based electrolyte, potentials as low as 5 V were sufficient to support the growth of an oxide layer. The viscosity of EG necessitates a larger applied potential in order to facilitate ion migration and charge transfer through the electrolyte. At the lower limit anodization voltage, charge transfer will cease and result in little or no flow of current. At the upper limit, the field-assisted dissolution of the metal into electrolyte overcomes growth of the oxide layer, and no nanostructures are supported. Temperature has also proven to have the potential for profound effects on resulting nanostructures. For the anodization of tantalum foil in DMSO, Allam<sup>27</sup> and Feng<sup>32</sup> observed no nanotube formation at room temperature. However they noted that the temperature of the electrolyte bath escalated over time during anodization. Upon raising the temperature of the bath even further, they were able to fabricate nanotubes.

With these considerations, the anodization voltage and temperature were systematically varied. Potentials in the elevated range of 60 - 90 V and temperatures in the range of 25 - 60°C were studied. Above 60°C it became difficult to reliably control the temperature of the electrolyte bath and keep the volume of the solution constant, as the elevated temperature facilitated evaporation of solvent and water. The small amount of water (1 vol %) means even a small loss in water may alter the electrolyte composition greatly.



Figure 28. Current transient data of anodization of copper foil in 0.03 M  $H_4F + 1\% H_2O$  in EG, at anodizing voltages: 60, 70, 80, and 90 V, broken down by temperature, from left to right: 25, 40, and 60°C.



Figure 29. Current transient data of anodization of copper foil in 0.03 M NH<sub>4</sub>F + 1% H<sub>2</sub>O in EG, at temperatures: 25, 40, 60 °C, categorized by anodization voltage: (a) 60 V; (b) 70 V; (c) 80 V; and (d) 90 V.

Figures 28 and 29 depict the current transient data graphically. Figure 28 groups the data by temperature and varies the voltage, while Figure 29 shows different anodization bath temperatures for a given potential. As can be expected, the overall current density increases as the temperature of the anodization bath is increased. It is evident from Figure 28 that at low temperatures (25°C), for the same voltages, the current density dip-gradual rise trench is deeper than at higher temperatures. In other words, there is a greater initial potential drop when the metal is etched and before the pits reach an equilibrium size. The decreasing current density is an indication of oxide formation. In addition, the current density difference is at a minimum at 90 V potential for all temperatures, and is increased for lower voltages. The largest

current density difference occurs in the sample anodized at 25°C and 80 V, where an approximately 9 mA/cm<sup>2</sup> drop is observed over only 10 s. Furthermore, in this sample the current density continues to increase at a slope greater than those at lower potentials. Based on this plot alone, a robust oxide layer with interesting nanoscale features was predicted.



Figure 30. FESEM images of copper foil anodized for 120 s at 80 V and 25°C in an electrolyte bath consisting 0.03 M  $NH_4F + 1\% H_2O$  in EG. (a) scale bar = 1  $\mu$ m; (b) inset: scale bar = 300 nm.

Investigation via FESEM confirmed the prediction made by the current transient of the 25°C, 80 V sample. Figure 30 shows the surface of the copper foil at two magnifications after anodization for 2 minutes in 0.03 M NH<sub>4</sub>F + 1% H<sub>2</sub>O in EG, at 80 V and 25°C. Here a definite nanoporous structure can be discerned, with some extent of longer range order as well. It appears as though the pits have reached an equilibrium size with diameter equal to roughly the size of the scale bar in Figure 30(b), 300 nm. The long range periodicity is only evident near the center of a particular grain and spans approximately 10  $\mu$ m, with the diameters in the center being larger than those on near the edges. The periodicity deteriorates nearer to the edge, yet is consistent across all the grains in Figure 30(a).

Figure 30 indicates that the copper oxide layer does indeed undergo pitting upon anodization in certain conditions, and is capable of self-organization. Although encouraging for the prospect of synthesizing nanotubes, none were observed in this sample or with any other electrolyte, voltage, and temperature combination. Figure 31 shows FESEM images of other selected samples with non-planar, porous nanostructures. Figures 31 (a) and (b) are room temperature anodizations at potentials of 70 and 60 V, and indicate similar porous nanostructures. Figure 31(c) and (d) have electrolyte bath temperatures elevated to 40 and 60°C, and it can be seen that the nanotube scaffold structure is no longer evident. The 60°C sample shows a clear reduction in porosity. Therefore, for the 0.03 M NH<sub>4</sub>F + 1% H<sub>2</sub>O in EG electrolyte bath, a narrow range of anodization conditions has shown the potential to grow oxide layers with ordered nanostructures.



Figure 31. FESEM images of anodization of copper foil in 0.03 M NH<sub>4</sub>F + 1% H<sub>2</sub>O in EG electrolyte under various conditions: (a) 25°C, 70 V, scale bar = 300 nm; (b) 25°C, 60 V, scale bar = 1  $\mu$ m; (c) 40°C, 80 V, scale bar = 200 nm; (d) 60°C, 80 V, scale bar = 200 nm.

With these nanostructures in mind, the next step was to analyze the evolution of the nanostructures over anodization time. Samples with non-linear current transients were chosen to study, and FESEM images were taken at different intervals of anodization. The first is chosen at the minimum of the current density, where the effects of pitting are at a maximum. Another point is when the current density reaches a steady state, and finally after long times in the steady state, giving the oxide layer a chance to grow. Figure 32 shows the current transient data of copper foil in a 0.03 M NH<sub>4</sub>F + 0.5% H<sub>2</sub>O in EG electrolyte bath at 40°C, anodized at 50 V. Figure 33 shows the corresponding FESEM images at those times. From these images it can be clearly seen that the most porous and uniform structure exists in Figure 33(b). If anodization is allowed to run for long times as in Figure 33(c), the morphology and porosity of the structure breaks down, rather than propagating and leading to enhanced nanofeatures such as nanotubes or nanowires.



Figure 32. Current transient data of 0.03 M NH<sub>4</sub>F + 0.5% H<sub>2</sub>O in EG electrolyte bath at 40°C, anodized at 50 V. Snapshots taken at (a) 10 s; (b) 60 s; (c) 300 s in Figure 33.



Figure 33. FESEM images of copper foil under anodization conditions described in Figure 32: (a) 10 s; (b) 60 s; (c) 300 s. Scale bar = 100 nm.

### 4.3 Thermal Annealing

The as-anodized samples were normally amorphous, and a mixture of compositions is expected on the surface of the copper film, including the potential for oxide, and hydroxide formation. In addition, impurities in the solvent may have introduced other compounds on the surface. Thus thermal annealing was necessary to induce crystallization and ensure conversion of all phases to CuO.

Crystallinity plays a key role in promoting charge transport.<sup>55</sup> Crystallization and phase transformation generally take place in the material through nucleation and growth processes.<sup>56</sup> Finding the lowest anneal temperature where crystallization is induced is advantageous, due to the adverse effects of internal stress differences between metallic copper substrate and copper oxide thin film. In many cases these internal stress differences lead to a weak adherence of the film to the substrate, and sonication or other cleaning methods destroy the integrity of the film. For this reason, a slow ramp rate of 0.5 °C/min was chosen to minimize internal stresses and prevent damage to the nanostructures, as previous studies have demonstrated destruction at higher ramp rates.<sup>57</sup>

Thermal annealing in  $O_2$  gas at 400°C for 4 hrs proved sufficient to crystallize the films, while  $O_2$  flow prevented contamination of the samples and ensured conversion to CuO. X-ray

diffraction was used to confirm the presence of crystallized copper oxide post-anneal. Figure 34 shows a typical XRD plot, with CuO peaks clearly dominating, as well as metallic Cu on which the oxide layer is adhered.



Figure 34. XRD data of anodized copper oxide thin film on Cu substrate post-anneal in  $O_2$  gas at 400°C for 4 hrs with ramp rate of 0.5 °C/min.

#### 4.4 Photoelectrochemical Measurements

Photoresponse was measured via photocurrent measurements. Photocurrent measurements are utilized to characterize the performance of a semiconductor anode under different bias conditions. During photocurrent measurements, the bias on the photoanode is swept from negative to positive values. Light can be provided by UV illumination, but typically simulated sunlight AM 1.5G is required for capture of broad spectrum solar energy. This notation refers to air mass 1.5 conditions, which occur when the sun is at the zenith angle of 48.19° and the device is inclined 27° towards the equator.<sup>58</sup>

Figure 35 shows the chopped light photocurrent of an anodized copper sample, post anneal. The edges of the anodized foil were masked in epoxy after soldering a copper wire lead,

and a 1 cm x 1 cm window was left exposed to a 1 M KOH electrolyte, in which the photocurrent density was measured as a function of bias. The setup consisted of an anodized copper foil as the working electrode, platinum as the counter electrode, and a saturated Ag/AgCI reference electrode. The chopped light photocurrent was measured, where the sample was subjected to 2 s intervals of alternating open (light) and closed (dark) conditions over a potential sweep of - 1 to 0 V (vs. Ag/AgCI). The lower curve in Figure 35 corresponds to the open (light) condition, whereas the upper curve is the dark current. The vertical lines connecting the light and dark currents indicate the switching from open to closed position, or vice versa. It can be seen in Figure 35 that an appreciable current density (-0.6 mA/cm<sup>2</sup> at ~ -0.75 V) can be drawn under simulated sunlight AM 1.5G illumination, and as large as 0.25 mA/cm<sup>2</sup> current density change is observed from dark to light illumination (at ~ -0.75 V).



Figure 35. Chopped light photocurrent of anodized copper foil in EG-based electrolyte post-anneal in O<sub>2</sub> gas at 400°C for 4 hrs with ramp rate of 0.5 °C/min.

The observation that the CuO film draws a negative current when a negative potential is applied confirms the p-type semiconductor nature of CuO. It should also be noted that there is a

non-negligible dark current in the CuO thin film. Ideally, for practical use in engineering applications, the dark current would be zero and current would be drawn only upon illumination. This dark current is possibly due to shorting in the sample. This also may be an artifact of the laboratory where the photocurrent measurements were conducted. Although care was taken to minimize stray light under dark conditions, realistically it is difficult to create a perfectly dark environment. For future studies, minimization of the dark current as a function of nanostructure, anodization conditions, and anneal conditions would be beneficial for the development of nanostructured CuO films into end-use commercial applications. Explicit suggestions for future study will be detailed in Section 6.3.

#### 4.5 Summary

This chapter has considered the fabrication of copper oxide nanostructured films in ethylene glycol electrolytes. Parameters that determine the resulting nanostructured morphology have been detailed. The results from this chapter provide insight to the electrochemical anodic growth process to determine how anodization parameters including voltage, acid concentration, water content, temperature, anodization time, and pH determine the resulting architectural features of the nanostructures. This chapter also helped bridge the gap between the relation between current density transients during anodization and the formation of novel nanostructures or lack thereof.

It was found that for anodization in ammonium fluoride as fluoride-bearing ion, and ethylene glycol as solvent, the condition of  $0.03 \text{ M NH}_4\text{F}$  with  $0.5 - 2 \text{ vol } \% \text{ H}_2\text{O}$  provided copper oxide nanoarchitectures with the greatest levels of porosity. NH<sub>4</sub>F concentration of 0.02 M was found to be too low to provide an environment where electrochemical etching was significant enough to allow pitting of the copper oxide surface layer, while 0.1 M NH<sub>4</sub>F provided too many fluoride ions. Etching was not controllable in this scenario, leading to a rapid decline in

nanoporosity or otherwise interesting nanofeatures with enhanced surface area and aspect ratio.

Furthermore, it was found that increasing the applied potential of the anodization bath from 30 V to upwards of 50 V introduced an element of long-range order for a nanoarchitecture that consists of what appears to be the beginning of nanotube formation. Modification of temperature of the anodization bath under these conditions proved to have no beneficial effects for the improvement of long-range order or enhanced thickness of the copper oxide layer.

Thermal annealing in O<sub>2</sub> gas at 400°C ensured (1) conversion of all phases of copper present on the surface to CuO, and (2) crystallization of the copper oxide thin film with strong adherence to metallic copper substrate, confirmed via XRD measurements. Photoelectrochemical properties of the annealed nanostructured films were analyzed via measurement of photocurrent, and confirmed the p-type semiconductor behavior or CuO and indicated the films' active response to broad wavelength white light.

# Chapter 5 Fabrication of Copper in Dimethyl Sulfoxide

### 5.1 Dimethyl Sulfoxide Properties

DMSO is an aprotic solvent; that is, it does not have a hydrogen atom bonded to an electronegative atom. The hydrogen atoms in aprotic solvents are only bonded to carbon atoms. Therefore aprotic solvents have very weak proton and hydrogen bond donating abilities.<sup>7</sup> DMSO has a basicity stronger than that of water, and this solvent easily solvates to small cations and is an excellent proton acceptor, whereas solvation to small anions is difficult. The solvent itself acts as a mild reducing agent, thus strong oxidizing agents are unstable in dipolar aprotic protophilic solvents such as DMSO. Hence the solubility of NH<sub>4</sub>F in DMSO is low, and HF is typically used as the fluoride-bearing molecule in DMSO-based electrolyte baths.<sup>7</sup>

## 5.2 DMSO Anodization Parameters

The use of DMSO as an electrolyte medium has been widely investigated for anodic formation of TiO<sub>2</sub>. Ruan et al.<sup>20</sup> managed to obtain 2.3 µm length nanotubes after anodizing titanium foil for 72 hrs at 20 V in an electrolyte containing 4% HF in a 1:1 mixture of DMSO and ethanol. Compared to aqueous electrolytes, the nanotubes formed in DMSO were relatively fragile, due to higher internal stresses in the film and poor adhesion to the substrate. Paulose et al.<sup>5</sup> obtained higher growth rates and much longer nanotube lengths of up to 93 µm by eliminating ethanol from a 2% HF DMSO electrolyte and increasing the anodization voltage up to 60 V. Further increases in HF concentration reduced the length of the nanotubes, indicating that chemical dissolution was detracting from growth of the oxide layer.

The anodization of copper foil in DMSO-based electrolytes was attempted, following the success of its use in forming long titania nanotubes via the same technique. An electrolyte bath of 1 - 2 vol % HF in DMSO was investigated. This bath composition was chosen with the knowledge that HF concentrations higher than 2% resulted in extensive dissolution in the case of titania. Copper, with less resistance to chemical dissolution than titanium, was expected to respond in kind.

Figure 36 shows the current transients of DMSO-based anodizations as a function of voltage and  $H_2O$  content. Note that the current density in DMSO is much lower than in other electrolytes such as aqueous or EG. Even with the application of higher potential, the current density does not respond with much increase. It can be seen that the 2%  $H_2O$  samples have slightly higher current densities than the 1%  $H_2O$  samples.



Figure 36. Current transient data of 1-2% HF and 1-2% H $_2$ O in DMSO at anodization voltages of 20 V, 40 V, 60 V, and 80 V.

# 5.3 Characterization

The current density profiles do not indicate any discernable non-linear trends which would indicate pitting or the development of novel nanoarchitectures. Nonetheless, some novel nanostructures were obtained contrary to the indication from current transient data. Figure 37 provides FESEM images showing how anodization at low potential, 40 V, results in almost

spherical nanostructures on the surface of the copper foil, but which do not appear to be porous or much higher surface area than that of a planar surface.

However, doubling the anodization potential to 80 V makes a drastic difference in the nanostructures formed. Figure 38 shows an array of nanowire-like structures. This type of nanoarchitecture was found uniformly across the surface of the copper foil, and results in a large increase in surface area compared to planar surfaces. The skinny nature of these nanowires, approximately 10 nm in diameter, means the diffusion length from oxide to electrolyte is much shorter than for a planar, bulk material. These short dimensions in the diffusion length should result in less recombination of charge carriers and subsequently an increase in efficiency and photoresponse of the material, as well as an increased dark current density.<sup>33</sup>

Based on these results, it was investigated whether a variation in the  $H_2O$  content of the electrolyte bath would favorably influence the morphology of the nanostructures. As expected, raising the  $H_2O$  content up to 5 vol % resulted in a planar morphology and an absence of any surface porosity. Upon reducing the  $H_2O$  content to 1%, a similar behavior was observed to that of 2%  $H_2O$ . At low anodization potential, nanostructures were found to be similar to those in Figure 37. Increasing the potential to above 70 V resulted in similar nanowire-like structures, seen in Figure 39. However in this case, the porosity of the structures was reduced. A majority of smaller gaps between each nanowire was filled, whereas the gaps remained mostly open in the case of 2%  $H_2O$ .



Figure 37. FESEM images of copper foil anodized in 2% HF + 2% H<sub>2</sub>O in DMSO electrolyte bath at 40 V. (a) scale bar = 200 nm; (b) inset: scale bar = 200 nm.



Figure 38. FESEM images of copper foil anodized in 2% HF + 2% H<sub>2</sub>O in DMSO electrolyte bath at 80 V. (a) scale bar = 200 nm; (b) inset: scale bar = 100 nm.


Figure 39. FESEM images of copper foil anodized in 2% HF + 1%  $H_2O$  in DMSO electrolyte bath at 80 V. (a) scale bar = 300 nm; (b) inset: scale bar = 100 nm.

Following these results, higher temperature electrolyte baths were attempted with the same electrolyte composition, which resulted in similar current transient profiles and no improvement upon the nanoarchitectures featured in Figures 38 and 39. In addition, voltages lower than 30 V were briefly attempted, but subsequently abandoned due to a miniscule current density and no visible changes in the appearance of the copper foil. If further improvements are to be made in DMSO electrolyte, other concentrations and/or compositions of acid will need to be attempted. Possibilities for future work will be discussed in Section 6.2.

#### 5.4 Summary

An interesting, high surface area nanoscale feature was obtained by anodizing copper foil in DMSO electrolyte. An array of ~10 nm diameter nanowires was fabricated in 2% HF + 2%  $H_2O$  in DMSO. The range of successful anodization conditions for this electrolyte composition was narrow. Only anodization above a threshold potential of approximately 70 V resulted in these nanowires; at lower potentials these features were non-existent. Also, reducing the  $H_2O$ content from 2 to 1 vol % reduced the porosity between the nanowires. The features were still able to form, but many more small pores between the features were closed when compared to those of 2% H<sub>2</sub>O.

# Chapter 6 Conclusion

## 6.1 Summary

As demonstrated in the previous chapters, this thesis has presented several aspects of electrochemical studies on the formation of copper oxide thin film nanoarchitectures. Specifically, the interaction of electrolyte composition and anodization conditions that result in novel nanostructures was established. One of the major pillars of this work was to maximize surface area of the oxide layer by introducing non-linear features on the nano-scale. In bulk materials, a significant portion of charge carriers is generated in the bulk of the oxide and are lost due to recombination. The improvement in the surface area of a nanostructured thin film serves to shorten the diffusion length of charge carriers, in order to minimize carrier recombination by photogenerated charges with small distance to the oxide – electrolyte interface, and thereby maximizing photo-electrochemical efficiency.

The parameter space for anodization conditions was explored for two organic solvents that have proven to promote high surface area nanoarchitectures in other metals. Ethylene glycol was found to produce high surface area nanostructures of copper oxide in anodization conditions performed primarily at room temperature, and at higher applied potential. For the electrolyte composition of 0.03 M NH<sub>4</sub>F + 2% H<sub>2</sub>O in EG, severe pitting was observed on the surface of the copper oxide film, and upon raising the anodization potential to upwards of 50 V, the beginning of nanotube formation appeared. However with further investigation into this parameter space, progressions in the growth of these structures into fully-developed nanotubes was elusive. Raising or lowering the acid concentration resulted in a destruction of this

structure. Further work must be done to fully understand the anodization conditions that will result in even higher surface area and aspect ratio nanostructures, detailed in Section 6.2.

Electrolytes consisting of dimethyl sulfoxide were also explored. It appears for the electrolyte composition consisting of HF + DMSO, an even narrower range of appropriate anodization conditions resulted in interesting nanofeatures. Although the structures resemble nothing in the way of nanotubes (such as in EG electrolyte), novel nanostructures were created within a narrow range of anodization conditions. Above the threshold potential of approximately 70 V, an array of ~10 nm nanowires was fabricated. Although these structures did not have any long-range order, the improvement in surface area is clear, as evidenced by FESEM images.

The anodized copper metal resulted in an amorphous nanostructured thin film material, although it is unclear exactly what the composition of the thin film is at the time of anodization. However, under appropriate anneal conditions, the thin film composition was converted to crystalline CuO. Crystallinity in the thin film is important in order to maximize charge transport efficiency, and the formation of CuO was advantageous due to its relatively low band gap (1.2 eV), which gives it the ability to utilize a large portion of the visible light spectrum unlike larger band gap materials. The p-type nature of the crystallized CuO thin films on metallic Cu foil was verified via photocurrent measurements, which indicated a clear photoresponse to visible light. These properties give the nanostructured CuO films the potential for use in a wide range of semiconductor and light harvesting applications.

## 6.2 Future Work

This work provides the basis for the exploration of anodization of copper. However, a great deal of work remains to understand the mechanisms of the formation of a nanostructured oxide layer. Many anodization parameters were explored in this thesis, but even more remain. For the electrolyte compositions studied, several anodization parameters were varied, including  $H_2O$  content, temperature, potential, and pH. Although it was concluded that a small amount of  $H_2O$  is necessary for the donation of  $OH^-$  ions to form the oxide layer, it is not necessary that the  $OH^-$  ions come from water. Replacing the  $H_2O$  with a base such as KOH may yield more novel nanostructures. The addition of KOH was briefly studied, but was used to influence the pH and not to replace  $H_2O$ . When using KOH in aqueous electrolyte, radically different nanostructures were found.

In addition, in Section 4.2.4 it was stated that it was difficult to raise the electrolyte bath temperature above 60°C without affecting the electrolyte composition and preventing H<sub>2</sub>O and solvent evaporation. Although this procedure is typically avoided for anodization because it abandons the elegance and simplicity of the technique, the anodization could be performed in a closed system, where pressure is controlled as well as temperature. This modification would allow higher temperatures to be explored, which may be necessary to support stable growth of nanotubes for the copper oxide system. For the same reason, lowering below room temperature should also be explored.

Further studies could also examine the effects of the acid. In these experiments, a fluoride-bearing ion was typically used. However, chloride ions have been successfully used to grow titania nanotubes, so exploration of acids such as NH<sub>4</sub>Cl in organic electrolytes would be a logical next step.

The effects of solvent composition should also be varied. In this study, ethylene glycol and dimethyl sulfoxide were chosen to be studied, given their robustness in anodization of other

metals. However with further research it may be proven that these electrolytes are not suitable for growth of porous nanoarchitectures with greater thickness or efficiency than demonstrated in this thesis. Solvents such as diethylene glycol (DEG), formamide (FA), and *N*,*N*dimethylformamide (DMF) have produced nanotubes in other materials.

With the current work, it is difficult to ascertain the composition of the as-deposited amorphous thin film. Although it is not necessary to know the compositions due to the thermal annealing step where conversion to oxide is achieved, for understanding the mechanisms of thin film formation for copper anodization, great insights could be gained. IR spectroscopy and XPS are two techniques which should be employed to understand what happens on the surface of the foils during anodization.

Once the formation of consistent nanostructures of copper oxide thin films with enhanced long-range order can be established, post-anodization techniques must be optimized in order to ensure their functionality in engineering devices. Cleaning methods such as aqueous washes, organic solvent washes, and sonication have been used. The effects of washing methods influence the adherence of the thin film to the substrate. Good adherence to the substrate is essential for optimal device performance.

In addition, anneal conditions can affect the resulting porosity and photoresponse of a device. Annealing at a high temperature may induce excellent crystallinity, but may also clog pores which reduce surface area and therefore overall efficiency. A systematic study of the effects of anneal conditions on device performance (via photocurrent measurements) would be useful. Annealing in air instead of  $O_2$  gas may encourage other phases to be mixed with CuO, altering the band gap and resulting photoelectrochemical properties and photostability of the thin film.

In conclusion, many parameters both pre- and post-anodization must be explored in further detail in order to develop stable and repeatable nanoarchitectures of this exciting material. The intrinsic properties of copper oxide make this material an attractive candidate for

use in a wide range of devices, but its synthesis via anodization requires further investigation before it can be implemented.

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