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AN INVESTIGATION INTO THE DOPING AND CRYSTALLINITY OF ANODICALLY FABRICATED TiO₂ NANOTUBE ARRAYS: TOWARDS AN EFFICIENT MATERIAL FOR SOLAR ENERGY APPLICATIONS

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by

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ABSTRACT

Anodically fabricated TiO₂ nanotube arrays have attracted significant attention in the scientific community because it has proven to be a robust and cost-effective functional material, widely investigated in many applications especially those related to energy conversion such as photoelectrochemical water splitting and solar cells. However, the properties of this material must be modified in order to increase its energy conversion efficiency. For example, the wide bandgap of TiO₂ (~ 3.0 eV for rutile and 3.2 eV for anatase) limits its absorption to UV radiation, which accounts for only \approx 5% of the solar spectrum energy. Also, despite many efforts, it remains a major challenge to successfully convert the amorphous walls of the as-fabricated TiO₂ nanotubes to crystalline walls while simultaneously retaining the barrier layer at a minimal thickness. The barrier layer formed during high temperature crystallization acts to hinder electron transfer in applications such as water photoelectrolysis, which in turn leads to reduction in the overall water splitting efficiency. The oxide growth from the underlying Ti foil layer can percolate up and destroy the tube morphology with very high temperature anneals. These properties are believed to be among the critical factors limiting the efficient use of this material especially in photoelectrochemical applications.

The important question is; how can TiO_2 be modified so as to achieve the requisite performance as a photoelectrode? The primary focus of this dissertation was to improve the properties of the anodically fabricated TiO_2 nanotube arrays; notably its band gap and crystallinity while retaining its tubular structure unaffected. The underlying hypothesis was that controlling the crystallinity and band gap while retaining the tubular structure will result in an enormous enhancement of the photoconversion capability of the material. To this end, a direct one-step facile approach for the *in-situ* doping of TiO_2 nanotube arrays during their electrochemical fabrication in both aqueous and non-aqueous electrolytes has been investigated. The effect of doping on the morphology, optical and photoelectrochemical properties of the fabricated nanotube arrays is discussed. Upon the use of different cathode materials for the anodization of titanium, it was possible to dope TiO_2 with various metal ions which were found to enhance the optical and photoelectrochemical properties of the material. The highest photoconversion efficiency of 6.9% under UV illumination (320-400 nm) was recorded for a $\sim 2.5 \mu m$ -sample prepared using a Fe cathode. In another set of experiments, mixtures of H₂O₂ and HCl in ethylene glycol electrolytes were found to drive modest amounts of carbon within the resulting TiO₂ structures which in turn led to an enhancement of the optical and photoelectrochemical properties of the resulted material as well. The highest Air Mass (AM) 1.5 spectrum efficiency of 0.42% was recorded for $\sim 6 \mu m$ -sample prepared in EG-containing electrolyte in the presence of 0.5M HCl and 0.4M H_2O_2 . This is ~15% more efficient than that reported for 30 µm long undoped TiO₂ nanowires under AM 1.5 (5M KOH, 0.61V_{SCE}) although our sample is 5 times shorter and tested in less concentrated KOH electrolyte. The incorporation of these ions into the TiO₂ nanotube arrays during their synthesis gives rise to the possibility of *in-situ* bandgap engineering of the material during its fabrication without any structural collapse. These results showed the validity of the hypothesis that doping the material while retaining its tubular structure enhances its photoactivity.

In an effort to improve the crystallinity of the anodically fabricated TiO₂ nanotube arrays while retaining the tubular morphology, novel processing routes have been investigated to fabricate crystalline TiO₂ nanotube array electrodes. For the sake of comparison, the nanotubes were annealed at high temperature using the conventionally used procedure. The samples were found to be stable up to temperatures around 580 °C, however, higher temperatures resulted in crystallization of the titanium support which disturbed the nanotube architecture, causing it to partially and gradually collapse and densify. The maximum photoconversion efficiency for water splitting using 7 μ m-TiO₂ nanotube arrays electrodes annealed at 580 °C was measured to be about 10% under UV illumination.

Could we enhance the photoelectrochemical properties of the material via any subsequent treatment? To this end, we investigated the effect of subsequent low temperature crystallization step. Combining high temperature furnace annealing with a 140°C (≈ 50 psi) ethanol vapor treatment successfully enhanced the photoconversion efficiency by about 30% under UV illumination and 40% under full AM 1.5 illumination. Despite this improvement, the barrier layer thickness was still the same as that of the thermally annealed sample. Consequently, it was believed that finding a technique which could be used to crystallize the nanotubes either at short time intervals and/or low temperature would result in better crystallinity of the tube walls as well as in a minimal barrier layer thickness which in turn would result in an enhancement of the photoconversion efficiency. Consequently, the possibility of both avenues has been investigated, i.e. the possibility of crystallizing the nanotubes at low temperature and/or at short time. Rapid infrared (IR) annealing was found to be an efficient technique for crystallizing the nanotube array films within a few minutes. The IR-annealed 7µm-nanotube array films showed significant photoconversion efficiencies $(\eta = 13.13\%)$ upon their use as photoanodes to photoelectrochemically split water under UV illumination. This was related, in part, to the reduction in the barrier layer thickness from 1100 nm for the thermally annealed sample down to 200 nm for the IR-annealed sample under same conditions. These results support the hypothesis that reducing the barrier layer thickness would result in better performance of the material. Could the fabrication temperature and in turn the barrier layer thickness be reduced any more? With this in mind, the possibility of low temperature crystallization was investigated with the hypothesis that this route might result in even thinner barrier layer.

Regarding the possibility of low temperature crystallization, this dissertation encompasses the first report on low-temperature synthesis of crystalline TiO_2 nanotube arrays. Nanotube arrays of up to 1.4 µm length using a two-step process have been demonstrated. The

two-step process consists of initial treatment of the Ti foil in an oxidizing agent (H_2O_2 or (NH₄)₂S₂O₈)-containing electrolytes, followed by potentiostatic anodization of the resulting foil in NH_4F -containing electrolytes. The as-synthesized crystalline nanotube arrays were successfully tested as anode electrodes for water photoelectrolysis, with performances comparable to samples annealed at high temperatures, and for liquid junction dye (N 719 dye)-sensitized solar cells. The photoconversion efficiencies for the as-synthesized nanotube arrays, under 320 nm - 400 nmillumination, were approximately 3% for the 800nm-H₂O₂-fabricated nanotubes and 4.4% for the 1.4 μ m-(NH₄)₂S₂O₈-fabricated nanotubes upon their use to split water photoelectrochemically. Although this method showed that low temperature crystallization drastically improved the photoelectrochemical properties of the material, the length of the resulted nanotube arrays was limited to 1.4 μ m, largely determined by the thickness of the oxide layer formed in the first step of fabrication. The obtained improvement in the photoconversion efficiency despite the limitation in the thickness of the fabricated nanotube arrays (η =4.4% for a 1.4µm nanotube sample) motivated me to investigate the possibility of achieving crystalline nanotubes directly from the anodization bath. This avenue would have the advantage of overcoming the limitation in tube length and controlling the barrier layer thickness since no high temperature would be employed.

With the ultimate goal to achieve room or low temperature, crystalline TiO_2 nanotube arrays, the effect of electrolyte composition on the possibility of inducing crystallinity in the vertically oriented TiO_2 nanotube array films during their synthesis via potentiostatic anodization was investigated. Is there any electrolyte composition that might enable *in-situ* crystallization? With the use of 3M HCl electrolytes, *partially* crystalline, vertically oriented TiO_2 nanotubes with thicknesses up to 300 nm were achieved between 10 V and 13 V. The addition of H_2O_2 to HClcontaining electrolytes was shown to extend the tube length up to 870 nm and to improve the crystallinity of the formed architectures. In regard to water splitting, the 870nm-*partially* crystalline as-anodized sample showed photoconversion efficiency of 0.025% under AM 1.5

illumination. Note that regularly fabricated TiO₂ nanotube arrays in fluoride-containing electrolytes show almost zero photoconversion efficiency. However, annealing the partially crystalline samples at 500°C resulted in an improvement in the photoconversion efficiency (0.14%). This is the first report on the fabrication of *partially* crystalline TiO_2 nanotubes and in *fluoride-free* HCl aqueous electrolytes. With the motivation of finding an electrolyte composition that might yield better crystalline nanotubes than that obtained in the HCl-containing electrolytes, the effect of using some polyol electrolytes (diethylene, triethylene, tetraethylene and polyethylene glycols) on the crystallinity and morphology of the fabricated TiO_2 nanotube arrays was investigated. The study showed that the use of these electrolytes helped to induce partial crystallinity in the formed nanotube arrays with the intensity of anatase (101) peak was found to increase with increasing the molecular weight of the polyol electrolyte. Water content in the electrolyte was found to be a critical factor in obtaining such partial crystallinity. The as-anodized nanotube arrays showed low photoconversion efficiency upon their use as photoanodes to split water photoelectrochemically indicating only partial crystallinity of the tubes. Annealing the tubes at only 300°C increased the photocoversion effciency to values comparable to those usually seen when nanotubes annealed at high temperature (above 500° C) were used. There is a possibility that the pre-existing anatase crystallites acted as nucleation sites (seed layer) facilitating the nucleation and growth of more crystallites at 300°C resulting in comparable crystallization to that obtained for totally amorphous nanotubes annealed at higher temperature (above 500° C).

Building upon my acquired expertise in synthesis of TiO_2 nanotube arrays, I have investigated the possibility of formation of Ta_2O_5 nanotube arrays. Ta_2O_5 is the starting material to fabricate TaON which was shown to split water efficiently and to be highly responsive to excitation wavelengths up to about 600nm with IPCE values up to 34%. The underlying hypothesis was that fabricating this material in the nanotubular structure would enhance its efficiency to split water due to the high surface area and better charge transfer. This thesis reports, for the first time, synthesis of high-aspect-ratio tantalum oxide nanotube arrays via one-step anodization of Ta foil. The use of aqueous electrolytes containing $HF:H_2SO_4$ in the volumetric ratios 1:9 and 2:8 results in formation of ordered nanodimpled surfaces with 40-55 nm pore diameters over the potential range 10-20 V. The addition of 5-10% of either ethylene glycol (EG) or dimethyl sulfoxide (DMSO) to the HF and H_2SO_4 aqueous electrolytes resulted in the formation of Ta oxide nanotube arrays up to 19 µm thick, either securely anchored to the underlying Ta film or as robust free-standing membranes, as dependent upon the anodization time and applied voltage.

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DEDICATION

I dedicate this work to my parents, my wife and my beloved son; Mouaaz, and to all my

brothers and sisters

Chapter 1

Introduction and Scope of the Thesis

1.1 Renewable Energy and the Terawatt Challenge

Air quality concerns and global climate impact constitute two major problems with our reliance on fossil energy sources. More than a century ago, Arrhenius put forth the idea that greenhouse gases such as CO₂ from fossil fuel combustion could cause the earth to warm as the infrared opacity of its atmosphere continued to rise.¹ The relations between fossil fuel burning, climate change, and environmental impacts are becoming better understood.² The amount of atmospheric CO₂ has reached an unprecedented 379.1 ppm in 2005 (Figure 1.1), it is expected to pass 550 ppm this century.³ Climate models indicate that 550 ppm CO₂ accumulation, if sustained, could eventually result in global warming comparable in magnitude (but opposite in sign) to the global cooling of the last Ice Age.⁴ The consequences could be unpredictably catastrophic and disastrous as recent hurricanes and tsunamis indicate.⁵



Figure 1.1: Atmospheric carbon dioxide record from Mauna Loa, Hawaii.⁵

Every year, a larger percentage of the current global population seeks to improve their standard of living by burning ever-increasing quantities of carbon-rich fossil fuels. Based on United Nations forecasts, another 2.5 billion people are expected by 2050 with the preponderance of them residing in developing countries.⁶

Coupled with this growing population's desire to improve their quality of life are the developed countries' activities which promise to add to the environmental pressure. Oil, coal, and natural gas are used to power cars, trucks, power plants, and factories, causing a dramatic buildup of greenhouse gases in the atmosphere, most notably CO_2 . The buildup of heat-trapping gases is intensifying the earth's natural greenhouse effect, causing average global temperatures to rise at an increasing rate. Most alarming is not the fact that the climate is changing but rather the rate at which the buildup of CO_2 is occurring. ⁵ Further, fossil fuels constitute a non-renewable, finite resource.⁷ That is to say; fossil fuels do not have a future in helping to meet this growing demand.

These environmental imperatives and energy resources limitation require us to quickly come to terms with the actual costs, including environmental externalities, of all of our energy use. Only then will the economic reality of energy consumption be realized. Therefore, the challenge is to maintain and improve the standard of living of the world's population and support economic growth while utilizing energy sources that are renewable and do not adversely affect the environment. Currently, renewable energy constitutes only a small fraction of the total energy mix in the U. S. and in other parts of the world (Figure 1.2). For example, in 2000, only about 6.6 quads (one quad is about 10^{18} J) of the primary energy in the U.S. came from renewables out of a total of 98.5 quads.⁸ Of this small fraction supplied by renewable energy, about 3.3 quads were from biomass, 2.8 from hydroelectric generation, 0.32 from geothermal sources, 0.07 from solar thermal energy and 0.05 quads from wind turbines.⁹ For the CO₂ emissions to be capped at environmentally safe levels, this profile would have to switch to an energy mix that resembles the right-side panel in Figure 1.2. This is what Professor Rick Smalley, the Nobel laureate in

Chemistry 1996, referred to as *the Terawatt Challenge*.¹⁰ Recent analyses¹¹ have posited that research, development and commercialization of carbon-free primary power to the required level of 10-30 TW (one terawatt = 10^{12} W) by 2050 will require efforts of the urgency and scale of the Manhattan Project and the Apollo Space Program.^{10,11}



Figure 1-2: The terawatt renewable energy challenge; the energy mix has to switch from the panel on the left to the panel on the right to cap CO₂ levels at safe limits. ¹²

1.2 Hydrogen as a Fuel of the Future

Hydrogen (H) is the simplest atom, consisting of one proton and one electron. Atomic hydrogen is very reactive and prefers to exist in a molecular form (H₂). When mixed with sufficient quantities of an oxidant (e.g., air, O_2 , Cl, F, etc.), it becomes a combustible mixture. **Table 1.1** shows some selected properties of gaseous hydrogen at 20 °C and 1 atm.

Physical Property	Amount		
Density	0.0838 kg/m ³		
Diffusion Coefficient in Air	6.10 cm ³ /s		
Thermal Conductivity	0.1825 W/m.K		
Specific Heat (C _v)	10.16 J/g. K		
Specific Heat (C _p)	14.29 J/g. K		
Enthalpy	4098 kJ/kg		
Entropy	64.44 J/g. K		

Table 1-1: Selected properties of gaseous hydrogen at 20 °C and 1 atm.¹³

Each fuel is limited to a fixed amount of energy it can release when it reacts with an oxidant. There are two values that can be experimentally tested for any fuel to determine the amount of energy it can release; the fuel's higher heating value (HHV) and lower heating value (LHV).¹³ The fact that hydrogen has the highest energy content per unit mass than any fuel¹³ makes it especially valuable. **Table 1.2** compares hydrogen properties with some other common fuels. Note that the energy density (ED) can be calculated as the product of LHV and the density of the fuel.

Fuel	Density (kg/m ³)	HHV (kJ/g)	LHV (kJ/g)	$ED (MJ/m^3)$
Hydrogen	0.0838	141.9	119.9	10.8
Methane	0.71	55.5	50.0	32.6
Gasoline	702	47.5	44.5	31,240
Diesel	855	44.8	42.5	36,340
Methanol	799	20.0	18.1	14,500

Table 1-2: Comparing hydrogen properties with other fuels.¹³

Obviously, the most important virtue of using hydrogen as a fuel, besides its high energy content, is its pollution-free nature. When burned in air, the main combustion product is water. Also, the use of hydrogen with O_2 in a fuel cell can be used directly to produce electricity. Indeed this, unlike fossil fuels, generates no CO_2 . These characteristics, among others, make hydrogen an ideal energy carrier. However, hydrogen is present in nature in limited quantities, which hinders its direct use. Therefore, the key question is where is the H_2 to come from and how can we produce hydrogen in a reasonable quantity?

1.3 Solar Energy and Hydrogen Production

Hydrogen is not a primary source of energy; rather it is an energy carrier much like electricity.¹⁴ Therefore, energy is required to extract hydrogen from substances like natural gas, water, coal, or any other hydrocarbon. **Figure 1.3** shows the primary energy sources and their use in hydrogen production.



Figure 1-3: Primary energy sources and their use in hydrogen production.¹⁴

1.3.1 Solar Energy

The sun is the ultimate renewable source of energy on earth. It radiates energy at the rate of 3.9×10^{26} W and has been doing so for several billion years.¹⁵ Each second, the sun burns about 637 million tons of hydrogen in a "nuclear furnace" to create about 632 million tons of helium with the 5 million tons difference transformed into energy (E = mc²).¹⁵ This energy gives rise to a surface temperature of around 6000 K, which in turn gives rise to the spectral distribution of the solar radiation, see Chapter two for more details. Solar irradiance is neither permanent nor of constant intensity around the world. Therefore, a suitable energy carrier for storage and transport of electricity is needed. To this end, hydrogen is thought to be an ideal energy carrier.

1.3.2 Hydrogen Generation by Water Splitting

A sustainable hydrogen economy requires hydrogen to be produced using a renewable method. As early as 1874 Jules Verne alluded to clean hydrogen fuels, writing: "*Yes, my friends, I believe that water will someday be employed as fuel, that hydrogen and oxygen, which constitute it, used singly or together, will furnish an inexhaustible source of heat and light....I believe, then, that when the deposits of coal are exhausted, we shall heat and warm ourselves with water. Water will be the coal of the future.*" ¹⁶ Nowadays, it becomes obvious that water would be the ideal and most sustainable source for H₂ production. **Table 1.3** summarizes various ways for generating H₂ using renewable sources. Note that although nuclear energy can be used to produce H₂, this way would not be significantly cheaper than using renewable power sources. Nuclear plants can generate H₂ in a non-electrolytic, thermal mode because of the intense heat generated in a thermonuclear reaction.¹⁷ This approach has not been demonstrated yet due to waste disposal problems and lack of public acceptance.¹⁷ Furthermore, producing 10 TW of nuclear power

would require the construction of a new 1-GW nuclear fission plant somewhere in the world every other day for the next 50 years!¹⁷ Similarly, the barriers set against the efficient use of biomass, wind and hydroelectric powers are listed in **Table 1.3**.

Source	Power available (TW)	Comments
Biomass	7-10	Entire arable land mass of the planet must be used excluding the area needed to house 9 billion people.
Wind	2.1	Would saturate the entire Class 3 (wind speed at 5.1 m/s at 10 m above ground) global land mass with windmills.
Nuclear	8.0	Requires the construction of 8000 new nuclear power plants.
Hydroelectric	1.5	Would require damming of all available rivers.

Table 1-3: The ability of nuclear and various renewable energy sources to meet the 14-20 TW demand of carbon-free power by 2050. 18

This means that we are left with the solar energy as a possible efficient and renewable source of energy to split water. **Figure 1.4** shows a number of possible pathways by which solar irradiation can be utilized to split water and generate H_2 . In the so called thermolysis process, the heat energy contained in the solar irradiation can be utilized directly to decompose water to hydrogen and oxygen at elevated temperatures without electrolysis.¹⁹ However, it was found that only about 25% of the water dissociates even at pressures as low as 0.05 bar and temperatures as high as 2500 K.²⁰ This was attributed to the rapid kinetics of the backward reaction between H_2 and O_2 to form water with the high temperature catalyzing the reaction. This makes thermolysis pathway a non-feasible approach.



Figure 1-4: Pathways of generating hydrogen.^{19,20}

Electrolysis and photolysis are the processes of splitting water using electricity and light, respectively. Water electrolysis is a very simple and reasonably efficient process. The net reaction is:

H₂O (liquid/vapor) + electrical energy
$$\rightarrow$$
 H₂ (g) + ½ O₂ (g) [1.1]

Today, water electrolyzers satisfy around 3.9% of the world's hydrogen demand through the production of hydrogen at levels ranging from a few cm³/min to several thousand m³/hour.²¹ The sluggish reaction kinetics at the electrodes aided by the overvoltage effects is still a serious limitation of this process. In photolysis, water splitting occurs through the direct use of sun light, i.e. the conversion of light into electrical current then the transformation of a chemical entity (H₂O) into useful chemical energy (H₂). This later process is the approach used in this thesis to split water. Therefore, it will be discussed in more detail later.

1.4 Towards Highly Efficient Photoelectrochemical Systems

Although the solar spectrum contains enough energy to split water, this reaction does not occur spontaneously at significant rates, due to the low absorption coefficient of water ($\sim 10^{-2} \text{ m}^{-1}$) in the UV-visible region of the electromagnetic spectrum.²¹ However, in theory, sunlight can be used to excite a semiconductor material, which in turn acts as a catalyst for the water splitting reaction in an electrochemical cell. In practice, the progress in the photoelectrochemical water splitting technology is materials-limited. The most challenging key factors in a water splitting system are; the existence of a material with a band gap suitable for capturing as much energy as possible from incident light, its stability in a wide range of aqueous electrolytes and minimization of charge carrier recombination.²¹ Further, the material has to be in a plentiful supply and environmentally benign for scalable applications. To this end, metal oxide semiconductors appear to exhibit superior properties as photo-electrodes in comparison to other types of materials.

1.4.1 Metal Oxide Semiconductors

The pioneering work of Honda and Fujishima in 1972 demonstrated that water splitting by illuminating a titanium dioxide (TiO₂) electrode with UV can be used to efficiently generate hydrogen.²² Subsequently, an enormous body of literature followed with the aim directed towards the development of robust, efficient, cost-effective, reliable, stable and scalable photoelectrochemical systems.

For the past three decades, metal oxide systems²³ have been studied extensively. Based on their availability and ease of fabrication, many of these materials have been tested as photoanodes in various photoelectrochemical systems, e.g. TiO_2 ,²²⁻²⁵ $SrTiO_3$,²⁶⁻²⁸ SnO_2 ,²⁹⁻³¹ Fe_2O_3 ,³²⁻³⁵ WO_3 ,³⁶ and WO_3/Fe_2O_3 nano-electrodes.^{37,38} The most critical key factors underlying the ability of the metal oxide to achieve useful device performance, amongst others, include its photocorrosion stability as a photoanode, the range of its wavelength response and its current-voltage characteristics.²¹ However, the investigated materials, up till now, have been found lacking in one property or another. For example, although lower band gap materials have the ability to absorb most of the visible spectrum, they are more prone to photocorrosion than their higher band gap counterparts and vice versa.²¹

1.5 Impact of Ordered Metal Oxide Nanoarchitectures

Numerous major advances in research and technology over the last decade or two have been made possible by the successful development of nanostructures made of metals, insulators and especially semiconductors. The practical interest in nanostructures is related to their unique properties and superior performance when compared to their bulk counterparts. One significant difficulty with nanostructures is how to prepare them in a well-ordered fashion. One can distinguish two approaches: top-down and bottom-up.³⁹ In the top-down approach, objects of ever-smaller dimensions are carved out of larger objects. However, the bottom-up approach consists of growing small objects to their desired size and shape. Porous nanostructures have attracted attention because they combine many of the advantages of the top-down and bottom-up approaches which made them unique functional architectures. For example, the use of porous nanocrystalline semiconductor films such as several micron thick porous crystalline TiO₂ films has led to substantial progress in the field of low-cost photoelectrochemical energy conversion.⁴⁰⁻

⁴⁴ The high efficiency imparted by these materials can be related to their enormous internal surface area which enables efficient light harvesting and maximization of the photogenerated charge in the porous nanocrystalline electrodes. Despite all these unique characteristics of the porous films, the structural disorder at the contact between two crystalline particles leads to an

enhanced scattering of free electrons, thus reducing the electron mobility, i.e. charge transport limitations.⁴⁵ Therefore, it is hypothized that ordered and strongly interconnected nanoscale structure would overcome these limitations by eliminating the random nature of the particles network. To this end, considerable interest has been focused on the fabrication of highly ordered one-dimensional nanostructures such as arrays of nanowires, nanorods and nanotubes. These structures are expected to enhance the electron percolation pathways and light conversion efficiencies.⁴⁶

1.6 Titanium Dioxide Nanotube Arrays

 TiO_2 is an n-type semiconductor exhibiting excellent charge transfer properties and hence superior photocatalytic activity.⁴⁷ Consequently, the photoactivation of TiO_2 has received enormous attention from scientists and engineers in the past decade; see Figure 1.5.



Figure 1-5: Annual number of papers published in which "TiO₂ or titanium dioxide" and "photo" are mentioned, beginning in 1992 through November 2005.⁴⁷

In regard to photoelectrochemical water splitting, although, the bandgap of TiO₂ includes the redox potential (E_{redox}) for the H₂O/'OH reaction allowing photo-generation of oxygen,²¹ the wide bandgap of TiO₂ (~ 3.0 eV for rutile and 3.2 eV for anatase) limits its absorption to UV radiation which accounts for only \approx 5% of solar spectrum energy. Various approaches are being pursued to circumvent the poor solar light response of photocorrosion-stable wide band gap semiconductors such as TiO₂. A tremendous advantage of the nanotube array geometry is the increased surface area. Highly-ordered vertically oriented TiO₂ nanotube-arrays fabricated by anodization of titanium constitute a material architecture that offers large internal surface area and, after being crystallized at high temperature, fairly reasonable electron percolation pathways for vectorial charge transfer between interfaces.²¹ Despite all these superior properties provided by the nanotubular structure, there are still some obstacles that need to be overcome to get the ideal optimized structure we need. For example, while TiO₂ nanotube arrays demonstrate a photoconversion efficiency of 16.25% under UV illumination, its efficiency under visible light AM1.5 is still limited to as low as 0.6 %.⁴⁹⁻⁵¹ Therefore, the following questions may be raised: what controls efficiency and how it can be improved?

1.7 Can Engineering the Bandgap and Crystallinity Help?

Highly crystalline structures offer unique advantages over amorphous architectures by providing a direct and fast pathway for electron transport ⁵² reducing electron recombination reactions with the oxidized species in the electrolyte, increasing the overall conversion efficiencies.⁵³ To date, titania nanotube arrays synthesized by Ti anodization are amorphous so that an elevated temperature heat-treatment, typically greater than 450°C, is required to induce crystallinity.⁵⁴ In regard to photoelectrochemical water splitting, annealing at temperatures sufficient to induce crystallinity usually leads to the formation of a thick barrier layer, separating

the nanotube array film from the underlying metal substrate⁵⁴ where recombination losses can occur, see **Figure 1.6**. This barrier layer acts to hinder electron transfer to the metal electrode (cathode) where water reduction takes place, in turn reducing the overall water splitting efficiency.



Figure 1-6: Schematic representation of the TiO₂ nanotube array structure obtained via potentiostatic anodization of titanium.

Therefore, it was the hypothesis of the current work that different crystallization routes (e.g. *in-situ* room temperature crystallization, low temperature crystallization, rapid thermal crystallization or conventional thermal annealing with controlled introduction of gases, type of gas ambient, temperature, and duration) might affect the rate of buildup of the oxide barrier layer differently and in turn reduce the series resistance and recombination losses. This would consequently improve the ability of TiO_2 structures to split water more efficiently. In addition to controlling the barrier layer thickness, control of grain size is also critical in improving the photoelectrochemical efficiency of TiO_2 .⁵⁵
Another contribution to the observed poor efficiency of the currently fabricated TiO₂ nanoarchitectures comes from the fact that TiO_2 has a wide bandgap which limits its absorption to UV radiation which accounts for only $\approx 5\%$ of the solar spectrum energy. Efforts to shift the bandgap of TiO₂ while maintaining its excellent charge transfer properties and photocorrosion stability have primarily focused on metal doping.55-57 Although various approaches of doping have been developed in the past, they usually suffer from multiple, tedious steps and often result in poor structure control.⁵⁵⁻⁵⁷ For example, aliovalent metal ion doping was shown to introduce mid-gap energy levels (see Figure 1.7) which are expected to control the bandgap response of the nanotube arrays and enhance their visible spectrum properties, however, the effect of doping is not well understood, and is complicated by some dopants affecting the morphology. The morphological defects imposed by dopants were believed to be, in part, due to the use of multi separate steps for fabrication and doping. Further, there is a lot of debate whether some dopants can improve the photoelectrochemical properties of TiO2.58-63 Therefore, it was the aim of the present work to investigate the possibility of in-situ doping of titania nanotubes during their synthesis via cation incorporation from the anodization bath and consequently to examine its effect on the morphology and photoelectrochemical characteristics of the fabricated TiO₂ nanoarchitectures.



Figure 1-7: Energy levels of aliovalent ions in TiO₂ (rutile) lattice.⁶⁴

1.8 Scope of the Thesis

Is it possible to develop highly efficient, easily fabricated materials for the solar generation of hydrogen by water photoelectrolysis? Building upon the earlier work in the development of highly ordered TiO_2 nanotube arrays,²¹ the author's hypothesis was that it might be possible to modify synthesis techniques to achieve *in-situ* low temperature crystallization, and control the bandgap response of the nanotube arrays to enhance their visible spectrum properties, while maintaining their excellent charge transfer behavior by *in-situ* doping of the titania during synthesis through cation incorporation from the anodization bath.

Chapter 2 gives a general overview on the science behind water photoelectrolysis and factors affecting the performance of a light harvesting device to aid the reader in following the discussions used throughout this work.

Chapter 3 reviews the relevant literature on the subject of synthesis, crystallization and doping of the TiO_2 nanoarchitectures as well as their use in water photolysis.

Chapter 4 gives the details of the experimental conditions employed for fabrication, characterization and testing of the fabricated photoanodes.

Chapters 5 through 8 include the results and discussion section of the thesis which is the core part of the dissertation.

Chapter 5 presents the results concerning the efforts towards engineering the band gap of TiO_2 via *in-situ* doping of the material. Two main avenues have been tried: (1) Study the effect of

using different cathode materials to control the morphology and properties of TiO_2 nanotube arrays. The results indicate the incorporation of ions into the TiO_2 nanotube arrays during their electrochemical synthesis, giving rise to the possibility of *in-situ* band gap engineering of the material during its fabrication without affecting their tubular morphology,⁶⁵ (2) Study the effect of different electrolyte bath chemistry on the possibility of *in-situ* doping of the formed TiO_2 .⁶⁶

Chapter 6 discusses the results of the high temperature thermal annealing treatments of the TiO_2 nanotube arrays. Conventional thermal annealing at high temperature was carried out in oxygen gas ambient at different temperatures and annealing durations. The samples were found to be stable up to temperatures around 580 °C, however, higher temperatures resulted in crystallization of the titanium support which disturbed the nanotube architecture, causing it to partially and gradually collapse and densify. The effect of vapor treatment on previously annealed TiO_2 electrodes ⁶⁷ and results on the rapid infrared annealing of the fabricated TiO_2 nanotubes are documented.⁶⁸

Chapter 7 This chapter reports the fabrication of crystalline TiO_2 nanotube at low temperature. A two-step process consisting of initial treatment of the Ti foil in an oxidizing agent (H₂O₂ or (NH₄)₂S₂O₈)-containing electrolytes, followed by potentiostatic anodization of the resulting foil in NH₄F-containing electrolytes has been used. The as-synthesized crystalline nanotube arrays were successfully tested as anode electrodes for water photoelectrolysis, with performances comparable to samples annealed at high temperatures, and for liquid junction dye (N 719 dye)-sensitized solar cells.⁶⁹

Chapter 8 presents different efforts towards *in-situ* crystallization of TiO_2 nanotubes during their fabrication. This includes the use of concentrated hydrochloric acid, mixtures of concentrated hydrochloric acid and hydrogen peroxide as anodization electrolytes in both aqueous and ethylene glycol-containing electrolytes. The as-anodized as well as thermally annealed samples were used as photoanodes to split water photoelectrochemically.

Chapter 9 considers fabrication of Ta_2O_5 nanotube arrays via one step anodization as an extension of the fabrication work to different metal systems.⁷⁰ Also, this material (after being converted to oxy-nitride) is a new material that can be used as a photoanode in the water photolysis applications.

Plans for Future Work suggests some extension plans for further work.

Appendix 1 Presents some basic fundamental aspects of semiconductors.

Appendix 2 contains the definition of IPCE along with the derivation of the (IPCE) formula.

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Chapter 2

Background

There are many concepts that underpin the development of photocatalytic materials for water splitting. This chapter presents some important background information relating to semiconductor materials and their interaction with the electrolyte when used as photoelectrodes in a photoelectrochemical cell. Special attention will be given to TiO_2 as a model photoelectrode. These concepts will be further discussed during the analysis of the results in the subsequent chapters.

2.1 Solar Radiation

The available solar energy for conversion processes depends upon the atmospheric conditions and the relative position of the sun to the absorbing plane. Figure 2.1a shows a representative solar spectral photon flux under the global AM 1.5 (air mass 1.5) condition, with the corresponding global spectral irradiance shown in Figure 2.1b. AM 1.5 represents the average atmospheric conditions in the United States which corresponds to a situation when the sun is at a zenith angle of 48.19° (AM = $[1/\cos (48.19)] = 1.5$).¹⁻³ In such a configuration, the light travels through the atmosphere 1.5 times the distance it travels when the sun is at 0° zenith angle (AM 1.0).



Figure 2-1: (a) Solar spectral photon flux (global AM1.5) and (b) The solar spectral irradiance.³

For the global spectrum, the flat absorber surface needs to be inclined 37 ° from the horizon and facing the sun.³ Note that 37 ° is the average latitude for the 48 contiguous states of the USA. The global AM 1.5 configuration is shown in **Figure 2.2**. The global irradiance includes both direct and diffused components of light from the sun with the total irradiance (I_r) calculated as:³

$$I_r = \int_0^\infty E(\lambda) d(\lambda)$$
 [2.1]



Figure 2-2: (a) Configuration for AM1.5 solar illumination, (b) Schematic illustration of light spectrum showing incidence of solar irradiance (I_r) available for conversion.^{3,4}

The total irradiance for the spectrum given in **Figure 2.1b** in the wavelength range $0.3-4.0 \mu m$ is reported to be about 963W/m^{2.4} However, considering the effect of variations in the atmospheric conditions (such as cloudiness, dust particles and relative humidity), the spectrum is normalized to $1000W/m^2$. This is generally regarded as 1 sun.⁴

2.2 The Semiconductor-electrolyte Interface

In order to enhance the photoelectrochemical cell performance, it is critical to understand the basic nature of the semiconductor-electrolyte interface that is developed when a semiconductor electrode comes into contact with an electrolyte.⁵ In this thesis, the discussion of semiconductor-electrolyte interface will be limited to an n-type semiconducting photoanode (e.g. TiO₂) submerged in an electrolyte with a metal electrode acting as the counter-electrode (cathode). The band structures of both electrodes at different conditions are shown in Figure 2.3.

Four electrochemical conditions can be distinguished in Figure 2.3: (a) initial condition before equilibrium is reached, (b) equilibrium condition in the dark, (c) illuminated condition, and (d) illuminated condition with a bias voltage applied.

Figure 2.3a shows the energy diagram before galvanic contact is made between the two electrodes. Initially the Fermi level of the electrolyte can be anywhere between the two water splitting redox potentials, the exact position depending on the concentration of hydrogen and oxygen in the electrolyte.⁵ At equilibrium in the dark (absence of light) (**Figure 2.3b**), the Fermi level of the semiconductor equilibrates with that of the electrolyte by flow of electrons from the n-type semiconductor (lower work function) to the electrolyte (higher work function), resulting in a region depleted of electrons at the semiconductor surface known as the *depletion layer* or *space charge layer*.⁵ This positively charged region attracts negatively charged ions in the electrolyte, which form a very thin (< 1 nm) *Helmholtz layer*.



Figure 2-3: Energy diagrams of PEC components: anode (n-type semiconductor), electrolyte, and cathode (metal): (a) before galvanic contact, (b) after galvanic contact in dark, (c) effect of light and (d) effect of light and externally applied bias on electronic structure of PEC components.⁵ Note that the vertical axis represents potential energy, and the three sections horizontally in each image show the semiconductor electrode, electrolyte and metal counter-electrode, respectively. U_{fb} is the flat band potential, U_{bias} is the bias voltage applied to the cell and V_B is the amount of band bending.⁵

The equilibration of the electrochemical potentials of the electrolyte and the semiconductor leads to "*band bending*" of magnitude $V_{B.}^{5}$ The potential drop across the Helmholtz layer, which increases the band bending, is determined by the interaction between the semiconductor and the electrolyte. The width of the depletion layer is represented by:⁵

$$w_d = \lambda_D \left(\frac{2e\left|U - U_{fb}\right|}{kT} - 1\right)^{1/2}$$
[2.2]

where λ_D is the Debye length, the distance over which significant charge separation can occur (see Eq. 2.3 below⁵), U is the applied voltage, U_{fb} is the flat band potential, k is Boltzmann's constant and T is the absolute temperature.

$$\lambda_D = \left(\frac{\varepsilon_r \varepsilon_0 kT}{N_D e^2}\right)^{1/2}$$
[2.3]

Here, ε_0 is the permittivity of free space, ε_r is the relative permittivity and N_D is the charge carrier concentration. The capacitance (C) per unit area (A) of the space charge layer can be expressed as:⁵

$$\frac{C}{A} = \frac{\varepsilon_r \varepsilon_0}{w_d}$$
[2.4]

Substituting w_d from Eq. 2.2 into Eq. 2.4 yields the following well-known *Mott-Schottky* relationship:²

$$\left(\frac{A}{C}\right)^2 = \frac{2}{\left(eN_D\varepsilon_r\varepsilon_0\right)} \left(\left|U - U_{fb}\right| - \frac{kT}{e}\right)$$
[2.5]

where A is the surface area of the electrode and other symbols have their usual meanings. A plot of $(A/C)^2$ as a function of applied voltage (U) will yield a straight line where the charge carrier concentration (N_D) and the flat-band potential (U_{fb}) can be determined from the slope and the intercept of this line, respectively.

It is important to note that the energy relation in dark is not favorable for water decomposition because the H^+/H_2 energy level is above the Fermi energy level of the cathode.² However, when the photoelectrochemical cell is illuminated, Figure 2.3c, charge carriers are generated, which are separated by the electric field in the space charge layer. In the case of an ntype semiconductor, the electrons move into the bulk and the holes migrate to the electrolyte interface.² As a result, a photovoltage is generated and the Fermi level is moved upwards toward the flat-band potential. The band bending is reduced as a result of electron-hole pairs being generated by the absorbed photons. Under these conditions no current is flowing. The overpotential of an electrode is the difference in potential of an electrode at equilibrium (with no current flowing) and when current is flowing.² It is a measure of the additional energy required to drive the reaction. The value of the overpotential will depend on the magnitude of the energy barriers involved in the chemical reactions, arising from factors such as the thermodynamics, kinetics, and charge carrier concentration differences between the solution and the interface.^{5,6} The total overpotential is the sum of the overpotential across the depletion region and that across the Helmholtz layer. The voltage drop in the electrolyte can be assumed to be small (in concentrated solutions) and can be ignored in most cases. The interfacial activation energies for electron and hole transfer are related to the overpotentials.⁵ Under illuminated conditions, Figure **2.3c**, the maximum Fermi energy possible is the flat band potential, which is still below the H^+/H_2 redox potential, so hydrogen generation is not possible. When a bias voltage (U_{bias}) is applied, **Figure 2.3d**, the Fermi energy in the metal electrode is raised above the H^+/H_2 potential, allowing the water splitting reaction to proceed.⁵ Note that the need for a bias voltage negatively affects the efficiency of the water splitting. Therefore, the properties of the semiconductor photoelectrode are critical in determining the efficiency of the water splitting process. Now, after reviewing the basics of semiconductor electrochemistry and the solar spectrum characteristics, it is important to know what is meant by a photoelectrochemical cell (PEC), how water splitting occurs, limitations

of the process and how the efficiency can be improved. In general, the performance of PECs depends on many factors such as the terms of:

- excitation of electron-hole pair in photo-electrodes;
- charge separation in photo-electrodes;
- electrode processes and related charge transfer within PECs;
- generation of the PEC voltage required for water decomposition.

2.3 Photoelectrochemical Water Splitting

The principle of photoelectrochemical water splitting is based on the conversion of light energy into electricity. In the simplest scenario, water can be split into hydrogen and oxygen gases by illuminating a semiconductor photoelectrode in a photoelectrochemical cell as shown in **Figure 2.4**.



Figure 2-4: A schematic for a photoelectrochemical cell for water photolysis using an n-type semiconductor (anode) and a metal (cathode) immersed in an aqueous electrolyte.^{3,5}

2.3.1 Reaction Mechanism

With reference to **Figure 2.4**, in an aqueous electrolyte the water splitting reaction using an n-type semiconductor photoanode and a metal counter-electrode (cathode) involves several processes within photo-electrodes and at the photoelectrode-electrolyte interface, including:³

 absorption of photons followed by light-induced intrinsic ionization of the photoanode resulting in the formation of electron-hole pairs:

$$2 hv \rightarrow 2e^{-} + 2h^{+}$$
[2.6]

This reaction takes place when the energy of photons (hv) is equal to or larger than the band gap. An electric field at the electrode-electrolyte interface is required in order to avoid recombination of these charge carriers.

2. oxidation of water at the photoanode by electron holes:

$$2h^{+} + H_2O_{(liquid)} \rightarrow \frac{1}{2}O_{2(gas)} + 2H^{+}$$
 [2.7]

- 3. transport of H^+ ions from the photoanode to the cathode through the electrolyte and transport of electrons from photoanode to the cathode through the external circuit.
- 4. reduction of hydrogen ions at the cathode by electrons:

$$2e^{-} + 2H^{+} \rightarrow H_{2 (gas)}$$

$$[2.8]$$

Accordingly, the overall reaction can be expressed as:

$$2hv + H_2O_{(liquid)} \rightarrow \frac{1}{2}O_{2(gas)} + H_{2(gas)}$$
 [2.9]

This overall reaction takes place when the energy of the photons absorbed by the photoanode is equal to or larger than the threshold energy (E):²

$$E = \frac{\Delta G_{H_2O}^o}{2N_A}$$
[2.10]

where $\Delta G_{H_2O}^o$ is the standard Gibbs free energy per mole of reaction (2.9) = 237.141 kJ/mol; N_A is Avogadro's number = $6.023 \times 10^{23} \text{ mol}^{-1}$. Substituting these numbers in Eq. 2.10 yields:

$$E = hv \approx 1.23 \text{ eV}$$
 [2.11]

Accordingly, the electrochemical decomposition of water is possible when the electromotive force of the cell (EMF) is equal to or larger than 1.23 V. Theoretically, a photon with energy of 1.23 eV has a wavelength around 1000 nm (near infra-red), i. e. the entire ultraviolet and visible parts of the solar spectrum should be available for solar water splitting. However, in practice around 2.0 eV (wavelength around 620 nm) is required.³ The extra energy is to account for unavoidable loss mechanisms such as electrode overpotentials, recombination of the photo-excited electron–hole pairs, resistance of the electrical connections and voltage losses at the contacts.^{3,4} The estimated value of these combined losses was shown to be ~ 0.8 eV.⁴

2.4 Efficiency of Photoelectrolysis

The efficiency of converting light energy into chemical energy, stored in the form of hydrogen, determines the usefulness of the water photoelectrolysis process. For water splitting, cell efficiency is mainly determined by the light harvesting and utilization properties of the photoelectrode because the redox properties of the electrolyte are almost constant.³ Although there are standard ways to determine the light-to-electrical energy conversion efficiencies in photovoltaics measurements, this is not the case in the calculations of the light-to-chemical energy conversion which can be related to the use of various definitions and cell configurations by different research groups.⁷

The overall photoconversion efficiency (η) can be defined as the ratio of the maximum energy output that can be obtained from the final water splitting products, hydrogen and oxygen, to the energy supplied in the form of light to produce them, i.e.:⁴

$$\eta_{c} = \frac{\Delta G_{H_{2O}}^{o} R_{H_{2}} - V_{bias} I}{I_{r} A}$$
[2.12]

where $\Delta G_{H_2O}^o$ is the Gibbs free energy of formation of one mol of liquid H₂O (237.141 kJ/mol), R_{H_2} the rate of hydrogen generation (mol/s), V_{bias} the bias voltage applied to the cell (V), I the current within the cell (A), I_r the incidence of solar irradiance (W/m²) and A is the irradiated area (m²). Note that I_r was proposed to assume a value of 970 W/m² as a standard level corresponding to an AM 1.5.⁴

In terms of power, η can be defined as the ratio of the power density that can be obtained from hydrogen to the power density of the incident light.³ In this thesis, the efficiency (η) of voltage-assisted water splitting is calculated as:³

 $\eta\%$ = [(total power output – electrical power input)/light power input] x 100

$$\eta(\%) = \frac{j_P (1.23 - |E_{measured} - E_{OCP}|)}{I_0} x100$$
[2.13]

where j_p is the photocurrent density, I_0 is the intensity of incident light, $E_{measured}$ is the measured voltage and E_{ocp} is the open circuit potential.

To achieve a highly efficient photoelectrochemical system, the photo-electrode should perform two fundamental functions efficiently and properly:²

- 1. optical function: required to obtain maximum absorption of solar energy;
- 2. catalytic function: required for water decomposition.

To date, most photo-electrodes that exhibit sustainable performance in PECs are fabricated from oxide materials.³ Although the application of other semiconductors (e.g. GaAs) has been studied, they are very prone to photocorrosion and require various protective coatings.^{3,4} These coatings are problematic per charge transfer.^{3,4} Therefore, semiconducting and electrochemical properties of photo-electrodes should satisfy several specific requirements including: suitable band gap and high corrosion resistance as well as rapid charge transport kinetics.

Although these properties have been identified, it is difficult to process materials such that all requirements are satisfied. The purpose of the subsequent sections is to consider the most important and challenging property requirements and limitations.

2.4.1 Bandgap

Figure 2.5 shows that the band gaps of possible oxide materials that can be used for photo-electrodes vary between 2.3 and 3.7 eV. Note that the energies are compared to the vacuum level as well as the normal hydrogen electrode (NHE) level in an aqueous solution of pH = 2.





As mentioned before, the optimal band gap for high performance photo-electrodes is ~ 1.7-2 eV.³ Note that the materials that have promising band gap width, such as GaP ($E_g = 2.23 \text{ eV}$),^{9,10} and GaAs ($E_g = 1.4 \text{ eV}$),¹⁰ were found to be unstable in aqueous environments and thus exhibit significant corrosion problems. For other materials such as In₂O₃ ($E_g = 2.6 \text{ eV}$) with indirect band gap, they will require higher energies than their corresponding band gaps.¹¹ Therefore, neither of these materials is suitable for photo-anodes. That is to say, the material which satisfies the band gap requirement and is corrosion resistant is not currently available. Therefore, there is a need to process such a material. **Figure 2.6** shows the maximum efficiency possible depending upon semiconductor bandgap, under xenon arc lamp and AM1.5 solar illumination.³



Figure 2-6: The maximum efficiency possible of a photoanode as a function of its bandgap.³

Despite their high band gap, TiO_2 and $SrTiO_3$ are frequently studied for use as photoanodes due to their high corrosion resistance.¹²⁻²⁶ Figure 2.7 shows the effect of pH on the energy bands of TiO_2 versus the vacuum level and NHE level in aqueous solutions. Note that higher pH values result in moving the H⁺/H₂ potential to the level at which the photoanode may act efficiently. However, the maximum EMF value obtained for the photo-voltage of a PEC equipped with a photoanode of TiO_2 is ~ 0.7–0.9 V.²⁷ Consequently, the application of this material as a photo-electrode still requires a bias in order to decompose water.



Figure 2-7: Effect of pH on energy of TiO₂ in terms of vacuum level and NHE level.⁴

Another possibility by which the bandgap of the photoanode can be engineered is through the imposition of a band located ~ 2 eV below the conduction band.³ Experimentally, this impurity band can be achieved through heavy doping of TiO₂ with aliovalent ions,^{28,29} see **Figure 1.7**. However, the reports concerning the effect of doping on the electrochemical properties of TiO₂ are not in agreement. ^{28,29} Therefore, further studies in this area are required. The author's hypothesis is that effective processing of a material with the desired semiconducting properties obtained through doping will require *in-situ* doping and evaluation of the establishment and progression of these properties during processing. This hypothesis will be tested during the course of the present work.

2.4.2 Corrosion and Photocorrosion Resistance

It is an essential requirement for the photo-electrode to be highly resistant to reactions that might result in degradation of its properties. These reactions include: electrochemical corrosion and/or photocorrosion. Certain oxide materials, such as TiO_2 and its solid solutions, are particularly resistant to these corrosion processes. Therefore, they are suitable candidates for photo-electrodes for electrochemical water splitting.

The electrochemical corrosion of an XY semiconductor, which leads to anodic and cathodic decomposition, may be represented by the following reactions, respectively:²

$$XY + nh^+ \rightarrow X^{n+} + Y + \Delta G_a; \qquad E_{p,d} = \frac{\Delta G_a}{nN_A}$$
 [2.14]

$$XY + ne^- \rightarrow Y^{n-} + X + \Delta G_c; \qquad E_{n,d} = \frac{\Delta G_c}{nN_A}$$
 [2.15]

where n is the number of electrons or holes, ΔG_a and ΔG_c the free energy change at the anode and cathode, respectively, $E_{p,d}$ the free enthalpy of oxidation per one electron-hole and $E_{n,d}$ the free enthalpy of reduction per one electron.

Gerischer put forward the following rules for testing the stability of photo-electrodes against electrochemical corrosion for the photoanode and photocathode, respectively:³⁰

$$E(O_2/H_2O) < E_{p,d}$$
 [2.16]

$$E(H^+/H_2) > E_{n,d}$$
 [2.17]

where $E(H^+/H_2)$ is the energy of the redox couple H^+/H_2 and $E(O_2/H_2O)$ is the energy of the redox couple O_2/H_2O .

Figure 2.8 shows band gap ranges and energies of the redox couples ($E_{p,d}$ and $E_{n,d}$) for a number of ionic and valence semiconductors. It can be seen that the stability condition (Eq. 2.16) required for the photo-anode is not met for all valence (non-oxide) semiconductors (viz., the $E_{p,d}$ level is less than the O₂/H₂O level). This implies that these materials are thermodynamically

unstable in aqueous environments. Also, several oxide semiconductors, such as TiO_2 , SnO_2 and WO_3 , are resistant to electrochemical corrosion while ZnO is stable only as a photocathode (viz., the $E_{n,d}$ levels are greater than the H^+/H_2 level).



Figure **2-8**: Position of decomposition potentials $E_{n,d}$ and $E_{p,d}$ versus E_c and E_v of selected semiconducting materials.³⁰

2.4.3 Nanostructure

When electrodes for use in photoelectrochemical cells are produced; crystallinity, crystallite size, interconnection of particles, shape and orientation significantly affect the chemical and physical factors that define the *energetics and kinetics* of the electrodes. Therefore, rationally controlling nano-scale structures of electrodes and understanding their effects on photoelectrochemical properties are critical in order to produce highly efficient and cost effective photoelectrodes.² In this regard, both well-aligned nanotubular morphology and crystallinity of the photoanodes are considered to be crucial factors. For example, highly crystalline, well-aligned structures provide a direct and rapid pathway for charge transport, thus decreasing the carrier path length which in turn reduces recombination losses.³

2.4.4 Charge Loss in Photoconversion Processes

In polycrystalline semiconductor materials, electron transport is mainly controlled by electron-phonon interactions, ionized impurities and grain boundaries. There are two major limiting processes that negatively contribute to the photoconversion efficiency in metal-oxide electrode systems:^{31,32} (1) bulk recombination and (2) surface recombination.

The transport process of photogenerated electrons is complex in nature involving trapping and de-trapping of electrons.³¹⁻³⁶ The traps arise from a variety of defects in the crystal structure of a semiconductor material, e.g. vacancies, impurities, dislocations and grain boundaries.³⁷ Defects in polycrystalline and nanostructured materials are typically located at the surface as well as the grain boundaries of the material.³⁷ Surfaces can have severe defects and be the site of many allowed states within the forbidden gap. Surface states can also arise due to adsorbed species. The effect of surface states on the overall electronic properties depends on the electronic occupancies of the formed energy states at the surface. Recombination of minority carriers will often occur through surface states and prevent desired chemical reactions between minority carriers and species in the electrolyte solution.^{35,36} Also, the grain boundary energy levels in the band gap can act as effective recombination centers, which effectively capture carriers from either band. **Figure 2.9** illustrates the charge loss in a photoelectrochemical system.³³



Figure **2-9**: An illustration of charge loss in a photoelectrochemical cell (a) bulk recombination (b) direct electron loss (c) surface recombination and (d) photocorrosion. The bold arrows represent the desired process of photolysis.³³

2.4.5 Charge Transport in Oriented 1D Nanostructures

Nanostructures are expected to have maximum absorption capabilities and enhanced charge transfer properties than their bulk counterparts due to their enormously high surface area.³ In nanoparticulate systems, the electron transport is characterized by the *random walk mechanism* which results in almost doubling the electron pathway length and consequently slow electron diffusion through the nanoparticle network.^{38,39} Ordered nanotubular/nanoporous structures vertically oriented to the surface permits vectorial charge transfer from the electrolyte to the conductive material, thereby reducing the losses observed in the nanoparticle network.⁴⁰ Therefore, an optimized one-dimensional nanoarchitecture with a surface area similar to that of a nanoparticle anode is expected to yield a higher overall efficiency through superior carrier transport/collection. It also enables easier access to the film surface and better control of the interface as well as enhancement of the light harvesting via light scattering within the porous

structure where photons are more effectively absorbed than in a flat electrode.^{41,42} Moreover, the vertically oriented nanowire, nanoporous and nanotubular structures facilitate the transport of the holes (minority carriers in n-type semiconductor) to the reaction electrolyte through the thin walls of these unique structures. The *diffusion length* (L) of the minority carriers in a semiconductor can be defined as:³

$$L = (D.\tau)^{1/2}$$
 [2.18]

where D is the diffusion coefficient and τ is the lifetime of the minority carriers. The diffusion coefficient (D) is related to the mobility (μ) via the Einstein relationship:³

$$D = \left(\frac{kT}{e}\right)\mu$$
 [2.19]

Consequently, the mobility can be expressed in terms of the diffusion length of charge carriers as:³

$$\mu = \left(\frac{L^2 e}{kT\tau}\right)$$
[2.20]

Study of particulate nanocrystalline photoelectrodes shows that a depletion layer cannot be formed in nanoparticles — the particles are simply too small.⁴³ Within the nanometer regime, it is generally accepted that as the size of the particle or grain decreases, its ability to sustain a significant amount of band bending also decreases.⁴³ As a consequence there is no significant local electric field present to assist in the separation of photogenerated electron–hole pairs.⁴³ Hence, one more advantage of thin-walled nanotubes is the possibility that they might be devoid of depletion region at the semiconductor-electrolyte junction. The absence of depletion layer implies that the initial charge separation of photogenerated charges will be dependent on the fast interfacial kinetics aided by the small particle size and the large nanostructured semiconductor/electrolyte interface, i.e. this may facilitate fast transport of photogenerated charges to the interface, which can compete with the recombination rate.⁴⁴ In summary, the following conditions must be satisfied for an efficient water photolysis system:³

- *I*. The energy of incident light photons (hv) should exceed the bandgap of the semiconductor (E_g);
- The bandgap of the semiconductor should be >1.23 eV but low enough (~1.7-2.0 eV) to absorb visible light;
- 3. The flat band potential (the potential where there is no net transfer of charge, and hence there is no band bending) of *n-type* photoanode should be more negative than the reversible potential of the hydrogen electrode reaction, whereas the flat band potential of the cathode should be more positive than the reversible potential of oxygen electrode reaction;
- 4. The semiconductor photoanode should be stable in aqueous electrolytes;
- 5. The photoanode material should allow fast charge transfer;
- 6. Ideally the semiconductor photoanode should be made of plentiful cost material (s).

2.5 Structural Properties of Titanium Dioxide

The electronic properties of titania have made it an attractive material for applications in various systems such as photocatalysis, solar cells, sensors, etc.⁴⁵ TiO₂ can exist in both crystalline and amorphous forms. The amorphous form of TiO₂ is photocatalytically inactive.^{46,47} The superior electronic properties of TiO₂ depend on its crystal structure, and can be changed by doping titania with different elements. In some cases this doping changes the local atom distribution, and in some others it changes the electron transfer without altering this distribution.⁴⁵ Therefore, to understand the electronic properties of titania, it is necessary to have some information regarding its crystal structure.

There are three crystalline phases of TiO_2 ; anatase, rutile and brookite.⁴⁶ Both anatase and rutile have been extensively studied for photocatalytic applications with the former found to be the most suitable for photocatalytic reactions.⁴⁶ Brookite is not commonly available and has not, apparently, been tested for photocatalysis.

Anatase and rutile are both tetragonal in structure while the brookite structure is orthorhombic.⁴⁷ All consist of TiO_6^{2-} octahedral with different manner of arrangement/bonding. In rutile, two (out of twelve) edges are shared forming a linear chain.⁴⁸ If each titanium octahedron (TiO_6^{2-}) was represented by a building block, then the basic structural unit of rutile can be represented by **Figure 2.10a**. For rutile, the linear chains are then joined to each other by the sharing of corner oxygen atoms, producing the overall rutile structure⁴⁸, **Figure 2.10b**.



Figure **2-10**: (a) The fundamental structural unit and (b) the overall structure of rutile.⁴⁸

Anatase has four edges shared per octahedron and no corner oxygen sharing.⁴⁹ The basic growth units possible for anatase are shown in **Figure 2.11**. This figure shows (a) two edges are shared per octahedron forming a right-angled configuration and (b) the third and fourth edges are shared into and out of adjacent layers. Effectively the arrangement of these octahedra gives the overall structure of anatase⁴⁸ shown in **Figure 2.11c**.



Figure 2-11: (a), (b) The fundamental structural units and (c) the overall structure of anatase.^{48,49}

The octahedral linkages in brookite are such that three edges are shared per octahedron.⁵⁰ The basic unit as well as the overall structures of brookite formed by TiO_6^{2-} octahedra are shown in Figure 2.12.



Figure **2-12**: (a) The fundamental structural units and (b) the overall structure of brookite.⁴⁹⁻⁵¹

2.5.1 Mechanism of Crystal Phase Formation in Solution

The mechanism of formation of rutile and anatase using different synthetic routes in solutions includes many steps. ^{48,52,53} First, two octahedra undergo condensation to form a bond (**Figure 2.13a**). Then, the placement of the third octahedron determines the formation of either rutile (**Figure 2.13b**) or anatase/brookite (**Figure 2.13c,d**). The first option (**Figure 2.13b**) occurs when the titania octahedra forms a bond such that a linear arrangement results. The linear arrangement is the most stable structure since the electrostatic repulsive energy is minimized, thus thermodynamically; the basic structure of rutile is favored.⁴⁸ The second option (**Figure 2.13c**) occurs when the octahedra bond together at right angles to give the basic unit structure for anatase.⁴⁹ The third option is possible when the octahedron edges share a bond⁴⁹ as shown in **Figure 2.13d**. This option is the basic growth unit for both anatase and brookite.



Figure **2-13**: (a) Condensation of two octahedra, (b) growth unit of rutile, (c) growth unit of anatase and (d) growth unit of anatase and brookite.^{48,49}

2.5.2 Crystallization of Anodically Fabricated TiO₂ Nanotube Arrays

Various techniques have been used to fabricate titania nanotubes of different geometrical shapes and crystallinity such as sol-gel, electrodeposition, sonochemical deposition and chemical treatment of fine titania particles.⁴⁵ While many of these fabrication routes are complicated due to the use of templates or the nature of the involved chemical processes, it has recently been demonstrated that self-organized vertically oriented titanium dioxide nanotube arrays can be fabricated using a simple anodization technique.⁵⁴ This technique can yield nanotubes of controlled diameters, wall thicknesses and lengths.³ However, all the anodically fabricated TiO₂ nanotube arrays to date are amorphous. Before utilization of these amorphous nanotubes in different applications, factors like the crystalline nature of the structure and stability of the desired crystalline phase as well as the stability of the structure itself must be examined.

Titania properties, and hence potential applications, depend on the crystallinity as well as the isomorph present at the desired operating conditions.^{55,56} For example, the anatase phase of titania is preferred in dye sensitized solar cells and catalysis because it is photoactive, whereas rutile is mostly used in the area of dielectrics and high-temperature oxygen gas sensors.^{45,46} In general, crystallization or phase transformations take place through *nucleation* and *growth* processes.⁵⁶

Based on the fact that titanium exhibits a capacity for dissolving a considerable amount of oxygen,⁵⁷ most of the crystallization methods used for the anodically fabricated TiO₂ nanotubes involve annealing the material at high temperature in oxygen atmosphere.⁵⁸ Oxidation during heating is generally accompanied by formation of stoichiometric oxide and gasimpregnated layers⁵⁸ which have a marked effect on the properties of the material as mentioned above.

On this basis, a model⁵⁸ was suggested to explain the crystallization of titania nanotubes (500 nm in length) as schematically shown in Figure 2.14. The nucleation of anatase phase was

shown to occur at temperatures between 230 and 280 °C, Figure 2.14a. These crystallites grow in size with increasing temperature, Figure 2.14b. Some of the closely spaced crystallites coalesce to form larger crystallites while some others establish grain boundary contacts. The size of the crystallites in the walls is restricted due to the constraints imposed by the walls. At temperatures around 430 °C, rutile formation was shown to occur at the nanotube–titanium support interface region (Figure 2.14c) leaving the anatase crystallite in the walls unaffected.



Figure **2-14**: Schematic representation of the crystallization of the titanium dioxide nanotube arrays: (a) nucleation of anatase crystals; (b) growth of the anatase crystals at elevated temperatures; (c) nucleation of rutile crystals; (d) growth of rutile crystals at higher temperatures; (e) complete transformation of crystallites in the walls to rutile at temperatures above approximately 620 °C.⁵⁸

The most common phase transformation in titania is the anatase to rutile transformation. The mechanisms responsible for this transformation involve breaking two of the six Ti–O bonds to form new bonds with the transformation activation energy calculated to be (264 kJ/mol) for the oxygen annealed samples.^{59,60} Nucleation and growth of rutile can occur through different processes.^{61,62} *Nucleation* can take place:⁶³

- 1. at the interface of two contacting anatase particles, **Figs. 2.14c,d**, which results in transforming the anatase grains into a large rutile grain.
- 2. in the bulk or on the surface of a large anatase grain.

During the nucleation process, the crystallites may rotate and reorient if sufficient volume is available.⁶¹ Hence, rutile nucleation cannot take place easily inside the walls of the nanotube. For example, it was reported that anatase crystallite sizes less than 14 nm are highly stable and will not be converted into rutile.⁶³

The growth of rutile may happen when:⁶³

- 1. a rutile crystallite comes into contact with an anatase crystallite forming a larger rutile crystallite; or
- 2. two rutile nuclei merge together.

As the oxidation proceeds, both titanium and larger anatase crystals at the interface can be directly transformed into rutile at temperatures between 480 and 580 °C.⁵⁸ However, smaller anatase crystallites grow at higher temperatures (~ 620 °C), yielding a larger anatase grain size. Eventually, the anatase crystallites in the walls are consumed by the developing rutile layer, **Figure 2.14d**. Hence, a complete rutile phase can be seen for sample annealed at 680 °C,⁵⁸ **Figure 2.14e**.

Although crystallization and phase transformations are essential for many applications, they have adverse effects on the stability of nanoarchitectures, especially when they occur at elevated temperatures. At elevated temperatures, high surface area makes them prone to solid-state sintering, which leads to grain growth, densification, and eventually complete collapse of the structure.⁶⁴⁻⁶⁶ Such processes are more pronounced during phase transformations when bond
breaking and enhanced mass transport take place, which can lead to grain growth and densification.⁶⁷ Hence, porosity and/or surface area reduction often accompany the sintering effects associated with nucleation and growth phase transformations.⁶⁸ That is why a part of the present work was devoted towards exploring different routes for low temperature (*in-situ*) crystallization of the anodically fabricated TiO_2 nanotubes to avoid any structural collapse and hence improving the efficiency of these unique architectures.

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Chapter 3

Review of Relevant Literature

Nanotubular structures are of great interest due to their high surface areas, directed charge transfer as associate with high aspect ratio and size dependent properties.¹ Several recent studies have indicated that TiO₂ nanotubes have improved properties compared to any other form of titania for various applications such as those in photocatalysis, photoelectrolysis, photovoltaics and sensing. A variety of methods have been used to fabricate titania nanotubes, and nanotube arrays, including deposition into nanoporous templates,² sol–gel³ and hydrothermal processes.⁴ However, none of these fabrication routes can be used to directly fabricate highly-ordered vertically oriented nanotube arrays, the architecture demonstrating by far the most remarkable properties.¹ Anodization of titanium in fluoride-based electrolytes seems to be the proper route to fabricate such unique arrays with precisely controlled dimensions. Uniform titania nanotube arrays of various pore sizes (22–110 nm), lengths (200 nm–1mm), and wall thicknesses (5–34 nm) are easily grown by tailoring electrochemical conditions.^{1,5} A variety of reports in the literature give evidence of the unique properties of this material architecture, making it of considerable scientific interest as well as practical importance.

It seems that the number of publications dealing with the fabrication, characterization and applications of TiO_2 nanotubes is quite large and the subject has been frequently reviewed.⁵⁻⁷ Therefore, only the aspects that are more relevant to the contents of this thesis will be reviewed.

3.1 Fabrication of Titania Nanotube Arrays by Anodization

In 1991, Zwilling and co-workers reported the fabrication of porous surface of titania films via titanium anodization in fluoride-based electrolytes.⁸ Almost a decade later Grimes and co-workers first reported formation of uniform titania nanotube arrays via anodic oxidation of titanium in hydrofluoric acid (HF) electrolyte.⁹ Further studies focused on precise control and extension of the nanotube morphology, length, pore size and wall thickness.^{6,7} Electrolyte composition, and its pH, determines both the rate of nanotube array formation, as well as the rate at which the resultant oxide is dissolved, i.e. it determines the resultant nanotube array nanoarchitecture and, potentially, its chemical composition.¹ In almost all reported cases, a fluoride ion containing electrolyte is needed for nanotube array formation. Examining the literature dealing with TiO₂ nanotube fabrication by anodization technique leads to the fact that three generations can be identified in developing the currently used titania nanotube array films.^{6,7}



Figure 3-1: FESEM micrographs of anodically fabricated TiO₂ nanotubes arrays.

3.1.1 First Generation of TiO₂ Nanotube Arrays

Anodization of titanium is commonly performed in a two-electrode electrochemical cell with a platinum foil as cathode and titanium foil as anode at a constant applied voltage, see Chapter four for more details. Gong and co-workers reported the anodization of Ti foils at different anodizing voltages (3-20 V) in 0.5 wt % HF aqueous electrolytes.⁹ At low anodization voltage (e.g. 3V), the morphology of the formed porous film is similar to that of porous alumina, with a typical pore size of 15-30 nm. As the applied voltage increased to 5V, the surface becomes nodular in nature. At 10V, discrete tube-like features appeared on the surface. Nanotube samples prepared using 10V, 14V and 20V anodization voltages have, respectively, inner diameters of 22 nm, 53 nm and 76 nm; wall thicknesses 13 nm, 17 nm and 27 nm; and lengths 200 nm, 260 nm and 400 nm. Uniform nanotube arrays were grown atop the supporting titanium metal foils, with an electrically insulating barrier layer separating the nanotubes from the conducting titanium foil, upon anodization of Ti samples for 45 min. Anodization at voltages greater than 23 V led to the loss of tubular structure with randomly porous structures being realized.

As reported by Mor and co-workers, the addition of acetic acid to the 0.5% HF electrolyte in a 1:7 ratio results in more mechanically robust nanotubes without changing their shape and/or size.^{10,11} However, anodization in this acetic acid-containing electrolyte at different temperatures (5, 25, 35 and 50 °C) led to changes in the wall thickness by approximately a factor of four and the tube-length by approximately a factor of two; the wall thickness increases with decreasing anodization temperature from 9 nm at 50°C to 34 nm at 5°C while the length of the nanotubes increases with decreasing anodization bath temperature from 120 nm at 50°C to 224 nm at 5°C.¹²

Ruan and co-workers investigated the anodization of titanium foil in aqueous electrolytes containing 1% HF + 2.5% HNO₃ in the presence and absence of boric acid.^{13,14} In this electrolyte mixture the applied potential was initially ramped from 0 to 20 V at a rate of 6 V/min; then held

constant at 20 V for 4 h. An initial ramp of the voltage was found to be critical because initial application of a 20 V anodization potential resulted in high current densities not allowing the formation of an oxide coating due to dielectric breakdown. The morphology of nanotube-array sample anodized in the absence of boric acid for 4 h showed a uniform, clean, regular structure with the nanotubes having an average pore size of about 100 nm and a wall thickness of \approx 20 nm with the length of nanotubes found to be \approx 400 nm. However, TiO₂ nanotube-arrays fabricated in the same electrolyte mixture with the addition of 0.5M H₃BO₃ were found to have a precipitate layer about 400 nm thick. The nanotube structures could be exposed after washing with a dilute HF solution. In these samples, there was a greater degree of pore irregularity, with sizes ranging from 10 nm to 120 nm, average wall thickness 20 nm, and nanotube length of about 560 nm.

In another study, Beranek and co-workers reported the fabrication of TiO_2 nanotube arrays using a mixture of H_2SO_4 and HF.¹⁵ Nanotube arrays up to 560 nm in length, single pore diameter of 140 nm and a pore spacing of 150 nm were achieved. The formation of self-organized TiO_2 nanotube layers at different HF concentrations and potentials in H_3PO_4 electrolytes was also investigated by Bauer and co-workers.¹⁶ It was found that for potentials between 1 and 25 V, nanotubes could be grown with diameters ranging from 15 to 120 nm combined with tube lengths from 20 nm to 1 µm. The diameter and the length depend linearly on the voltage.

A factor limiting the application of this first generation of nanotubes was their production in HF-based electrolytes which is accompanied by very high rate of chemical dissolution of TiO_2 and in turn the nanotubes could be grown only up to a maximum length of 1 μ m.

3.1.2 Second Generation of TiO₂ Nanotube Arrays

In the second generation, nanotube arrays several microns in length were fabricated by Grimes and co-workers using electrolytes containing fluoride salts instead of HF at variable pH values.^{6,7} For example, Cai and co-workers found, in electrolytes containing 0.1M KF and 1M H_2SO_4 , that the potential window for nanotube formation was in the range 10-25V with no tube formation observed outside this potential range.¹⁷ At 5V, the electrochemical etch rate was slow due to lower applied potential and only a few pits could be seen on the sample surface. On contrary, at 30V, the electrochemical etch was much faster, which prevents nanotube formation so that only highly disturbed porous structures obtained. The nanotube pore size was found to be proportional to the applied potential and independent of the anodization time and electrolyte concentration. The diameter of the resulting nanotubes increased from 40 nm to 110 nm upon increasing the potential from 10V to 25V. No significant difference was observed in the pore size for anodization times of 1 hr and 6.5 hr or for electrolyte concentrations of 1M H_2SO_4 and 2M H_2SO_4 .¹⁷

It was reported by Cai and co-workers that the electrolyte pH plays a crucial role in the fabrication of TiO₂ nanotube arrays.¹⁷ With increasing the pH of the electrolyte, the rate of chemical dissolution becomes slower and consequently longer nanotubes could be formed.¹⁷ For example, at 25V, on increasing the pH from strong acidity (pH<1) to weak acidity (pH 4.5), the nanotube length was increased from 0.56 μ m to 4.4 μ m; for 10V, the length increased from 0.28 μ m (pH<1) to 1.4 μ m (pH 5). It was also shown that for a particular pH, the length increases with applied potential. When the potential increased from 10V to 25V, the length increased from 0.59 μ m to 1.5 μ m for pH=2.8 and from 1.05 μ m to 4.4 μ m for pH=4.5. Also, at a particular pH, the pore size of the nanotubes was found to be increasing with anodization potential. However, the anodization time has no effect on the tube length in strongly acidic solutions (pH<1), however it

is time dependent in weak acid electrolytes. Studies showed that the best pH range for formation of relatively longer nanotubes is between pH 3 and pH 5; lower pH forms shorter but clean nanotubes, while higher pH electrolytes result in longer tubes that suffer from unwanted precipitates. Alkaline solutions are not favorable for self-organized nanotube formation.^{1,17}

Therefore, the limiting factor of the application of this second generation of nanotubes is the unwanted precipitates that partially or totally cover the tube surface.

3.1.3 Third Generation of TiO₂ Nanotube Arrays

This generation is based on the use of organic electrolytes with the hypothesis that the donation of oxygen in organic electrolytes is more difficult in comparison to aqueous electrolytes. The reduction in water content reduces the chemical dissolution of the oxide in the fluorine containing electrolytes, and hence aids longer-nanotube formation.^{6,7} Therefore, it appears that the key factor in achieving very long nanotube arrays is to minimize water content in the anodization bath to less than 5%. Many electrolyte compositions have been reported including formamide (FA), N-methyl formamide (NMF), ethylene glycol, dimethyl sulfoxide (DMSO) and glycerol.

Paulose and co-workers were the first to investigate the anodization of Ti foil in formamide-containing electrolytes.¹⁸ They were able to fabricate nanotube arrays nearly 70 μ m long in formamide electrolytes containing 1-5 wt % of deionized water and 0.3-0.6 wt % NH₄F upon anodization for 48 hours at a constant potential of 35 V. The average outer diameter of these nanotubes was determined to be 180 nm, wall thickness \approx 24 nm, resulting in an aspect ratio of \approx 390. Lower anodization potentials result in shorter nanotubes with smaller diameters. The increase in nanotube length with larger anodization voltage was attributed to the increased driving force for ionic transport through the barrier layer at the bottom of the pore, resulting in faster movement of the Ti/TiO₂ interface into the Ti metal. In the FA/NMF electrolytes, an increase in the outer nanotube diameter was found to increase with anodization voltage.¹⁸ This observation agrees with the reported behavior of nanotube arrays formed in aqueous electrolytes. Nanotubes with a smaller pore diameter and $\approx 10\%$ greater lengths were obtained using NMF rather than FA electrolytes.¹⁸ Shankar and co-workers further investigated the effect of five different cationic species on the formation of TiO₂ nanotube arrays by anodization of titanium in formamide-water mixtures containing fluoride ions.¹⁹ It has been shown that the cation choice is a key parameter influencing both the nanotube growth rate and the resulting nanotube length.

Yoriya and co-workers found that samples fabricated by anodization in an electrolyte of dimethyl sulfoxide (DMSO) containing 2% HF electrolyte at 40V for 69 hours had a length of approximately 45 μ m, pore diameter \approx 120 nm, and wall thickness \approx 15 nm.²⁰ The top-surface of the as-prepared samples was typically covered with debris from the anodization bath. The pores appear clogged in such cases, with sonication needed to remove the debris. Anodization in the range 20 - 60 V for 70 hours yielded regular, well-aligned nanotube-array architectures with an increase in length from about 10 μ m to 93 μ m. As the HF concentration varied from 1% to 4% the length of the nanotubes grown at 20 V increased from 4.4 μ m to 29 μ m. Pre-anodization at 20 V in 0.5% HF in deionized water followed by anodization at 40 V in DMSO containing 2% HF solution yielded 82 μ m long nanotubes, almost a factor of two increase in length from that obtained without using the pre-anodization step.

Further, titania nanotube arrays were shown to be formed upon the anodization of Ti foil in the voltage range 20-65V in ethylene glycol (EG) electrolytes containing 0.1 - 0.5 wt% NH₄F and 1% - 4% H₂O.^{6,7} For 17 hour anodization of titanium foil at 60 V, it was reported that: ^{6,7,21}

- 1. for a given concentration of water, the length increases with increasing NH_4F up to 0.3 wt %;
- 2. for NH_4F concentrations up to 0.3 wt %, the nanotube length increases with increasing H_2O concentration up to 2 vol %;

- 3. in the range of 0.1 0.3 wt % NH₄F and 1-2 vol % H₂O, the previously used electrolyte, in comparison to a fresh solution, exhibited an increase in nanotube length ranging from 15 μ m -70 μ m for the same applied potential and duration; and
- 4. self-standing membrane comprised of a close-packed array of vertically oriented titania nanotubes was formed upon extended ultrasonic cleaning, of approximately 1 minute duration, of the nanotube arrays fabricated in 0.3 wt % NH₄F and 2 vol % H₂O in ethylene glycol electrolyte.

Double-sided anodization, where both sides of the starting titanium foil (1 mm thick) are exposed to the anodizing electrolyte, resulted in the formation of 2 mm thick nanotube array membrane, comprised of two 1 mm long nanotube arrays. This is the longest nanotube arrays reported so far.²¹

Although these three generations showed great progress towards controlling the morphology of the anodically fabricated TiO_2 nanotube arrays, no improvement in the crystallinity and/or band gap of the as-anodized samples was reported, i.e. the fabricated nanotubes are always amorphous and undoped. Another important point is that, for all previous studies, fluorine ions were reported to be the most essential ingredient of the anodization electrolyte constituents with no study towards the investigation of the use of fluoride-free electrolytes to achieve TiO_2 nanotube arrays. To this end, the materials in this thesis present efforts to address these issues; notably the fabrication of partially crystalline nanotubes directly from the anodization bath and *in-situ* doping of the fabricated TiO_2 nanotube arrays as well as the fabrication of TiO_2 nanotubes in fluoride-free electrolytes.

3.2 Mechanistic Model of TiO₂ Nanotube Array Formation

The formation mechanism of the TiO_2 nanotubes is believed to include the following key processes:^{8, 23-25}

- Oxide growth at the surface of the metal substrate as a result of the interaction of the metal with O²⁻ or OH⁻ ions;²⁶
- 2. *Migration of anions* through the oxide layer reaching the metal/oxide interface where they react with the metal.
- Migration of metal ions (Ti⁴⁺) from the metal at the metal/oxide interface; Ti⁴⁺ cations will be ejected from the metal/oxide interface under application of an electric field that move towards the oxide/electrolyte interface.
- 4. Field assisted dissolution of the oxide at the oxide/electrolyte interface; due to the applied electric field the Ti-O bond undergoes polarization and is weakened promoting dissolution of the metal cations. Ti⁴⁺ cations dissolve into the electrolyte, and the free O²⁻ anions migrate towards the metal/oxide interface, see Figure 3.2 (a), to interact with the metal.²⁷
- 5. *Chemical dissolution* of the metal, or oxide, by the acidic electrolyte takes place during anodization. Chemical dissolution of titania in the HF electrolyte plays a key role in the formation of a nanotubular versus nanoporous structure.

Figure 3.2 (a,b) shows the formation and growth of an oxide layer atop the metal surface.

With the onset of anodization, a thin layer of oxide forms on the titanium surface, **Figure 3.2 (b)**, due to the interaction of the surface Ti^{4+} ions with oxygen ions (O²⁻) in the electrolyte.

The overall reactions for anodic oxidation of titanium can be represented as:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
 [3.1]

$$Ti + O_2 \rightarrow TiO_2$$
 [3.2]



Figure **3-2**: Schematic diagram of the evolution of straight nanotubes at constant anodization voltage, see text.¹

In the initial stages of the anodization process field-assisted dissolution dominates chemical dissolution due to the relatively large electric field across the thin oxide layer.²⁷ Then, small pits originate in this oxide layer due to the localized dissolution of the oxide, **Figure 3.2 (c)**, making the barrier layer at the bottom of the pits relatively thin which, in turn, increases the electric field intensity across the remaining barrier layer, resulting in further pore growth^{6,7} as seen in **Figure 3.2(d)**.

$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O$$
 [3.3]

The pore entrance is not affected by electric field assisted dissolution and hence remains relatively narrow, while the electric field distribution in the curved bottom surface of the pore causes pore widening, as well as deepening of the pore. The result is a pore with a scallop shape.²⁸ As the Ti-O bond energy is high (323 kJ/mol),²⁸ in the case of titania it is reasonable to assume that only pores having thin walls can be formed due to the relatively low ion mobility and relatively high chemical solubility of the oxide in the electrolyte, hence un-anodized metallic

portions can initially exist between the pores. As the pores become deeper, the electric field in these protruding metallic regions increases, enhancing the field assisted oxide growth and oxide dissolution. Hence simultaneously with the pores, well-defined inter-pore voids start forming **Figure 3.2(e)**. Thereafter, both voids and tubes grow in equilibrium. The nanotube length increases until the electrochemical etch rate equals the chemical dissolution rate of the top surface of the nanotubes;¹ after this point is reached, the nanotube length will be independent of anodization duration.

The chemical dissolution step, the key for the self-organized formation of the nanotube arrays, reduces the thickness of the barrier layer, keeping the electrochemical etching (field assisted oxidation and dissolution) process active. No nanotubes can be formed if the chemical dissolution is too high or too low.^{6,7} The electrochemical etch rate depends on the anodization potential as well as concentration of electrolytes. If the electrochemical etch proceeds faster than the chemical dissolution, the thickness of the barrier layer increases, which in turn reduces the electrochemical etching process to the rate determined by chemical dissolution. The chemical dissolution rate is determined by the F⁻ concentration and solution pH, see Eq. 3.3. With increasing F⁻ and H⁺ concentrations, chemical dissolution increases. Recent investigations have shown that only in a certain F⁻ concentration range can nanotube arrays be achieved.^{6,7} The anodic potential at which nanotubes are formed is related to the F⁻ concentration, with higher potentials requiring electrolytes of higher F⁻ concentration.

In polar organic electrolytes such as FA, NMF, DMSO and EG, the water is usually the main source of oxygen in anodizing solutions, atmospheric oxygen is supposed to play lesser role. While the exact mechanism by which water contributes oxygen to an anodic oxide film is not well-understood, it is believed that hydroxyl ion can be injected from the electrolyte into the anodic oxide film during anodization.²⁹ When a large amount of water is present, hydroxyl ions are injected into the body of the oxide layer and affect the structure sufficiently to impede ion

transport through the barrier layer,³⁰ which is necessary for further movement of the metal-oxide interface into the metal. However, when less water is present, the difficulty in extracting oxygen and/or hydroxyl ions from the solution limits the rate of growth of the overall oxide film. Also, the barrier oxide layer exhibits increased ionic conductivity caused by the non-stoichiometry induced by the reduced hydroxyl ion availability to the oxide. The amount of hydroxyl ion injection is dependent on the solvent structure. ^{18,19,21,31}

3.3 Modification of the Band Gap and Crystallinity of TiO₂

Although TiO₂ is identified as the best available candidate for the photoanode, the highly efficient use of TiO₂ nanomaterials is usually limited by its wide band gap. The band gap of bulk TiO₂ lies in the UV regime (3.0 eV for the rutile phase and 3.2 eV for the anatase phase), which allows absorption of only a small fraction of the sun's energy (<5%). This limits water-splitting efficiency under AM1.5 global solar illumination to a theoretical maximum of 2.2% for rutile and 1.3% for anatase, well under the 10% generally considered to be required for economic hydrogen production.³³

Thus, one of the goals for improving the performance of TiO_2 nanomaterials is to increase their optical absorption by shifting the onset of the response from the UV to the visible region. It was shown that the light absorption of TiO_2 may be increased substantially by modification of its semiconducting and electrochemical properties through doping with aliovalent ions and producing solid-solutions with other oxides.³⁴ Although the chemical composition of TiO_2 can be altered by doping, it is desirable to maintain the integrity of its crystal structure in such a way to produce favorable changes in electronic structure. It appears easier to substitute the Ti^{4+} cation in TiO_2 with other transition metals than to replace the O^{2-} anion with other anions due to differences in charge states and ionic radii.³⁴

3.3.1 Metal-Doped TiO₂ Nanoarchitectures

Although various metals have been doped into TiO_2 nanomaterials, the methods used can be divided into the following three categories:³⁵

- 1. wet chemistry,
- 2. high temperature treatment,
- 3. ion implantation.

Wet chemistry methods usually involve hydrolysis of a titanium precursor in a mixture of water and other reagents, followed by heating.³⁵ However, high temperature treatments involve heating the material in an atmosphere containing the dopant ion (s).³⁵ Ion implantation is a surface modification process in which ions are injected into the near-surface region of a substrate. High-energy ions, typically 10–200 keV in energy, are produced in an accelerator and directed as a beam onto the surface of the substrate.^{36,37} The ions impinge on the substrate with kinetic energies 4–5 orders of magnitude greater than the binding energy of the solid substrate and form an alloy with the surface upon impact.^{36,37}

Both theoretical and experimental studies have shown that the desired band gap narrowing of TiO_2 can be achieved by using metal dopants.^{38,39} Herein a summary of some of these studies regarding the effect of some metal dopants on structural, electrical and photoelectrochemical properties of TiO_2 is presented.

Umebayashi and co-workers have performed DFT calculations regarding the densities of states of V-, Cr-, Mn-, Fe-, Co-, and Ni-doped TiO₂.³⁹ They found that when TiO₂ was doped with V, Cr, Mn, Fe, or Co an electron occupied level was formed and the electrons were localized around each dopant. As the atomic number of the dopant increased, the localized level was shifted to lower energy. For V-, Mn- or Fe-doped TiO₂, the absorption spectra shifted to a lower energy region with an increase in the dopant concentration. This red shift was attributed to the charge-transfer transition between the d-electrons of the dopant and the CB (or VB) of TiO₂. Choi

and co-workers performed a systematic study of doping TiO₂ nanoparticles with 21 different metal ions by the sol-gel method and found the presence of metal ion dopants significantly influenced the interfacial electron transfer rates, charge carrier recombination rates and consequently the photo-activity of the material.³⁸ Metal ion doped TiO₂ prepared by ion implantation with various transition-metal ions such as V, Cr, Mn, Fe and Ni was also found to have a large shift in the absorption band toward the visible light region, with the order of the effectiveness in the red shift being V > Cr > Mn > Fe > Ni. ^{36,37}

Among the widely studied metal dopants, Cr has gained extensive attention. Anpo and co-workers found that the absorption band of Cr-ion-implanted TiO₂ shifted smoothly toward the visible light region, with the extent of the red shift depending on the amount of metal ions implanted.³⁷ Also, Ghicov and co-workers reported that Cr-ion-implantation of annealed TiO₂ nanotube arrays showed photoresponse in the visible range of the solar spectrum with reannealing the tubes increased the magnitude of the photoresponse.⁴⁰ On the contrary, chemically Cr-ion-doped TiO₂ showed no shift in the absorption edge of TiO₂; however, a new absorption band appeared at around 420 nm as a shoulder peak due to the formation of an impurity energy level within the band gap, with its intensity increasing with the number of Cr ions.³⁷ Tsai and co-workers studied the photoelectrochemical activity of hydrothermally intercalated Cr-doped TiO₂ and found that it was higher than that of the undoped sample.⁴¹ The photoelectrochemical activity of photoelectrochemical activity with increasing chromium doping and a red shift in the band gap was observed.

Moreover, the nature and concentration of dopants was found to affect the crystal structure of the TiO_2 host material. Gracia and co-workers synthesized M (Cr, V, Fe, Co)-doped TiO_2 by ion beam induced CVD and found that TiO_2 crystallized into the anatase or rutile structures depending on the type and amount of cations present, with partial segregation of the cations in the form of M_2O_n after annealing.⁴² Also, Wang and co-workers found that the

formation of rutile was strongly promoted with iron doping compared to the anatase phase being prevalent in the undoped TiO₂.⁴³ Cao and co-workers prepared Sn⁴⁺-doped TiO₂ nanoparticle films by the plasma enhanced CVD method and found that, after doping by Sn, more surface defects were present on the surface.⁴⁴ Bessekhouad and co-workers investigated alkaline (Li, Na, K)-doped TiO₂ nanoparticles prepared by sol-gel and impregnation technology and found that the crystallinity level of the products was largely dependent on both the nature and the concentration of the alkaline, with the best crystallinity obtained for Li-doped TiO₂ and the lowest for K-doped TiO₂.⁴⁵

3.3.2 Non-metal-Doped TiO₂ Nanoarchitectures

Various non-metal elements such as B, C, N and S have been successfully doped into TiO₂ nanomaterials via many different fabrication routes. For example, C-doped TiO₂ has been obtained either by heating titanium carbide,⁴⁶ annealing TiO₂ under CO gas flow at high temperatures (500-800 °C),⁴⁷ or direct burning of a titanium metal sheet in a natural gas flame.⁴⁸ N-doped TiO₂ nanomaterials have been synthesized either by hydrolysis in a water/amine mixture and the post treatment of the TiO₂ sol with amines,^{49,50} ball milling of TiO₂ in a NH₃ water solution,⁵¹ heating TiO₂ under NH₃ flux,⁵² decomposition of gas-phase TiCl₄ with an atmospheric microwave plasma torch⁵³ or by sputtering/ion-implanting techniques with nitrogen or N₂⁺ gas flux.^{54,55} S-doped TiO₂ nanomaterials were synthesized by mixing titanium tetraisopropoxide with ethanol containing thiourea,⁵⁶ heating sulfide powder⁵⁷ or by using sputtering or ion-implanting techniques with S⁺ ion flux,⁵⁸ with different doping methods resulting in different valence states of the dopants. For example, the incorporated S from thiourea had S⁴⁺ or S⁶⁺ state, while direct heating of TiS₂ or sputtering with S⁺ induced the S²⁻ anion.

Recent theoretical and experimental studies have shown that the desired band gap narrowing of TiO₂ can also be achieved by using nonmetal dopants.^{53,54,57} Asahi and co-workers

calculated the electronic band structures of anatase TiO2 with different substitutional dopants, including C, N, F, P, or S.⁵⁴ They showed that C dopant introduced deep states in the gap. Nakano and co-workers found three deep levels located at approximately 0.86, 1.30, and 2.34 eV below the conduction band in C-doped TiO2.59 On the contrary, Lee and co-workers, in their first principles calculations of electronic properties of C-doped TiO₂, found that the bands originating from C 2p states appeared in the band gap of TiO₂; however, the mixing of C with O 2p states was too weak to produce a significant band gap narrowing.⁶⁰ C-doped TiO₂ showed long-tail absorption spectra in the visible light region. Shankar and co-workers reported on the photoelectrochemical properties of propane flame annealed TiO₂ nanotube arrays.⁴⁸ Although flame annealing was found to increase the amount of the incorporated carbon in all samples, it significantly enhanced the visible spectrum absorption and the solar-spectrum induced photocurrents of short nanotubes but not significantly affected the absorption spectrum of the longer nanotubes with flame deterioration of the morphology of the nanotubes observed.⁴⁸ Similarly, Park and co-workers doped TiO₂ nanotubes with carbon by annealing in a carbon monoxide (CO) atmosphere, and found that about 30–40% of the photocurrent under illumination by a xenon arc lamp with water filter was due to visible light at wavelengths longer than 420 nm.⁴⁷ However, their visible light measurements still give values well below untreated TiO₂ nanotubes of good quality. In both cases (Shankar and Park), the photocurrents corresponded to a water-splitting efficiency below 1%, consistent with that expected for TiO₂ under solar illumination. Also, Hahn and co-workers reported on carbon doping by thermal acetylene treatment of self-organized TiO₂ nanotube layers.⁶¹ Their results showed that the acetylene treated tube layers exhibit a significant photoresponse over the whole range of visible light up to the near-IR region (1.5 eV). They claim that their treatment did not lead to any structural damage to the morphology of the nanotubes but no SEM images of the doped samples were given.

In another set of measurements (which were later found to be extremely overestimated and so have been challenged by many experts in the field), some authors showed drastic enhancement in the photoconversion efficiency of C-doped TiO₂ nanotube arrays. For example, Mohapatra and co-workers⁶² as well as Raja and co-workers⁶³ fabricated carbon-doped TiO₂ nanotubes by annealing TiO_2 nanotubes in a mixture of acetylene, hydrogen and carbon, and by producing nanotubes from ethylene glycol using a sonochemical method, respectively. They reported visible absorption and large photocurrents (up to 3 mA/cm²) for large bias voltages under illumination by a solar simulator. No IPCE data were presented to confirm their results. Also, Khan and co-workers have reported chemically modified n-type TiO₂ by controlled combustion of Ti metal in a natural gas flame.⁶⁴ They claimed that this material, in which carbon substitutes for some of the lattice oxygen atoms, absorbed light at wavelengths below 535 nm and has a lower band-gap energy than rutile (2.32 eV). They showed that this chemically modified ntype TiO_2 performed water splitting (at an applied potential of 0.3 volt) with a total conversion efficiency of 11% and a maximum photoconversion efficiency of 8.35% when illuminated at 40 mW/cm². However, many authors have challenged the reported values by Khan and co-workers since, even assuming 100% incident photon conversion efficiency, the maximum theoretical efficiency obtainable for a band gap of 2.32 eV under AM1.5 global solar irradiation is 8.0% and not 8.35% for the stated bias voltage of 0.3 eV.65 Their results have not been found to be reproducible.

In contrast, Neumann and co-workers found no significant water-splitting activity for visible light illumination, and a reduction in water-splitting activity for UV illumination compared with undoped TiO₂ photoanodes, and concluded that carbon doping led to the formation of defect states located in the band gap, at which holes recombined before they could oxidize water.⁶⁶ This seems to be in agreement with Serpone who proposed that the commonality in all doped titania rests with formation of oxygen vacancies and the advent of color centers that

absorb the visible light radiation, and he argued that the red shift of the absorption edge is in fact due to formation of the color centers.⁶⁷

Regarding nitrogen doping of TiO₂, Asahi and co-workers reported that substitutional doping of N is the most effective in band gap narrowing.⁵⁴ Di Valentin and co-workers studied nitrogen doping in both anatase and rutile polymorphs.^{68,69} In anatase, the dopant caused a red shift of the absorption band edge toward the visible region, while, in rutile, an overall blue shift was found. Experimental evidence supported the statement that nitrogen-doped TiO₂ formed nitrogen-induced mid-gap levels slightly above the oxygen 2p valence band. Wang and Doren found that N doping introduced some states at the valence band edge and thus made the original band gap of TiO_2 smaller, and that a vacancy could induce some states in the band gap region, which acted as shallow donors.⁷⁰ Nakano and co-workers found, in N-doped TiO₂, that deep levels located at approximately 1.18 and 2.48 eV below the conduction band were attributed to the O vacancy state as an efficient generation-recombination center and to the N doping which contributed to band gap narrowing by mixing with the O 2p valence band, respectively.⁷¹ However, Okato et al. found that, at high doping levels, N was difficult to substitute for O to contribute to the band gap narrowing, instead giving rise to the undesirable deep-level defects.⁷² In N-doped TiO₂, it was shown that the band gap absorption onset shifted to 600 nm compared to 380 nm for the undoped TiO₂. The optical absorption of N-doped TiO₂ in the visible light region was primarily located between 400 and 500 nm, while that of oxygen deficient TiO₂ was mainly longer than 500 nm. Also, N-F-co-doped TiO₂ prepared by spray pyrolysis was found to absorb light up to 550 nm in the visible light spectrum.⁷³ Livraghi et al. recently found that N-doped TiO₂ contained single atom nitrogen impurity centers localized in the band gap of the oxide which was responsible for visible light absorption with promotion of electrons from the band gap localized states to the conduction band.⁷⁴ The incident photon-to-current efficiency as a function of wavelength (IPCE) for N-doped TiO_2 and undoped TiO_2 showed that the photoelectrochemical

onset for TiO_{2-x}N_x was shifted to around 550 nm (into the visible region of the spectrum) and some ultraviolet (UV) efficiency for TiO_{2-x}N_x is lost compared to that of undoped TiO₂, suggesting the TiO_{2-x}N_x has a typical photoelectrochemical behavior of a material with states in the band gap which act as recombination centers for light-induced charge carriers. Vitiello and co-workers reported N-doping of anodic TiO₂ nanotubes using heat treatment in ammonia.⁷⁵ Their XPS measurements revealed the presence of nitrogen in two forms; as a nitride and as a chemisorbed N₂, indicating that some oxygen sites were substituted by nitrogen and that indeed the formation of TiO_{2-x}N_x occurred, resulting in a significant visible light response. Kim and coworkers reported on the fabrication of N-doped anodic TiO₂ nanotubes grown from nitrogencontaining Ti alloys.⁷⁶ Upon anodization of the alloy, the N-rich phase was shown to have significantly smaller nanotubes while at low N-concentrations nanotubes with larger diameter were formed. However, XPS and photoelectrochemical measurements demonstrated successful nitrogen doping of the resulting nanotube layers, which led to a significant visible photoresponse from this material.

Shankar and co-workers reported N-doped TiO₂ thin films with chemical composition $TiO_{2-x}N_x$, up to x = 0.23, fabricated by anodic oxidation of a pure titanium sheet in electrolyte solutions containing ammonium ions, nitrate ions and fluoride ions.⁷⁷ XPS indicates that nitrogen atoms substitute for oxygen sites within the TiO₂. The UV-visible spectroscopy indicated a shift in the primary absorption threshold as well as significant optical absorption in the visible wavelength range from 400 to 530 nm.

S dopant induced a similar band gap narrowing as nitrogen,⁵⁴ and the mixing of the sulfur 3p states with the valence band was found to contribute to the increased width of the valence band, leading to the narrowing of the band gap.^{57,58} When S existed as S⁴⁺, sulfur 3s states induced states just above the O 2p valence states, and S 3p states contributed to the conduction band of TiO₂.⁵⁶ The S-doped TiO₂ also displayed strong absorption in the region from 400 to 600

nm.⁵⁶ The red shifts in the absorption spectra of doped TiO₂ were generally attributed to the narrowing of the band gap in the electronic structure after doping.⁵⁴ The photocurrent spectra for the pure and S-doped crystals showed that the photocurrent spectrum edge shifted to the low-energy region below 2.9 eV for the S-doped crystal, compared to 3.0 eV for pure TiO₂, due to the transition of electrons across the narrowed band gap between the VB and the CB.⁵⁸ Nishijima and co-workers showed that the activity of S- doped TiO₂ for hydrogen evolution was higher than that of N- doped TiO₂ photocatalysts under visible light.⁷⁸ Nakahira and co-workers reported on the synthesis and characterization of S-doped TiO₂ made by anodic oxidation of titanium in sulfuric acid.⁷⁹ XPS results showed the incorporation of some sulfur species into TiO₂ coating after anodic oxidation. These S-incorporated TiO₂ coatings showed high photocatalytic activity.

Li and co-workers used the electro-deposition method to fabricate B-doped TiO₂ nanotubes.⁸⁰ XRD spectrum indicated improved crystallinity of boron-doped TiO₂ nanotube arrays, relative to undoped TiO₂ nanotube arrays. A shift of the absorption edge toward the visible region and a new absorption shoulder (380-510 nm) of B-doped TiO₂ nanotube arrays were observed via diffuse reflectance spectroscopy (DRS) and the photocurrent conversion efficiency was enhanced because of boron doping. However, the nanotubes suffered from an observable disintegration of morphological integrity.

Further, multi-non-metal-doped TiO_2 nanotubes were fabricated by electrochemical anodization of Ti in the mixed acid electrolyte of $C_2H_2O_4.2H_2O$ and HIO_3 containing NH_4F .⁸¹ The results indicated non-metals of N, F and I were successfully doped into TiO_2 with the samples displayed a significant visible-light response.

In summary, it seems that the question of whether doping of TiO_2 can lead to photoelectrochemical water splitting under visible illumination remains controversial. For example, Murphy has recently reviewed the work of carbon-doped TiO_2 and concluded "*there is no convincing evidence in the literature of water splitting under visible light in carbon-doped* TiO_2 ".⁶⁵ Also, most of the reported doping routes include tedious steps that led, in most cases, to collapse of the tubular structure. Therefore, it was one of the tasks of the present work to try to achieve *in-situ* doping of TiO₂ enabling simultaneous nanostructuring and doping of the growing anodic oxide and to investigate its effect on the photoelectrochemical water splitting capabilities of this material.

3.3.3 Crystallization of TiO₂ Nanoarchitectures

Highly crystalline structures offer unique advantages over amorphous architectures by providing a direct and fast pathway for electron transport thus decreasing the electron lifetimes in the semiconductor electrode.⁸² Shorter lifetimes reduce the electron recombination reactions with the oxidized species in the electrolyte, increasing the overall conversion efficiencies.¹

Among the widely used processing routes to fabricate crystalline TiO₂ are hydrothermal, sol-gel and calcination processes. However, crystallization by hydrothermal treatment is not convenient as it leads to a strong reduction of the textural properties due to excessive coalescence of the inorganic framework, and structural damage results when hydrothermal treatment is performed on mesostructured titania.⁸³ With sol–gel, titania nanoparticles usually exhibit a high tendency to aggregate.⁸⁴ Similarly, with calcination the thus-generated TiO₂ crystals are usually too large to be accommodated within mesopore walls, resulting in structural collapse.⁸³ Therefore, low temperature synthesis routes, where a high temperature annealing step for crystallization is not required, are needed to obtain the full benefit of this unique material architecture. The work presented in this thesis reports for the first time the fabrication of crystalline TiO₂ nanotubes at low temperature via a facile fabrication route. Also, efforts towards *in-situ* room temperature crystallization of TiO₂ nanotubes have been investigated as well.

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Chapter 4

Experimental Methods and Materials

4.1 Potentiostatic Anodization

Prior to anodization, pure titanium foil samples (2.0 x 1.0 cm x 0.25 mm) were ultrasonically cleaned with acetone followed by a deionized (D.I.) water rinse. The anodization was performed in a two-electrode electrochemical cell with the titanium foil as the working electrode and platinum foil as the counter electrode (unless stated otherwise) under constant applied voltage at room temperature (approximately 22°C) in either fluoride or chloride-containing electrolytes. Agilent E3612A D C power supply was used for potentiostatic anodization. The time-dependent current behavior under constant potential was recorded using a computer controlled Keithley 2000 multimeter. A schematic representation of the anodization setup is shown in Figure 4.1. After anodization, the samples were rinsed thoroughly with deionized water and isopropyl alcohol and then blow-dried with 99.99% pure nitrogen.



Figure 4-1: Schematic of the anodization set up.

4.2 Morphological and Crystal Structure Characterization

The morphology of the samples was examined using a JEOL JSM-6300 field emission scanning electron microscope (FESEM) and high-resolution transmission electron microscope (HRTEM, JEOL 2010F). Samples were prepared for TEM by scraping the substrate with a needle. Material was allowed to fall onto a copper grid with a lacey carbon film. The crystalline phases were detected and identified by a glancing angle Scintag x-ray diffractometer (GAXRD) on a Philips X'pert MRD PRO x-ray diffractometer (Almelo, The Netherlands) with Copper source and Si (Li) Peltier detector as well as TEM.

The compositional analysis of the samples was investigated using X-ray photoelectron spectroscopy (XPS) using a Kratos Axis Ultra spectrometer with an Al anode (Al KR: 1486.6 eV). The anode voltage and current were 14 keV and 20 mA, respectively. Photoelectrons were collected in hybrid mode over an analysis area of about 1.5 mm² with the plane of the sample surface normal to the analyzer entrance. Spectra were charge referenced to C 1s at 285 eV.

4.3 Thermal Annealing

4.3.1 Conventional Thermal Annealing

The as-anodized samples were loaded in an alumina boat and subjected to thermal annealing in an alumina tube furnace with constant flow of chosen gas maintained during the annealing process for different time intervals with heating and cooling rates of 1^{0} C/min.

4.3.2 Rapid Thermal Annealing

The as-anodized TiO_2 nanotube arrays were subjected to infrared annealing in air using RTC infrared furnace (LA 306) at 300, 400, 500 and 600 0 C for time intervals of 5, 7, 10 and 15 min under air ambient with a flow rate of 50 Standard Cubic Feet per Hour (SCFH).

4.4 Optical and Photoelectrochemical Measurements

The optical characterization of the films was performed using a Cary UV-Visible spectrophotometer. To prepare the sample for the photoelectrochemical measurements, copper contacts were drawn from the annealed sample with conducting silver epoxy and then were mounted on a microscope glass slide using '2-ton' epoxy resin. Photoelectrochemical properties were investigated in 1.0 M KOH solution using a three-electrode configuration with a TiO₂ nanotube-array photoanode, saturated Ag/AgCl as a reference electrode, and platinum foil as a counter electrode. A scanning potentiostat (CH Instruments, model CHI 600B) was used to measure dark and illuminated currents at a scan rate of 10 mV/s, see Figure 4.2.



Figure 4-2: Illustrative drawing of the experimental set-up for hydrogen generation by water photoelectrolysis.^{1,2}

A 50W mercury arc lamp (Exfo lite) was used as the light source with optical filters restricting the incident light to UV wavelengths between 320 and 400 nm. The incident power was determined as 100mW/cm² using a thermopile detector (Spectra Physics, CA, USA) after eliminating the light reflection and absorption effects at the Pyrex glass window. In some other measurements, sun light was simulated with a 300W xenon lamp (Spectra physics) and AM 1.5 filter (Oriel). The light intensity was set using a NREL calibrated crystalline silicon solar cell, equivalent to AM 1.5 light at 100 mW/cm². Incident photon to current conversion efficiency (IPCE) measurements were performed with the spectral irradiance of the light from the 300 W xenon lamp, integrated with a parabolic reflector, passing through an AM 1.5 filter and monochromatic determined using an Oriel calibrated silicon photodiode.

Note that the common standard solar reference spectrum is the air mass 1.5 (AM 1.5) global solar spectrum which describes the effect of the Earth's atmosphere on the incident solar spectrum, where $AM = 1/cos(\alpha)$, where α is the zenith angle, the angle between the overhead and actual position of the sun. Figure 4.3 shows the spectral power in Watts/cm²/nm of the xenon lamp with an A M 1.5 filter overlapped with the AM 1.5 solar irradiance from NREL.



Figure 4-3: Solar spectral irradiance (global AM 1.5) obtained from NREL plotted against irradiance from the xenon lamp with AM 1.5 filter used for photoelectrochemical measurements.³

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Chapter 5

Towards In-situ Doping of Vertically Oriented TiO2 Nanotube Arrays

As mentioned in the previous chapters, TiO_2 remains the most investigated semiconductor photocatalyst since its first demonstration in 1972¹, however, its efficient use is usually limited by its wide band gap which limits its capability to split water under AM1.5 global solar illumination to a maximum theoretical limit of 2.2% for rutile and 1.3% for anatase.² Despite many efforts, as discussed in details in Chapter 3, it remains a question whether one can successfully shift the bandgap of TiO_2 , specifically the TiO_2 nanotubes, while maintaining their excellent charge transfer properties. Is it possible to develop facile and direct routes for the *in-situ* doping of TiO_2 nanotube arrays during their fabrication? If so, will these new routes retain the tubular structure and enhance the photoconversion performance of the material? In this chapter we try to address these questions and investigate their validity. Two approaches are employed; investigation of the effect of using different cathode materials and effect of electrolyte composition on the possibility of *in-situ* metal and non-metal doping of the as-anodized TiO_2 nanotube arrays.

5.1 In-situ Metal Ion Doping of TiO₂ Nanotube Arrays

5.1.1 Effect of Cathode Material

Metal anodization is one of the most commonly developed surface treatment techniques, used in a variety of applications.³⁻⁶ With metal anodization the potential difference across the anodic film may be varied at will, whereas in other methods the ion concentration gradient and the potential across the film are controlled by the system thermodynamics.³ The metal electrode selectively influences the rates of certain reaction steps, thus influencing the overall performance. For example, hydrogen evolution reaction (HER) rates differ by several orders of magnitude

between metals.⁷ Moreover, it has been demonstrated that overvoltage effects for the anodic and cathodic reactions parallels the electrode material selectivity to intermediate products.⁸ For these reasons and many others, the following question may be raised: which electrode system is best for Ti anodization to get the proper TiO_2 material?

Careful inspection of the TiO_2 nanotube array literature, see Chapter 3, indicated no published study on the effect the cathode material used in the anodization process has on the properties of the resulting nanotube arrays and their structures. The effect of some cathode materials, from different locations in the periodic table, on the morphology, composition and electrochemical properties of the fabricated TiO_2 nanotubes in aqueous and ethylene glycol electrolytes containing NH₄F and H₃PO₄ is investigated here for the first time. The motivations behind this work were to:

- investigate whether it is possible to alter the absorption characteristics of the TiO₂ nanotube arrays by incorporation of dissolved ions, from the cathode, during their synthesis (*in-situ* doping);
- 2. determine if cathode material selection can help in controlling the resulting nanotube array architecture; and
- find alternative cheaper cathode materials as compared to Pt while sustaining the TiO₂ nanotube architectures.

In this study, pure titanium foil was cleaned as mentioned in Chapter 4 then the anodization was performed using a two-electrode cell with titanium foil as the working electrode and different materials (foil samples of Pt, Pd, Ni, Fe, Co, Cu, Ta, W, Sn, and Al) as the counter electrode. Anodizations were carried out for 10 hours at a constant applied voltage of 20 V at room temperature ($\approx 22^{\circ}$ C) in either: (A) 0.2M NH₄F + 0.1M H₃PO₄ aqueous electrolyte, or (B) ethylene glycol (EG) containing 0.2M NH₄F + 0.1M H₃PO₄ + 2% H₂O electrolyte. The

amorphous as-anodized samples were crystallized by oxygen annealing at 525°C for 4 hours with a heating and cooling rate of 1°C/min. The stability of the cathode materials was tested in terms of mass loss rate (R) in mg cm⁻² h^{-1} as calculated by:²⁰

$$R = \frac{\left(W_1 - W_2\right)}{A \times t} \tag{5.1}$$

where W_1 and W_2 are the weights of the cathode material before and after anodization, A is the surface area of the cathode material in cm² and t is the anodization time in hours.

Table 5.1 lists the tested cathode materials with the average diameters and lengths of the nanotube arrays fabricated using these cathode materials, 10 hr anodization duration, in both aqueous and EG electrolytes.

Group	Cathode	Fabricated Nanotubes in Aqueous		Fabricated Nanotubes in EG	
	Material	Electrolytes		Electrolytes	
		Average Diameter	Average Length	Average	Average Length
		±5-7 (nm)	$\pm 10 (nm)$	Diameter ± 5	$\pm 10 (nm)$
				(nm)	
Pt-group	Ni	143	1200	65	1510
Elements	Pd	134	1435	61	2500
	Pt	105	1520	65	1725
Non-Pt	Fe	99	2470	68	2000
Transition	Со	135	1900	143	2100
Tansition	Cu	81	1265	83	1130
Elements	Та	140	1175	70	1300
	W	91	690	114	2400
Non-	Al	96	570	85	1600
transition	Sn	147	1220	90	1060
ti ansition					
Elements					

Table 5-1: The cathode materials tested, grouped according to their position in the periodic table.

5.1.1.1 Anodization in Aqueous Electrolytes

FESEM micrographs of samples obtained upon anodization of Ti foil in electrolyte (A) using Ni, Pd and Pt cathodes, platinum group elements, showed that the TiO₂ nanotube arrays

formed using Ni and Pd cathodes have similar architectural features compared to those obtained using a Pt cathode with a slight variation in their diameters and lengths, see **Table 5.1**. Since the obtained architectures are quite similar, FESEM images of tubes obtained using the Pt cathode are only shown, see **Figure 5.1**. Ni and Pd can be considered as alternative cathode materials for Ti anodization with the resulting architectures very close to those obtained using Pt.



Figure 5-1: FESEM image of nanotube arrays fabricated using Pt cathode in aqueous electrolyte. The nanotubes of the inset are approximately 1.5 μm long.

For non-Pt group transition elements, tubes obtained using a Fe cathode, shown in **Figure 5.2a**, and Co and Cu cathodes showed the formation of well-aligned nanotubes of different length: 2.469 μ m, 1.900 μ m and 1.270 μ m, respectively. Top view micrographs showed a variation in pore diameter that did not correlate with length: Fe – 99 nm, Co – 135 nm, and Cu – 81 nm. Nanotube arrays obtained using Ta showed the largest pore size, 140 nm versus 105 nm for Pt, while the nanotube arrays obtained using a W cathode, see **Figure 5.2 b**, were the shortest.



Figure 5-2: FESEM images of nanotube arrays fabricated using (a) Fe and (b) W cathodes in aqueous electrolytes.

For the non-transition elements, the nanotube arrays fabricated using Sn and Al showed great variation in their dimensions with Al cathodes resulted in formation of the shortest nanotubes, $0.57 \mu m$, with relatively poor tube uniformity, see Figure 5.3.



Figure 5-3: FESEM image of nanotube arrays fabricated using Al cathode in aqueous electrolyte.

5.1.1.2 Anodization in Ethylene Glycol Electrolytes

FESEM images of Ti foil samples anodized in electrolyte (B) using Ni and Pt (Figure 5.4a) cathodes showed the TiO_2 nanotube array surfaces to be covered with precipitate debris. In contrast, nanotube arrays fabricated using a Pd cathode showed no such debris, see Figure 5.4b. Cross sectional images showed the Pd fabricated nanotube arrays to be more highly aligned than those fabricated using either Pt or Ni.



Figure 5-4: FESEM images of nanotube arrays fabricated using (a) Pt and (b) Pd cathodes in EG electrolytes.

Figure 5.5a shows FESEM micrographs of nanotube arrays synthesized using a Fe cathode, with no indication of precipitate debris upon the surface. Although cross-sectional views of the nanotubes fabricated using Co, Cu, Ta and W cathodes showed the formation of well-organized nanotube arrays, top view micrographs showed that the tubes were clogged with surface debris; **Figure 5.5b** shows nanotube arrays fabricated using a Co cathode.



Figure 5-5: FESEM images of nanotube arrays fabricated using (a) Fe and (b) Co cathodes in EG electrolytes.

Nanotube arrays fabricated using Sn and Al cathodes showed the formation of wellaligned structures with no or very little debris on the surface. **Figure 5.6** shows the morphology of nanotube arrays obtained using an Al cathode.



Figure **5-6**: FESEM image of nanotube arrays fabricated using an Al cathode in an EG electrolyte.

These results indicate that the nature of the cathode material plays a role in the appearance of surface precipitate. The overpotential of the cathode is a critical factor that affects the dissolution kinetics of the Ti anode, in turn controlling the activity of the electrolyte and morphology of the formed architectures. Yoriya and co-workers reported that the more dissolved Ti in the electrolyte there is, the higher the electrolyte conductivity, which in turn helps to prevent debris formation.²¹ It appears that the different cathode materials lead to the fabrication of

different morphologies due to differences in their overvoltage within the test electrolyte. Note that in all cases it was possible to achieve TiO_2 nanoarchitectures in their tubular form. Now, what is the effect of cathode material on the chronoamperometric behavior of titanium during its anodization? Is there any drastic change in the current magnitude? Is the shape of current curve different from that usually seen when using Pt as a cathode to anodize titanium?

5.1.1.3 Chronoamperometric Measurements

The time dependent anodization current behavior during anodic oxidation of Ti in both aqueous and EG electrolytes show similar trends, however the initial current amplitudes are higher for the aqueous electrolytes. Therefore, the discussion below is limited to the results obtained using aqueous electrolytes. **Figure 5.7** shows the Ti foil anodization current-time response for the different cathode materials. The curves are essentially identical in shape to that obtained using a Pt cathode, but with a variation in current amplitude that Newbery ²² reported could be related to the overpotential difference between different cathode materials, as well as differences in the resulting oxide layer thickness. ²³



Figure 5-7: Current-time response of Ti samples anodized using different cathodes in aqueous electrolytes.

With reference to **Figure 5.7**, initially, a compact layer of TiO_2 is assumed to be formed through hydrolysis of titanium, i.e.

$$Ti_{(s)} + 2H_2O_{(l)} = TiO_{2(s)} + 4H^+ + 4e^-$$
 [5.2]

This oxide layer results in a dramatic decrease in the recorded current due to its poor electrical conductivity. After that, TiO_2 starts to dissolve, forming pores, leading to the observed slight increase in current with time. This can be explained on the basis of the high field model (HFM)²⁴ and its modified form; ²⁵ under sufficient applied voltage magnitude the electric field will be strong enough to migrate titanium ions ^{24,25} leaving behind voids in the interpore areas ²⁶ that, in turn, will separate one pore from one another leading to the formation of discrete tubes oriented vertically to the substrate.

According to the HFM,^{24,25} the current under high field conditions during the formation of the oxide layer takes the simple form:

$$i = \alpha . e^{\beta F}$$

$$[5.3]$$

where *i* represents the current, α is the jump probability of a cation interstitial and is given by Eq. 5.4, β is calculated for Ti by Eq.5.5, and *F* is the electric field strength (V/cm):

$$\alpha = \frac{0.24ekT}{a^2\varphi_o\tau}e^{-\frac{\varphi_o}{kT}}$$
[5.4]

$$\beta = \frac{4ae}{8kT}$$
[5.5]

In the above equations e is the electron charge, k is Boltzmann's constant, T is the absolute temperature, a is one half of the jump distance, φ_o is the minimum potential barrier, and τ is the time of vibration. Note here that the charge associated with formation of a titanium cation is 4e. The electric field linearly decreases with thickness, while from Eq. 5.3 we see that current will decay exponentially with film thickness. The nanotube length is a result of the equilibrium established between the electrochemical formation of TiO₂ and its simultaneous chemical

dissolution in the fluoride-containing electrolytes.²⁷ Now, what about the stability of cathodes in the test electrolytes? Is it possible that these cathode materials are not stable? if so, is it possible that the dissolved ions from cathodes be doped/incorporated into the resulted TiO₂ nanotube arrays? What is the effect of these incorporated ions, if any, on the photoelectrochemical and optical properties of the material?

5.1.1.4 Cathode Material Stability

Table 5.2 shows the rate of mass loss of the tested cathode materials; see Eq. 5.1, in aqueous electrolyte during a 10 hr anodization. Pd has stability comparable to that of Pt since both indicate zero mass loss, while Ni gives a mass loss rate of about 81.4 μ g cm⁻² h⁻¹. Among the tested non-platinum transition elements, Ta shows the greatest stability (3.2 μ g cm⁻² h⁻¹) while W was the least stable (712.8 μ g cm⁻² h⁻¹). The cathode materials can be arranged, according to their stability in aqueous electrolytes, in the following order:

$$Pt \approx Pd > Ta > Al > Sn > Cu > Co > Fe > Ni > W$$

Within the limits of our microbalance sensitivity, $0.1 \mu g$, the cathode materials showed no mass loss in the ethylene glycol based electrolytes over the 10 hour test period.

Table 5-2:The rate of mass loss of the tested cathode materials, see Eq. 5.1, in aqueous electrolyte
during a 10 hr anodization.

Group	Cathode Material	Average Rate of Mass Loss (µg/cm ² /hr)
	Ni	81.4 ± 0.2
Pt-group Elements	Pd	0
	Pt	0
Non-Pt Transition	Fe	46.7 ± 0.1
Flomonts	Со	34.9 ± 0.1
Elements	Cu	8.3 ± 0.1
	Та	3.2 ± 0.1
	W	712.8 ± 0.3
Non-transition	Al	6.0 ± 0.1
Elements	Sn	7.6 ± 0.1

5.1.1.5. Photoelectrochemical and Optical Properties

5.1.1.5.1 TiO₂ Photoanodes Fabricated in Aqueous Electrolytes

Figure 5.8a shows the photocurrent less dark current versus applied potential obtained for the annealed TiO₂ nanotube electrodes prepared using different cathode materials in aqueous electrolyte under 100 mW/cm² 320 nm – 400 nm illumination. The electrodes show n-type behavior, i.e., positive photocurrents at anodic potentials.²⁸ The photocurrent values obtained for some electrodes are higher than those measured for electrodes fabricated using Pt cathode under same conditions. Although this can be related to the difference in tube length, the measured values here are higher than those values reported for TiO₂ nanotubes fabricated using Pt cathodes with a comparable length.²⁹ The corresponding light energy to chemical energy conversion (photoconversion) efficiency η was calculated using Eq. 2.13. Figure 5.8b shows the corresponding (three electrode) photoconversion efficiency; the highest photoconversion efficiency of 6.9% was recorded for samples prepared using a Fe cathode.



Figure **5-8**: (a) Photocurrent (light-less-dark) versus voltage characteristics for the annealed nanotubular TiO₂ electrodes prepared by anodization of Ti foil in aqueous electrolytes using different cathode materials, illuminated by 100 mW/cm² 320 to 400 nm. (b) Corresponding photoconversion efficiency.

For the given nanotube array geometry, photocurrent generally scales with surface area as shown by Shankar and co-workers ³¹, however the nanotube arrays prepared using a W cathode showed high photocurrent and photoconversion efficiency in spite of their shorter tube length (4.3%, 690 nm). In contrast significantly longer nanotube arrays prepared using a Cu cathode showed a comparatively low photoconversion efficiency (3.1%, 1260 nm). Why is that? To help resolve this issue, XPS analyses were performed for the W and Cu samples which showed incorporation of both W and Cu into the TiO₂ architectures. Figures 5.9a,b shows the XPS spectra for W 4d and W 4f, respectively. Petrovic' and co-workers reported the same peaks of W 4f for W-Ti thin films³², assigning the peak at 38 eV to W-oxide and that at 33 eV to metallic W. The formation of the metallic W can be explained based on thermodynamic considerations because the formation of TiO₂ (with enthalpy of formation $\Delta H = -944$ kJ/mole) is energetically more favorable than the formation of the WO₃ phase ($\Delta H = -841$ kJ/mole). Colton and coworkers³³ and Park and co-workers³⁴ found a peak at 38.1 eV and related this peak to the W⁶⁺ oxidation state. The observed peak at 33.6 eV can be related to the W⁴⁺ oxidation state. These results indicate that W, in the (IV) and (VI) oxidation states, has been incorporated into the TiO_2 nanotubes.



Figure **5-9**: XPS spectra of TiO₂ nanotube arrays fabricated using W cathode in aqueous electrolyte; (a) W 4d, and (b) W 4f.

Park and co-workers reported that higher valence cations than Ti^{4+} such as W^{6+} can replace Ti^{4+} , leaving extra electrons weakly bound to the dopant center and thus contributing to the conduction band. ³⁴ Incorporation of a higher valence cation (W^{6+}) into the TiO_2 will decrease its work function and enhance the electron density³⁵ via the following defect-site reaction:

$$WO_3 \leftrightarrow W_{Ti}^{**} + 2O_0^{*} + \frac{1}{2}O_{2(g)} + 2e^{-1}$$
 [5.7]

where e^{-} refers to a quasi-free electron i.e. there is a possibility that tungsten forms donor-type centers (W_{Ti}^{-}) in the crystal lattice of TiO₂.^{36,37}

TiO₂ nanotube arrays incorporating copper, see **Figure 5.10a**, showed significantly lower photocurrent and photoconversion efficiency. Similarly, Liqiang and co-workers found that Cu doping of a TiO₂ matrix led to severe decrease in its photocatalytic activity.³⁸ However, the absorption spectra of Cu-doped TiO₂ nanotubes showed a shift in the visible region, see **Figure 5.10b**. Note that both cupric and cuprous oxides are p-type semiconductors which can act as trap states.



Figure 5-10: (a) Cu 2p XPS spectra of TiO_2 nanotube arrays fabricated using Cu cathode in aqueous electrolyte and (b) Diffuse reflectance spectra of TiO_2 nanotube arrays fabricated using Pt, W and Cu cathodes.

Finally, it is noted that XPS of nanotube arrays synthesized using Fe and Co cathodes showed indication of elemental doping which can be used, besides the tube length, to explain the obtained high photoconversion efficiencies, see **Figure 5.11**.



Figure 5-11: XPS spectra of TiO_2 nanotube arrays fabricated using (a) Fe and (b) Co cathodes in aqueous electrolytes.

5.1.1.5.2 TiO₂ Photoanodes Fabricated in EG electrolytes

Figure 5.12a shows the measured light-less-dark photocurrent versus potential obtained for the TiO₂ nanotube electrodes prepared using different cathode materials in ethylene glycol electrolytes. The photocurrent values obtained for some electrodes are higher than those measured for electrodes fabricated using a Pt cathode under the same conditions, a difference that can be related to tube length, see **Table 5.1**. The highest photoconversion efficiency of 5.45% was recorded for samples prepared using a Pd cathode, see **Figure 5.12b**. Note here that photoanodes fabricated using Pd, W, Co and Fe showed higher photoconversion efficiency than the photoanode fabricated using Pt cathode. These results along with the obtained unique morphologies using these materials as cathodes suggest that these less-expensive metals can replace Pt during the fabrication of TiO_2 nanomaterials via anodization. Note that no XPS analysis is performed because there was no mass loss of the cathode material during their use in EG-containing electrolytes which omits the possibility of metal ion doping from cathodes.



Figure **5-12**: (a) Photocurrent (light-less-dark) versus voltage characteristics for the annealed nanotubular TiO₂ electrodes prepared by anodization of Ti foil in EG electrolytes using different cathode materials, illuminated under 100 mW/cm² 320 to 400 nm. (b) Corresponding photoconversion efficiency.

5.2 In-situ Non-metal Doping of TiO₂ Nanotube Arrays

As discussed in Chapter 3, there has recently been a surge of interest in the area of semiconductor doping documenting different experimental approaches towards carbon doping of titania³⁹⁻⁴² However, as reviewed by Murphy, there is a great debate in literature whether the improvement in the photoelectrochemical properties of C-doped TiO₂ is related to the effect of carbon doping.⁴³ Some authors related the observed enhancement in the photoelectrochemical properties of C-doped TiO₂ to the structural artifacts resulted during the doping process as most of the previously reported processes involved multi steps resulting in poor structural control.⁴³ Therefore, the immense question here becomes: is it possible to dope TiO₂ by carbon while

retaining its high quality structure? If so, will we still be getting high photoconversion efficiency using these C-doped nanotubes? Herein, we investigated the possibility of *in-situ* carbon doping of TiO_2 nanotube arrays while avoiding any structural artifact/collapse.

5.2.1 Effect of Carbon Cathode

TiO₂ nanotube arrays have been fabricated via anodization of Ti foil in similar electrolytes used for metal-ion doping shown in the previous section (electrolytes A and B) with the exception of using carbon rod as the cathode material. **Figure 5.13a,b** shows the FESEM micrographs of the fabricated samples in aqueous and EG-containing electrolytes, respectively. For the sake of comparison, the FESEM micrographs of the corresponding titania nanotube arrays fabricated in similar electrolytes using Pt cathodes are shown in **Figures 5.1** and **5.4a**. It is worthy mentioning that carbon shows great stability in both electrolytes (rate of mass loss of $1.5 \,\mu\text{g cm}^{-2} \,\text{h}^{-1}$ in aqueous electrolyte and no mass change in EG electrolyte).



Figure 5-13: FESEM images of nanotube arrays fabricated using C cathode in (a) aqueous and (b) EG-containing electrolytes.

Although the nanotube arrays formed using C cathode in both electrolytes are vertically aligned with comparable tube lengths, the nanotubes fabricated in EG electrolytes showed less debris than

those fabricated in aqueous electrolytes. Note that no collapse of the tubular structures was observed in either case.

 Table 5.3 shows the dimensions of the fabricated nanotube arrays using C and Pt

 cathodes in both aqueous and EG electrolytes. In both media, the nanotube arrays fabricated using

 C cathodes are shorter than those fabricated using Pt cathodes while their diameters are larger.

Cathode	Fabricated Nanot	ubes in Aqueous	Fabricated Nanotubes in EG		
	Electro	olytes	Electrolytes		
Material	Average Diameter	Average Length	Average Diameter	Average Length	
	±5-7 (nm)	± 10 (nm)	\pm 5 (nm)	± 10 (nm)	
Pt	105	1520	65	1725	
С	143	1300	81	1220	

Table 5-3: The nanotubes fabricated using carbon cathode as compared to those fabricated using pt.

The light energy to chemical energy conversion (photoconversion) efficiencies of the fabricated TiO_2 nanotube arrays using C and Pt cathodes were calculated using Eq. 2.16 and shown in **Figure 5.14**. The nanotubes fabricated in aqueous electrolyte using C cathode showed the highest photoconversion efficiency. Note that the photoconversion efficiency of the other fabricated nanotube arrays (using C cathode in EG and using Pt in both aqueous and EG electrolytes) scales almost linearly with their tube lengths.



Figure **5-14**: Photoconversion efficiency versus voltage characteristics for the annealed nanotubular TiO₂ electrodes prepared by anodization of Ti foil in aqueous and EG electrolytes using carbon and Pt cathodes, illuminated under 100 mW/cm² 320 to 400 nm.

To investigate the reason behind getting high photoconversion efficiency in case of the nanotubes fabricated using C cathode in aqueous electrolyte, XPS analysis was performed to see if any carbon doping/incorporation is there. **Figure 5.15** shows the C1s XPS spectra for a typical sample anodized in aqueous electrolyte using C cathode. The C1s spectrum shows a strong peak at 284.8 eV arising from adventitious carbon and another peak at about 288.5 eV which Ren and co-workers assigned it to the presence of C-O bonds.⁴⁴ These data reveal that carbon may result in the formation of a Ti–O–C structure, which can be used to explain the observed enhancement in the photoconversion efficiency. This is in parallel with Shankar and co-workers who showed that carbon incorporation increases the photoconversion efficiency of the flame annealed TiO₂ nanotube arrays.⁴⁵ These results confirm the possibility that carbon doping can enhance the photoelectrochemical properties of TiO₂ and that this enhancement is not related, at least not completely, to structural artifacts.



Figure 5-15: XPS spectra of TiO₂ nanotube arrays fabricated using C cathode in aqueous electrolyte.

5.2.2 Effect of the Anodization Bath Chemistry

It is well known that H_2O_2 can oxidize ethylene glycol to a mixture of low carboncontaining acids. The following was shown to be a possible reaction pathway for the oxidation of EG with H_2O_2 : ⁴⁶



While oxalic acid is oxidized to formic acid, the rate is less than that for other intermediates, 7.7 x 10^6 mole/s for oxalic acid compared to 8.6 x 10^8 mole/s for glycolic acid.⁴⁶ Also, it was shown that chlorine (if present as one constituent of the anodization medium) can act as a catalyst enhancing the formation of a ternary TiO₂-C-Cl complex, i.e. it enhances carbon incorporation into TiO₂.⁴⁷

Based on the above two reported findings, it seems that a mixture of EG, chlorine and H_2O_2 might result in C-doped TiO₂ architectures. However, the remaining challenging question was: what is the optimum electrolyte composition that enables the fabrication of C-doped TiO₂ nanostructures? To this end, formation of the nanotubes by anodization in ethylene glycol (EG) electrolytes containing 0.5 M HCl + 0.1-0.5 M H_2O_2 and 2 *vol.*% H_2O was investigated under applied voltages in the range 5 V to 20 V. It was found that various nanotube '-ish' architectures could be obtained over the voltage range 8-18 V while the Ti sample starts to corrode above 18 V. I say tube'ish in that some pore openings could be seen under FESEM imaging, however they may well be a mix of wires and tubes. Figure 5.16a,b shows FESEM micrographs of the

architectures formed upon anodizing Ti foil at 10 V in EG-containing electrolytes composed of 0.5M HCl with 0.1M and 0.4M H₂O₂, respectively. The nanotube bundles, individual nanotube outer diameter \approx 30 nm, start to form after only \approx 90 s of anodization, with similar surfaces seen for anodization durations up to ten minutes, after which the sample tends to corrode. The nanotube bundles formed in solutions containing 0.1M (Fig. 5.16a) and 0.2M H₂O₂ (not shown) were irregular agglomerates in nature, however, these bundles start to show orientation in the presence of 0.3M H₂O₂ or higher (Fig. 5.16b). It is also clear that the surface coverage increases as the H₂O₂ concentration increases since the nanotube growth starts randomly at certain points on the surface and then spreads out to cover almost the whole surface, in agreement with the results reported by Richter ⁴⁸ and Hahn ⁴⁹ who showed the formation of similar nanotube bundles. Note that nanotube bundles of \approx 6 µm in length and 600 nm in width are formed upon the use of 0.4 M H₂O₂.



Figure 5-16: Illustrative FESEM image of a TiO₂ nanotube bundles achieved by anodization of Ti foil for 120 s in ethylene glycol electrolytes containing 0.5 M HCl + xM H₂O₂ at 10 V; (a) x=0.1M and (b) x=0.4M.

Plots of current versus time as a function of H_2O_2 concentration (10 V, 0.5 M HCl) are shown in **Fig. 5.17**. Depending upon H_2O_2 concentration, a variety of time-current behaviors have been seen, including the classic dip-rise-gradual fall seen using fluoride ion containing electrolytes, as well as ones similar to those associated with nanoscale 'pitting'.



Figure 5-17: The anodization current-time response of Ti samples as a function of H_2O_2 concentration anodized for 120 s in ethylene glycol electrolytes containing 0.5 M HCl + xM H_2O_2 at 10 V.

Figure 5.18a is an FESEM image of baleen-looking structure from a mechanically fractured sample fabricated at 18 V, 0.5 M HCl + 0.4 M H₂O₂ for 80 s. The use of low concentrations of H₂O₂, namely 0.1 and 0.2M, resulted in the formation of flower-like structures while the use of higher concentrations led to the formation of well-aligned bundles. Nanotube bundles of up to approximately 6.5 μ m in length can be formed upon the use of 0.4 M H₂O₂ however, the addition of 0.5 M H₂O₂ leads to sample corrosion. Figure 5.18b shows the current-time relations recorded for samples anodized at 18 V as a function of H₂O₂ concentration. The plots are similar to those usually obtained in aqueous media except for the electrolyte solution containing 0.5 M H₂O₂ which shows a sharp increase in current after its initial drop leading to sample corrosion.



Figure 5-18: Illustrative FESEM image of a TiO_2 nanotube bundles achieved by anodization of Ti foil for 80s in ethylene glycol electrolytes containing 0.5 M HCl + 0.4M H₂O₂ at 18 V; (b) The corresponding anodization current-time response of such samples for a variety of H₂O₂ concentrations.

The above reaction scheme of EG with H_2O_2 indicates the possibility of EG oxidation by H_2O_2 to form a mixture of organic acids of lower viscosity. Richter and co-workers reported the fabrication of TiO₂ nanotube bundles in chloride-containing electrolytes with a combination with either oxalic or formic acid electrolytes.⁴⁸ They were able to get these nanotube bundles over an applied voltage range of 11-20 V, a behavior in close agreement with our present findings suggesting that EG is partially oxidized to a mixture of oxalic and formic acids. The transport number of 0.1-1.0 M HCl (t_{H^+}) in ethylene glycol at 298.15 K is almost constant (0.830) ⁵⁰ indicating that EG will not significantly alter the etching properties of HCl in our electrolyte system.

The next step was to investigate the optical and photoelectrochemical properties of the fabricated nanoarchitectures and to characterize them for any carbon doping. Figure 5.19a shows illuminated-less-dark photocurrent versus voltage values for 500°C annealed nanotubular TiO_2 electrodes prepared at 10 V and 18 V anodization potentials in EG solutions containing 0.5M HCl

and 0.4M H₂O₂, under AM 1.5 simulated sunlight in 1.0 M KOH. Also shown, for the 18 V EG fabricated sample, is the photocurrent generated by only the visible portion of the AM 1.5 spectrum. The dark current was less than 5 μ A/cm² for all samples over the displayed potential range. The electrodes show n-type behavior, i.e., positive photocurrents at anodic potentials.^{28,29} The AM 1.5 photocurrent values obtained are slightly better than those reported for TiO₂ nanotubes fabricated in fluoride-containing media²⁹ with the longer tubes obtained at 18 V giving higher values.

Figure 5.19b shows the squared AM 1.5 photocurrent as a function of applied voltage. The current gradually increases, becoming linear with applied bias, indicating that the photogenerated charges are being efficiently separated by the electric field of the depletion layer.⁵¹ At higher potentials the squared photocurrent-potential plot deviates from linearity due to saturation resulting from the near complete collection of photogenerated charge carriers.



Figure 5-19: (a) Current-voltage characteristics (light less dark currents) for the annealed TiO_2 electrodes prepared in EG solutions containing 0.5M HCl + 0.4M H₂O₂ anodized at different potentials and (b) the corresponding squared AM 1.5 photocurrent as a function of applied voltage.

The corresponding light energy to chemical energy conversion (photoconversion) efficiencies (Eq. 2.13) for AM 1.5 illumination are shown in Figure 5.20. The highest AM 1.5

spectrum efficiency, due almost entirely to the UV portion of the AM 1.5 spectrum, of 0.42% was recorded for 18 V samples prepared in EG-containing electrolyte in the presence of 0.5M HCl and 0.4M H₂O₂. This is ~15% more efficient than that reported by Sultana and co-workers⁵² for 30 μ m long undoped TiO₂ nanowires under AM 1.5 (5M KOH, 0.61V_{SCE}) although our samples are 5 times shorter and tested in less concentrated KOH electrolyte. So, what is the reason behind this enhancement in the photoconversion efficiency? Is there any other quantitative measurement to confirm the high efficiency of the fabricated material?



Figure 5-20: AM 1.5 photoconversion efficiency as a function of measured potential for the annealed TiO_2 electrodes prepared in EG solutions containing 0.5M HCl + 0.4M H₂O₂ anodized at different potentials.

To quantitatively confirm the ability of the fabricated nanoarchitectures to split water, we have measured the amount of generated hydrogen during the water photoelectrolysis process. **Figure 5.21** shows the hydrogen generated as a function of time, in μ L, under AM 1.5 illumination using a 1 cm² ethylene glycol anodized sample, 18 V, 0.5M HCl, 0.4M H₂O₂, anodization duration 2 minutes, 500°C annealed. The samples were mounted on a glass base and the electrical contacts were taken from the titanium substrate using copper leads and silver epoxy after removing the oxide layer at the titanium surface. All the regions except a 1 cm² sample were covered using an insulating epoxy. The hydrogen evolution rate is approximately 391 μ L/hr

 $(1 \text{cm}^2 \text{ electrode under 100 mW/cm}^2 \text{ AM } 1.5 \text{ illumination})$, with a time-power normalized evolution rate of 3.9 mL/W•hr. The water-splitting reaction was confirmed by the 2:1 ratio of evolved hydrogen to oxygen (GC; SRI, model 8610C); no performance degradation was observed during a 24 hr continuous test.



Figure **5-21**: Hydrogen generated as a function of time, in μL, under AM 1.5 illumination using a 1 cm² ethylene glycol electrolyte anodized sample, 18 V, 0.5M HCl, 0.4M H₂O₂, 2 minute anodization, annealed in oxygen for three hours at 500°C.

Based on the observed extraordinary rapid formation of TiO₂ architectures in the EG/HCl/H₂O₂ electrolyte, an oxide layer approximately 6 μ m long grown in \approx 80 s, and the very reasonable photoconversion efficiency, the possibility of impurity incorporation in the TiO₂ was investigated, which, in the case of an organic electrolyte will mainly be carbon,⁴⁷ using XPS analyses. Figure 5.22a,b shows the C1s XPS spectra for samples anodized in ethylene glycol containing 0.5 M HCl and 0.4 M H₂O₂ at 10 V and 18 V, respectively. In both cases the C1s spectrum shows a strong peak at 285.7 eV, arising from adventitious carbon, and a weak peak at 281.4 eV that can be assigned to carbon associated with Ti-C bonds in the TiO₂ architectures.⁵³ Irie and co-workers observed a similar peak, around 281.8 eV, in C-doped TiO₂ prepared by oxidizing TiC ⁵⁴ that they assigned to the C1s peak of the Ti-C bond. Figure 5.22b shows another peak at about 289 eV. Ren and co-workers observed a similar peak at 288.6 eV and assigned it to

the presence of C-O bonds.⁴⁴ The data indicates that carbon incorporation may result in the formation of a Ti-O-C structure. A slight inflection can be seen at 287.6 eV that could be assigned to interstitial carbon atoms.⁴⁴



Figure 5-22: C1s XPS spectra for samples anodized in ethylene glycol containing 0.5M HCl + 0.4M H₂O₂ at (a) 10 V and (b) 18 V.

To investigate the effect of carbon doping/incorporation on the optical properties of TiO₂, the diffuse reflection spectra for the TiO₂ architectures fabricated in the ethylene glycol electrolyte containing 0.5M HCl and 0.4M H₂O₂ at 10 V and 18V were examined, Figure 5.23. Shankar and co-workers observed similar behavior in the spectra of flame annealed carbon-doped TiO₂ nanotubes fabricated in fluorine-based electrolytes.⁴⁵ Also, Wang and co-workers reported shift in the photoresponse of TiO₂ from UV to near infrared region and related that shift to substitutional and interstitial carbon atoms in the lattice of TiO₂, which led to the formation of complex midgap states.⁵⁵ The chlorine chemistry may facilitate the incorporation of carbon derived from the organic medium into the fabricated architectures. The author notes Richter and co-workers suggested that chlorine can act as a catalyst enhancing the formation of a ternary TiO₂-C-Cl complex.⁴⁷ Therefore; *in-situ* carbon doping was possible via controlling the

electrolyte composition. The doped material showed better optical and photoelectrochemical properties than its undoped counterpart.



Figure 5-23: UV-visible diffuse reflection spectra of the prepared TiO_2 nanotube architectures by anodization at different voltages in EG solutions containing 0.5M HCl + 0.4M H₂O₂.
Conclusions

A direct one-step facile approach for the *in-situ* metal and non-metal ion doping of TiO_2 nanotube arrays during their electrochemical fabrication in both aqueous and non-aqueous electrolytes has been developed. The effect of doping on the morphology, optical and photoelectrochemical properties of the fabricated nanotube arrays is documented. The following conclusions can be drawn from this study: (1) The incorporation of ions into TiO2 nanotube arrays during their electrochemical synthesis is giving rise to the possibility of *in-situ* bandgap engineering of the material during its fabrication without any structural collapse, (b) The use of different cathode materials led to the incorporation/doping of ions into the TiO_2 nanotube arrays which in turn enhanced its optical and photoelectrochemical properties, except for Cu which forms a p-type oxide that can act as trap states in n-type TiO_2 , (c) Doping TiO_2 with carbon while retaining its original structure led to an enhancement in its optical and photoelectrochemical properties, confirming that this enhancement is not related to the artifacts developed during the doping processes developed by others, (d) It appears the H_2O_2 + HCl combination in ethylene glycol electrolytes drives modest amounts of carbon incorporation within the resulting TiO_2 structures, (e) A wide range of comparatively inexpensive materials can be efficiently used as cathodes during the anodization process of titanium in fluoride-containing aqueous and EG electrolytes to fabricate vertically oriented TiO₂ nanotube arrays with scalable dimensions and finally (f) This study opens the way for the possibility of *in-situ* doping of 1D nanoarchitectures via the modification of the anodization bath chemistry with the advantage of simplicity and retaining the original material morphology.

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Chapter 6

High Temperature Crystallization of Anodically Fabricated TiO₂ Nanotubes

In this part of the thesis, the effect of different high temperature crystallization routes has been investigated in order to determine the optimal annealing conditions for TiO_2 nanotube arrays. For example, the conventionally used tube furnace annealing is investigated along with combined processes of thermal annealing and solvothermal treatments. Also, the effect of rapid infrared annealing is introduced.

For the sake of comparison, the investigated TiO_2 nanotube arrays in this study have been fabricated under the same conditions. Cleaned titania samples (see Chapter 4 for details) were anodized at room temperature (approximately 22°C) at 20V for 20h in a formamide-based electrolyte containing 0.2M NH₄F, 0.1M H₃PO₄ and 3 vol.% H₂O.

6.1 Conventional High Temperature Thermal (Furnace) Annealing

Figure 6.1 shows FESEM images of the fabricated nanotube arrays. It can be seen that the nanotube array is uniform over the substrate. The cross-sectional view of the nanotube arrays is shown in **Fig. 6.1b**. The tubular structure with nearly uniform wall thickness throughout the length of the tube is evident from the figure. The as-prepared samples were found to have a length of approximately 7 ± 0.2 µm.



Figure 6-1: (a) FESEM top-view image of the fabricated TiO_2 nanotube arrays upon anodizing Ti foil in a formamide-based electrolyte containing 0.2M NH₄F, 0.1M H₃PO₄ and 3 vol. % H₂O at 20V for 20 hours, (b) the corresponding cross-sectional view .

Figure 6.2 shows the GAXRD patterns of the as-anodized as well as annealed samples at different temperatures in dry oxygen ambient. The as-anodized nanotube arrays were found to be amorphous. In the diffraction patterns, the anatase phase starts to appear at 300 °C. The 230 °C annealed sample was amorphous with only small reflection appears at $2\theta \sim 40^{\circ}$ that can be related to reflection from the titanium substrate. It is clear also that the sample starts to crystallize in the anatase phase at a temperature close to 300 °C. The intensity of the anatase (101) increases with increasing temperature up to 550 °C. Near 480 °C, the rutile phase emerges in the x-ray diffraction pattern. After this temperature, the relative intensity of the rutile (110) peak with respect to anatase (101) peak increased.



Figure 6-2: Glancing angle x-ray diffraction patterns of 7 µm long nanotube arrays as a function of annealing temperature in oxygen ambient.

Although the rutile ratio increases with increasing the annealing temperature, complete transformation to rutile does not occur even upon annealing to 700 °C.

The variation of the size of the anatase and rutile crystallites (D) with temperature was calculated using the Scherrer equation:¹

$$D = \frac{0.9\lambda}{FWHM\cos(\theta)}$$
[6.1]

where λ is the wavelength of Cu K_a radiation (1.5418 Å), 0.9 is the Scherrer constant, θ is the Bragg reflection angle, and FWHM is the full-width at half-maximum intensity of the anatase (101) peak. Relative standard deviation of the determined average particle size is ~ 7%. The instrument broadening was corrected for using NIST 640c silicon. **Fig. 6.3** shows that the grain size of rutile progressively increased with temperature after its nucleation. In contrast, the average size of the anatase grains shows a decreasing trend starting at the temperature where the rutile phase starts to appear. This might indicate that above 480 °C the large anatase grains transform into rutile with the smaller grains remaining anatase.²



Figure 6-3: Variation of the anatase and rutile crystallite sizes of the TiO_2 nanotube samples with the annealing temperature.

Evolution of the nanotube architecture as a result of high-temperature annealing shows that the nanotubular structure is retained up to around 580 °C, **Fig. 6.4a**. No discernible changes in the pore diameter or wall thickness were observed even after annealing for 6 h at this temperature. However, annealing at higher temperatures (> $600 \ {}^{0}$ C) was accompanied with structural collapse of some portions of the nanotubes, **Fig. 6.4b**, as evidenced by shortening in the nanotube length. It is noteworthy mentioning that the tubular structure does not disappear (collapse) completely even upon annealing at 700 °C. This can be used to explain the existence of anatase (101) peaks in the GAXRD patterns for samples annealed at all temperatures since it is believed that the anatase crystallites form within the tube walls.³



Figure 6-4: Effect of annealing temperature on the surface morphology of TiO_2 nanotube array samples annealed in O_2 ambient at (a) 580 °C and (b) 620°C

These results showed that the fabricated titania nanotube architectures remain stable up to temperatures near 580 °C when annealed in oxygen, without any notable change in the pore diameter, wall thickness or tube length. The protrusions emanating from the underlying titanium support in the form of rutile crystallites is believed to be the major cause of the material degradation above this temperature. Were the appeared rutile peaks in the GAXRD pattern of the annealed samples associated with the supporting titanium substrate? To investigate this possibility, bare titanium foil samples were annealed at different temperatures under same conditions to those used to anneal the nanotubes. GAXRD of the substrate showed an almost similar result as that observed in the case of a nanotube sample subjected to identical treatment, but the relative intensity of the rutile (110) peak to anatase (101) peak was found to be higher in

the case of bare titanium foil even at lower temperatures compared to those of the nanotube samples, **Fig. 6.5**. Note that complete transformation to rutile is observed at temperature near 580 $^{\circ}$ C which was not the case for the annealed nanotube arrays. Hence, it is clear that part or all of the rutile phase observed in the GAXRD patterns of the nanotube array annealed samples, **Fig. 6.2**, is from the substrate. Another observation that supports this possibility is the lower anatase crystallite size above 480 $^{\circ}$ C (**Fig. 6.3**) as compared to that at temperatures below 480 $^{\circ}$ C. This smaller crystallite size indicates the possibility that the larger anatase crystallites in the nanotube–titania support interface region were converted into rutile leaving those on the nanotube walls unaffected. This is in parallel with Zhang and Banfield who reported that anatase crystallite sizes less than 14 nm are highly stable and will not be converted into rutile.⁴



Figure 6-5: Glancing angle x-ray diffraction patterns of bare titanium foil as a function of annealing temperature in oxygen ambient.

Figure 6.6a shows the I-V characteristics of 7 μ m nanotube arrays annealed at different temperatures under UV (320 nm to 400 nm) illumination with an intensity of 100 mW/cm² on the surface; the dark current in all cases is approximately 10⁻⁷ to 10⁻⁶ A. The photocurrent increases

with increasing annealing temperature to 580°C, after which it reduces, with samples annealed at 625°C showing a lower photocurrent than samples annealed at 550°C.



Figure 6-6: (a) Photocurrent generated from 7 μm long nanotube arrays with respect to annealing temperature in oxygen ambient, and (b) the corresponding photoconversion efficiencies.

The corresponding light energy to chemical energy conversion (photoconversion) efficiencies, **Fig. 6.6b**, were calculated using Eq. 2.13. An efficiency of about 10% was obtained for samples annealed at 580°C. The increase in photocurrent and efficiency can be related to the increased crystallinity of the nanotube-walls, with the reduction of the amorphous regions and grain boundaries in turn reducing the number of charge carrier recombination centers. However, at temperatures near 625°C the densification of the bottom part of the nanotubes,³ as indicated by the increase in the rutile to anatase ratio (**Fig. 6.2**), starts isolating the undestroyed nanotubes from the metal substrate reducing the number of charge carriers reaching the electrode.² Also, the low conversion efficiency at high annealing temperatures can be related, in part, to the partial structural collapse of the tubes, see **Fig. 6.4b**.

6.1.1 Effect of Vapor Treatment

Solvothermal methods are well known routes for crystal size enhancement.^{5,6} Reactions take place in a closed system under autogeneous pressure, which can be varied by choice of solvent, reaction temperature and volume filling of the reaction vessel.^{7,8} However, when solvothermal treatments were performed on water immersed nanotube array samples, disorientation of the vertically aligned nanotubes and detachment of the tubes from the underlying substrate were observed. These problems were eliminated when ethanol ^{9,10} was used instead of water, with the samples exposed to the resulting ethanol vapor rather than keeping them in physical contact with the liquid medium. Based on these advantages, could we improve the crystallinity of the as-anodized TiO₂ nanotubes by the high-pressure ethanol vapor treatment on the crystallinity and photoelectrochemical properties of TiO₂ nanotube arrays? To this end, the effect of high-pressure ethanol vapor treatment of as-anodized as well as otherwise optimally thermally annealed samples on their crystallinity and photoconversion efficiency to split water was investigated.

The ethanol vapor treatment was carried out in a 23 ml Teflon lined stainless steel chamber. Optimal enhanced crystallization conditions were found with a reaction temperature of 140° C and ~ 25% filling volume, corresponding to a reaction chamber pressure of approximately 50 psi. Hence for the treatment of all samples, 6 ml of ethanol was placed within the Teflon beaker, with the nanotube array sample mounted on the top of a grooved Teflon stub to avoid direct contact with the liquid medium. The sealed chamber was then kept at 140°C for 18 hrs.

Figure 6.7a shows the glancing angle x-ray diffraction pattern of an as-anodized titania nanotube array sample, and a similar sample after being subjected to the ethanol vapor treatment. It is evident that the 140°C vapor treatment results in some minimal degree of crystallization but



Figure 6-7: GAXRD of: (a) ethanol vapor-treated titania nanotube array sample and (b) as anodized amorphous titania nanotube array sample

Figure 6.8a shows the photoresponse of a thermally annealed sample (580°C for 6 hrs in oxygen) and a similar thermally annealed sample subjected to the ethanol vapor treatment irradiated by near-ultraviolet light (320-400nm). Note that the 580°C was chosen because samples thermally annealed at this temperature showed the best photoconversion efficiency, see Fig. 6.6b. The photocurrent of the vapor treated thermally annealed sample shows a sharp increase to saturation. The effective series resistance of a photoelectrochemical cell is due to the semiconductor itself, semiconductor-metal interfaces, connecting leads, electrolyte and counter electrode. The sharp increase in current seen in Figure 6.8a indicates the possibility of a reduction in the series resistance of the cell, which in turn is related to the reduction in barrier layer thickness and/or improvement in the sample crystallinity. Since both samples were subjected to the same thermal treatment, they possess the same underlying oxide layer thickness, hence the photoresponse improvement appears due to enhanced crystallinity of the treated samples. For all samples the dark current was negligible, several orders of magnitude less than

the photocurrent values. The nanotube array anodes irradiated by near-ultraviolet light (320-400nm) showed a photoconversion efficiency of 13% for the high temperature annealed ethanol vapor treated samples. This is almost 30% more than the efficiency shown by the thermally annealed sample, η =10%. **Figure 6.8b** shows the response of the vapor treated and untreated thermally annealed nanotube array samples when exposed to AM 1.5 illumination. As in the case of UV irradiation, the vapor treated samples show significantly improved photocurrents. The vapor treatment of the thermally annealed sample increases the photoconversion efficiency from 0.40% to 0.56%, i.e. a 40% increase.



Figure 6-8: Photocurrent density vs potential in 1 M KOH solution under (I) UV and (II) AM 1.5 for: (a) 580°C annealed titania nanotube array sample; (b) nanotube array sample annealed and then subjected to ethanol vapor treatment; (c) dark currents.

Figure 6.9a shows GAXRD patterns of a thermally annealed sample, and a vapor treated thermally annealed sample (samples of the same dimensions and identical instrument conditions were used for recording the spectra). The patterns from both samples show identical peak positions and the presence of both anatase and rutile phases. It is known from previous studies that the anatase reflections are primarily from the nanotube walls and rutile reflections from the thermally oxidized metal layer underneath the nanotubes.² All major reflections from the vapor treated thermally annealed sample are stronger than those of the untreated sample, indicating a

significant increase in the degree of crystallization with the ethanol vapor treatment.

To further investigate the enhanced charge transport properties of the vapor treated nanotube array films, the incident photon to current conversion efficiency $(IPCE)^2$ of the treated and untreated samples were measured over the wavelength range 350-500 nm in KOH electrolyte while applying a constant bias of 0.5 V between the photoanode and cathode, see **Appendix B**:

$$IPCE\% = \frac{I_{sc}(amp/cm^2)}{P\left(\frac{W}{cm^2}\right)} \times \frac{1240}{\lambda(nm)} \times 100$$
[6.2]

An IPCE close to 80%, **Figure 6.9b**, is indicative of very efficient light to chemical energy conversion by the nanotube array architecture. The higher IPCE of the vapor treated samples indicates that the number of carrier recombination centers was reduced, which can be attributed to an increase in crystallization as a result of the ethanol vapor treatment.



Figure 6-9: (I) GAXRD patterns and (II) IPCE of: (a) 580°C annealed titania nanotube array sample without ethanol treatment; (b) sample annealed and then subjected to ethanol vapor treatment.

6.2 High Temperature Rapid Infrared Annealing

Although high-pressure ethanol vapor treatment of otherwise optimally thermally annealed TiO₂ nanotube samples led to an enhancement in the crystallinity of the material, it has no effect on the barrier layer thickness. Moreover, the need for a high temperature anneal of extended duration to achieve crystallization limits use of the nanotube arrays with temperature-sensitive materials. The development of relatively thick barrier layer, which acts as recombination trap centers, is a function of both temperature and time of the thermal treatment. However, the above results showed that high temperature is necessary to develop reasonable degree of crystallinity for the as-anodized nanotubes. Therefore, the remaining challenging questions were: was it possible to find a technique which could be used to crystallize the nanotubes at high temperature over very short annealing time intervals? Could this technique retain the original tubular structure of the material? was it possible to reduce the barrier layer thickness upon annealing the material using this technique? what is the effect of reducing the barrier layer thickness, if any, on the photoelectrochemical properties of the resulted material?

Consequently, the potential of using the rapid infrared annealing (IR) treatment to crystallize the as-anodized nanotubes was investigated, with the hypothesis that the rapid nature of the technique (annealing occurs within minutes) would limit the growth of thick rutile barrier layer, hence, reducing the number of carrier trap states and in turn enhancing the charge carrier transport which would result in an enhancement of the conversion efficiency.

The 7 μ m as-fabricated nanotube arrays (**Figure 6.1**) were subjected to infrared annealing using RTC infrared furnace (LA 306) as described in Chapter 4. Glancing angle x-ray diffraction (GAXRD) patterns of the IR annealed TiO₂ nanotube array films at different temperatures (300°C to 600°C) for different time intervals (5 min to 15 min) indicate a crystalline nature for all samples annealed at temperatures \geq 400°C for 5 min or more, see **Figure 6.10**.



Figure 6-10: 2° glancing angle x-ray diffraction (GAXRD) patterns of the IR-annealed TiO₂ nanotubes at different temperatures and time intervals.

Note that the IR annealing time was limited to a maximum of 15 min since annealing at 600°C for 30 min led to collapse of the tubular structure, see **Figure 6.11**.



Figure 6-11: FESEM top view micrograph of sample annealed at 600 ⁰C for 30 min using IR-technique. (a) and (b) show higher magnification of damaged and undamaged areas, respectively.

Figure 6.12 compares the GAXRD diffraction pattern obtained from two typical IR and thermally annealed samples. The rutile signature for the thermally-annealed sample is due to the relatively thicker barrier layer. IR annealing appears efficient in terms of ease, time, and performance through formation of a minimal barrier layer which in turn facilitates electron transfer to the metal electrode (cathode).



Figure 6-12: 2° glancing angle x-ray diffraction (GAXRD) patterns of 7 μm long TiO₂ nanotube arrays thermally (600°C, 4 h) and IR (600°C, 15 min) annealed.

To investigate the influence of the IR annealing on the anatase crystallite size (D) of the crystallized nanotube arrays, the variation of the size of the anatase crystallites with temperature, **Figure 6.13**, was estimated using Scherrer's formula,¹ see Eq. 6.1 above. It can be seen that the anatase crystallite size progressively increased with temperature after its nucleation.



Figure 6-13: Variation of anatase crystallite size as a function of IR annealing temperature and time. Note that the relative standard deviation of the determined average particle size is $\sim 7\%$.

Anatase has two low energy surfaces, (101) and (001), however the (101) surface is the most prevalent face for anatase nanocrystals.¹¹ **Figure 6.14** shows the variation in the anatase (101) peak intensity with IR annealing duration and temperature. The intensity of the (101) peak increases with both anneal duration and temperature. No rutile is apparent in the GAXRD patterns of the IR annealed samples. It is known from previous studies that the nanotube walls are anatase, and the thermally oxidized metal layer underneath the nanotubes is mainly rutile.² The thickness of the barrier layer formed with a 600°C 15 min IR anneal is approximately 200 nm. In contrast, a 600°C 4 h thermal anneal results in a barrier layer approximately 1.1 μ m thick. This confirms the potential of this crystallization technique to control the barrier layer thickness via reducing the annealing time needed to crystallize the anodically fabricated TiO₂ nanotubes.



Figure 6-14: Change of anatase (101) peak intensity measured via 2° glancing angle x-ray diffraction (GAXRD) for the IR-annealed samples as a function of annealing time and temperature.

The next step was to investigate the photoelectrochemical properties of the IR-annealed samples. **Figure 6.15a** shows the measured photocurrent density versus potential, in 1 M KOH under 320 nm – 400 nm 100 mW/cm² illumination, of IR annealed 7 μ m long nanotube arrays, for 15 min duration, as a function of temperature. **Figure 6.15b** shows the photocurrent density versus potential in 1 M KOH solution under UV (320 – 400 nm, 100 mW/cm²) illumination for thermally (600°C, 4 h), and IR (600°C, 15 min) annealed 7 μ m long TiO₂ nanotube array samples. As seen in Figure 6.15b, the photocurrent in the IR annealed sample is significantly greater than that of the thermally annealed sample due, we believe, to the thinner barrier layer and improved crystallinity.



Figure 6-15: Photocurrent density vs potential in 1 M KOH solution under UV (320 - 400 nm, 100 mW/cm^2) illumination for thermally (600° C, 4 h), and IR (600° C, 15 min) annealed 7 μ m long TiO₂ nanotube array samples.

The light energy to chemical energy conversion (photoconversion) efficiency η was calculated using Eq. 2.13. As indicated in **Figure 6.16**, the photoconversion efficiencies for the IR-crystallized nanotube arrays increase with both annealing temperature and time, generally tracking the variation in anatase (101) intensity as seen in **Figure 6.14**. The highest photoconversion efficiency of $\approx 13.13\%$, see **Figure 6.15b**, was obtained for the 7 µm long TiO₂ nanotube arrays annealed at 600°C for 15 min, a value significantly greater than that obtained for the 7 µm thermally annealed nanotube array sample, 600°C for 4 h with 1°C/min rate of change, which showed a photoconversion efficiency of η =10%.



Figure 6-16: Change in photoconversion efficiency of the IR-annealed $7 \,\mu\text{m}$ long TiO₂ nanotube array photoanodes, measured in 1 M KOH under 100 mW/cm² 320 - 400 nm illumination, as a function of annealing time and temperature.

Conclusions

Novel processing routes have been demonstrated to fabricate crystalline TiO₂ nanotube array electrodes using different high temperature annealing treatments with the following conclusions can be drawn: (1) TiO₂ nanotube arrays were found to be stable up to ~ 580 °C upon their thermal annealing, with higher temperatures resulting in the oxidation of the titanium support which disturbed the nanotube architecture causing it to partially and gradually collapse and densify. The 580°C-thermally annealed TiO₂ electrode showed a maximum photoconversion efficiency of 10% under UV illumination, (2) high-pressure ethanol vapor treatment of otherwise optimally thermally annealed TiO₂ nanotube samples successfully enhanced the photoconversion efficiency by about 30% under UV illumination and 40% under full AM 1.5 illumination, (3) infrared annealing was found to be an efficient technique for crystallizing the nanotube array films within a few minutes with the IR-annealed nanotube array films showed significant photoconversion efficiencies (η =13.13% for 7 µm long nanotubes).

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Chapter 7

Low Temperature Fabrication of Crystalline TiO₂ Nanotube Arrays

Although rapid infrared annealing of the nanotubes was shown to reduce the barrier layer thickness compared to that obtained when thermal furnace annealing is used, the need for high temperature limits their use with temperature-sensitive materials, such as polymers, for applications such as photocatalytic membranes. Therefore, low temperature synthesis routes, where a high temperature annealing step for crystallization is not required, are needed to obtain the full benefit of this unique material architecture. Also, the use of low temperature routes is expected to result in thinner barrier layers even than those obtained in case of IR annealing which in turn is expected to result in a higher photoelectrochemical performance. Based on these expected advantages of low temperature processing, various methods for the synthesis of crystalline TiO₂ architectures at moderate to low temperatures have been reported in literature. Among the widely used processing routes to fabricate crystalline TiO_2 are hydrothermal and solgel processes. However, crystallization by hydrothermal treatment at low temperature usually results in a little improvement in the crystallinity of TiO₂, see Chapter 6. The use of higher temperatures during the hydrothermal treatment leads to a strong reduction of the textural properties due to excessive coalescence of the inorganic framework, and structural damage results when hydrothermal treatment is performed on mesostructured titania.¹ With sol-gel, titania nanoparticles usually exhibit a high tendency to aggregate.² So, is it possible to develop a fabrication route which makes this equation possible, i.e. low temperature, retaining tubular structure and thin barrier layer? Herein we investigated the possibility of developing a facile and novel method to fabricate crystalline TiO_2 nanotube arrays at low temperature (80-120°C) for use as electrodes in water photoelectrolysis and liquid junction dye sensitized solar cells.

Prior to anodization, pure titanium foil samples were polished using 500 grade silicon carbide paper (to have rough surfaces), cleaned as mentioned in Chapter 4. Then the samples were immersed in solutions similar to those reported in literature to obtain crystalline TiO_2 films ²⁻⁴ with only a slight modification in the electrolyte composition: either (a) 30% H_2O_2 + 5mM Na_2SO_4 + 0.5M H_3PO_4 at 80°C for 50-72 hours or (b) 0.05M (NH_4)₂S₂O₈) at 120°C for 3-5 hours. The resulting samples were then washed with 1M HCl for at least two hours at room temperature. The anodization was performed as described in Chapter 4. The resulted as-anodized samples were washed with D.I. water and dried using a nitrogen stream then characterized and tested as described in Chapter 4.

A schematic of the two-step process used to fabricate crystalline TiO_2 nanotube arrays is shown in **Figure 7.1**. The Ti foil sample is first treated with an oxidizing agent-containing electrolyte; H_2O_2 at 80°C or $(NH_4)_2S_2O_8$ at 120°C, then anodized at constant voltage in a fluoride-containing electrolyte. This process appears general, hence may be extended to other valve metal oxides. We have confirmed the crystallinity of the as-anodized architectures using XRD and TEM measurements. The two steps are not symmetrical; treating as-synthesized amorphous TiO₂ nanotube arrays with the oxidizing agent-containing electrolyte destroys the nanotubes. Our ability to achieve crystalline nanotube arrays at low temperatures is significant, enabling the titania nanotube architecture to be used in combination with flexible polymeric substrates as well as other temperature-sensitive substrates intended for semiconductor devices.



Figure 7-1: Schematic presentation of the two-step fabrication process used to directly synthesize crystalline TiO₂ nanotube arrays.

After the initial treatment of the Ti foil sample in an 80°C peroxide electrolyte, the resulting surfaces were then anodized in aqueous solutions containing NH_4F . Figure 7.2 shows the GAXRD results for an as-anodized sample, indicating that the nanotube arrays are purely anatase. The inset shows an FESEM top-view image of the nanotube array architecture.



Figure 7-2: 2° glancing angle x-ray diffraction (GAXRD) pattern of well-developed nanotube arrays formed by anodizing peroxide treated Ti foil sample in an aqueous electrolyte containing $0.25M \text{ NH}_4\text{F} + 0.1M \text{ H}_3\text{PO}_3 + 0.05M \text{ H}_2\text{O}_2$, inset shows FESEM top-view image of this same sample.

Figure 7.3a shows a TEM micrograph for a similarly fabricated nanotube array sample, and Figure 7.3b shows the corresponding diffraction pattern which indicates a best fit to anatase. Figure 7.3c gives the intensity from a rotationally averaged pattern with expected Bragg lines from anatase. Since the anodic formation of self-organized valve metal oxide nanotubes have several common mechanistic aspects⁵ The two-step process may be readily extended to form nanoporous/nanotubular metal oxides in other valve metals as well. This is in parallel with Ondo and Yoshikawa who reported the fabrication of high performance-anatase TiO₂ nanoporous films on metallic titanium by anodization in an acidic electrolyte composed of H₂SO₄, H₃PO₄ and H₂O₂ subsequent to pre-nitridation treatment with the pre-nitridation carried out by pre-annealing metallic titanium at 750-950 0 C for 6 hours under nitrogen atmosphere of 0.1 MPa.⁶



Figure 7-3: (a) TEM image of nanotubes formed by described technique; (b) corresponding selected area diffraction pattern; and (c) intensity from rotationally averaged pattern compared with expected Bragg lines for anatase.

The 80°C peroxide pretreatment of the Ti foil produces a crystalline oxide layer approximately $1.2 \,\mu\text{m}$ thick.²⁻⁴ Subsequent anodization in a fluoride containing electrolyte initially produces a crystalline nanotube array structure by structuring of the crystalline oxide layer. As the anodization continues with time, due to field assisted oxidation and dissolution, as well as chemical dissolution, the Ti-oxide interface gradually moves deeper into the Ti metal and the outer surface dissolves, see Chapter 3 for more details. Therefore, with increasing anodization duration (longer than 3h) the crystalline oxide layer initially present is replaced with

an amorphous nanotube array structure, hence the GAXRD observed crystallinity of the nanotube arrays decreases for extended anodization durations. This anodization time restriction limits the tube length to about 800 nm. Strategies to overcome this limitation include the use of strong oxidizing agents and/or higher temperatures in the pre-treatment step to produce a thicker crystalline oxide layer which is then converted into nanotubular architecture by subsequent anodization. To this end, we immersed Ti foil samples in ammonium persulfate $((NH_4)_2S_2O_8)$, a stronger oxidizing agent, at 120°C for 3 hours. This pretreatment of the Ti foil produces a crystalline oxide layer approximately 1.6 µm thick; temperatures lower than 120°C resulted in thinner films, while higher temperatures resulted in an insulator-like film which we were unable to anodize. Subsequent anodization of the resulting surfaces in aqueous solutions containing NH₄F enabled fabrication of nanotube arrays 1.4 µm in length. Figure 7.4 shows the GAXRD results for an as-anodized persulfate sample, indicating that the nanotube arrays architecture.



Figure 7-4: 2° glancing angle x-ray diffraction (GAXRD) pattern of well-developed nanotube arrays formed by anodizing persulfate treated Ti foil sample in an aqueous electrolyte containing 0.25M $NH_4F + 0.1M H_3PO_3 + 0.05M H_2O_2$, inset shows FESEM top-view image of this same sample.

A preliminary, proof-of-concept photoelectrochemical activity test for water photoelectrolysis using the as-synthesized TiO_2 nanotube arrays was carried out. Figure 7.5a shows photocurrent (light less dark) - photovoltage characteristics and photoconversion efficiencies for the as-anodized crystalline nanotubular TiO_2 electrodes under 95 mW/cm² ultraviolet illumination (320-400 nm) in 1M KOH. The current-voltage characteristics of an illuminated TiO_2 electrode in contact with a redox electrolyte can be described using the following equation:⁵

$$i = i_{ph} - i_0 \left[\exp\left(\frac{e_0 V}{kT}\right) - 1 \right]$$
[8.1]

where *i* is the net current obtained by adding the majority and minority current components, i_0 is the reverse bias saturation current and i_{ph} is the illumination current which is proportional to the photon flux, *k* is Boltzmann's constant, *T* is the absolute temperature and *V* is the potential. The tested nanotube-array electrodes show n-type behavior, i.e., positive photocurrents at anodic potentials. For this type of semiconductor, the surface electron density (N_s) decreases with the applied anodic potentials (E_a) as:⁷

$$N_s = N_b \exp\left[-e\left(\frac{E_a - V_{fb}}{kT}\right)\right]$$
[8.2]

where N_b is the bulk electron density in the semiconductor, V_{fb} is its flat-band potential, e is the elementary charge, k is Boltzmann's constant and T is the absolute temperature. Note that $N_s < N_b$ for an n-type semiconductor at all potentials positive of V_{fb} .

The corresponding light energy to chemical energy conversion (photoconversion) efficiency η was calculated using Eq. 2.13. The photoconversion efficiencies for the assynthesized nanotube arrays, under 320 nm – 400 nm illumination, are approximately 3% for the H₂O₂-fabricated nanotubes and 4.4% for the longer (NH₄)₂S₂O₈-fabricated nanotubes.



Figure 7-5: Measured data from application of 800 nm long anatase nanotubes synthesized by described technique: (a) Current-voltage characteristics and photoconversion efficiency for a water-splitting photoelectrochemical cell, and (b) electrical characteristics of a N-719 dye sensitized solar cell.

For solar cell measurements, the as-anodized crystalline nanotube array samples were coated with dye by leaving them overnight in a 0.5 mM solution of the N-719 dye (Solaronix, Switzerland). For solar cell fabrication, electrode spacing was ensured by the use of 25μ m thick SX-1170 spacer (Solaronix Inc., Switzerland). A liquid junction solar cell was prepared by infiltrating the dye coated TiO₂ electrode with commercially available I₃-/I₂ redox electrolyte MPN-100 (Solaronix, Switzerland). A conductive glass slide sputter-coated with 0.5 nm of Pt was used as the counter electrode. The electrolyte was introduced into the clamped electrodes by capillary action and the solar cell was subjected to the backside illumination geometry. Photocurrent (I) and photovoltage (V) of the liquid junction cell were measured using simulated sunlight at AM1.5 produced by a 500W Oriel Solar Simulator whose output was measured using an NREL calibrated standard Silicon solar cell. The cell efficiency (η) was calculated via:⁸

$$\eta = \frac{V_{OC}.J_{SC}.FF}{E}$$
[8.3]

where V_{OC} is *the* open-circuit voltage, J_{SC} the short-circuit current, *E* the irradiation power and *FF* is the fill-factor which is defined as:⁸

$$FF = \frac{P_{\text{max}}}{V_{OC}.J_{SC}}$$
[8.4]

where the maximum power point, P_{max} , is the product of $i \cdot V$ at the maximum power point.

The I-V characteristics of a typical N-719 ((cis-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bis-tetrabutyl ammonium)-sensitized TiO₂ nanotube-arrayelectrode solar cells, comprised of either a H₂O₂ 800nm long nanotube- array sample or a $(NH_4)_2S_2O_8$ 1.4 µm nanotube- array sample, are shown in Figure 7.5b. The active area of the devices, typically 0.4-0.5 cm², was measured using digital Vernier calipers and verified by examination under a calibrated optical microscope. The solar cell showed a short circuit photocurrent density (J_{sc}) of 1.75 mAcm⁻², an open circuit potential (V_{oc}) of 730 mV for an overall photoconversion efficiency of 0.46%. The typical persulfate solar cell showed a J_{sc} of 3.72 mA cm^{-2} and a V_{oc} of 752 mV for an overall photoconversion efficiency of 1.31%. Using dye desorption measurements the coverage of N-719 dye on the surface of the as-anodized anatase 800 nm long nanotube arrays was determined to be 12.6 nmol cm⁻². The surface dye coverage of a thermally annealed 6.6 µm long TiO₂ nanotube array formed in aqueous electrolyte was previously determined to be 50 nmol cm⁻² while that of a 10 μ m thick nanoparticulate film was reported to be 130 nmol cm^{-2,7} With the perspective provided by these numbers, it is noted that the surface dye coverage of the as-anodized anatase samples is better than that expected for a 800 nm long nanotube array indicating that the surface of these nanotubes are nanoscopically rougher and therefore provide more surface sites for dye adsorption; similar results were found for the persulfate nanotubes.

Conclusions

In conclusion, the low-temperature synthesis of crystalline TiO₂-nanotube arrays of up to 1.4 μ m length using a two-step process has been demonstrated. The two-step process consists of initial treatment of the Ti foil in an oxidizing agent (H₂O₂ or (NH₄)₂S₂O₈)-containing electrolytes, followed by potentiostatic anodization of the resulting foil in NH₄F-containing electrolytes. The crystallinity of the nanotube array films are confirmed using GAXRD and TEM measurements. The as-synthesized crystalline nanotube arrays were successfully tested as anode electrodes for water photoelectrolysis, with performances comparable to samples annealed at high temperatures, and for liquid junction dye (N 719 dye)-sensitized solar cells. This study opens the way for the possibility of low temperature fabrication of crystalline metal oxide nanoarchitectures.

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Chapter 8

Towards In-situ Room Temperature Crystallization of TiO₂ Nanotube Arrays

With the obtained enhancement in the photoelectrochemical performance of TiO₂ nanotube arrays crystallized at low temperature (see Chapter 7) the author was motivated to investigate the possibility of *in-situ* crystallization of the anodically fabricated nanotube arrays during their fabrication at room temperature. To achieve the TiO₂ nanotubular structure in crystallization was shown to be strictly determined by migration of Ti⁴⁺ outward from the substrate, and O²⁻/OH⁻ inward to form crystalline oxide in a ratio that favors crystal growth¹, see Chapters 2 and 3. Additionally, because crystallization of anodic titania can be correlated with ionic transport during the film growth^{2,3} it appears that the chemical properties of the anodization electrolyte is a key parameter that controls the crystallization process. Is there an electrolyte composition that might enable *in-situ* crystallization of TiO₂ during fabrication? Herein, the possibility of *in-situ* room temperature fabrication of crystalline, highly ordered TiO₂ nanotube arrays was investigated by tailoring the anodization conditions, especially the electrolyte composition.

8.1 Anodization in pure HCl electrolyte

It is well-known that the presence of inorganic acids and/or salts as components in the starting solution influences the reaction rate and in turn the nucleation, crystal growth and morphology of the fabricated nanoarchitectures.⁴⁻⁶ Among the widely investigated acids, HCl was shown to have a decisive influence on the crystallinity of TiO_2 .⁴ For example, with [HCl] ≤ 0.5 M, the product was found to be mainly anatase and contained a little brookite. However, when 0.8 M

 \leq [HCl] \leq 1.0 M is used; a mixture of anatase, rutile, and brookite was formed. When [HCl] \geq 1.3 M, the anatase phase disappeared and only a pure rutile phase was found. Conversely, the absence of salt or acid leads to the formation of poorly crystalline TiO₂ structures.⁶ Despite these advantages of using HCl, it remains a challenge to fabricate even amorphous well-aligned TiO₂ nanotube arrays in fluoride-free HCl electrolyte rather than getting crystalline structures. Accordingly, I started by investigating the potential of using HCl (0.15 M to 3.0 M) to anodize Ti-foil with the aim of getting crystalline nanotubes. With HCl concentrations below 3 M, it was not possible to achieve either porous or nanotubular titania surfaces over the voltage range 5 V to 60 V. This is in agreement with Jaszay and co-workers⁷ who reported that 2M HCl was not sufficient to initiate pitting corrosion on titanium.

Figure 8.1a is an illustrative FESEM top-surface image of a nanoporous sample, obtained by anodization of Ti foil at 9 V in 3M HCl. Inspection shows characteristic rings on the surface (see arrows in **Fig. 8.1a**) indicating that nanotubular morphology is near. **Figure 8.2b** shows the corresponding anodization current-time response of the sample; notable are unusual spike-like oscillations in the current amplitude similar to those recorded for meta-stable pitting.⁸



Figure 8-1: (a) Illustrative FESEM top-surface image of a nanoporous sample, obtained by anodization of Ti foil at 9 V in 3M HCl. (b) The corresponding anodization current-time response of the sample.

Nanotube arrays have been achieved in 3 M HCl between 10 V and 13 V; at higher voltages the sample simply corrodes. For example, well-developed nanotube arrays with thicknesses up to \sim 300 nm are observed upon anodizing titanium at 13 V in 3M HCl for only 10 min, see **Figures 8.2**.



Figure 8-2: Illustrative cross sectional image of a TiO₂ nanotube array sample fabricated by anodizing titanium at 13 V in 3M HCl for 10 min.

The corresponding current-time behavior, see **Figure 8.3**, is essentially identical to that seen when nanotube arrays are achieved via anodization of Ti in aqueous HF solutions. Nanotube array films could be achieved in as little as 5 minutes, while anodization periods greater than approximately 20 minutes result in sample corrosion. The anodization voltage could be extended up to 20 V by stepwise increments, from 5 V to 20 V at a rate of 1 V/minute. However, the resulting nanotubes, up to ≈ 600 nm in length, are not nearly as well-organized as those fabricated using a constant anodization voltage. This is the first report on the fabrication of TiO₂ nanotube arrays in fluoride-free HCl electrolytes. Consequently, the following question was asked: what is the mechanism of nanotube formation in chloride media? Is it similar to that for fluoride-containing electrolytes?



Figure 8-3: The current-time behavior seen during anodization of Ti foil sample at 13 V, 3M HCl; the behavior is essentially identical to that seen when nanotube arrays are achieved via anodization of Ti in aqueous HF solutions.

Considering Figure 8.3, initially, it is supposed that a compact layer of TiO_2 is formed through hydrolysis of titanium, i.e.

$$Ti_{(s)} + 2H_2O_{(l)} = TiO_{2(s)} + 4H^+ + 4e^-$$
 [8.1]

The low free energy of formation of TiO_2 (-820 kJ/mol)⁹ accounts for its stability in aqueous media. The above reaction involves more elementary steps:

$$Ti + H_2O = TiO^{2+} + 2H^+ + 4e^-$$
 [8.2]

$$TiO^{2+} + H_2O = TiO_2 + 2H^+$$
 [8.3]

This oxide layer leads to a dramatic decrease in the recorded current due to its poor electrical conductivity. Note that the current decreased drastically (**Fig. 8.3**) from an initial value of about 500 mA to about 50 mA within a few seconds. After that, TiO_2 starts to dissolve (forming pores) leading to the observed slight increase in current with time. As is the case in fluoride-containing electrolytes, this can be explained on the basis of the high field model (HFM)¹⁰ and its modified form.¹¹ Under sufficient applied voltage magnitude, the electric field will be strong enough to migrate the titanium ions, leaving behind some voids in the interpore areas¹² which in turn will separate one pore from one another leading to the formation of discrete tubes oriented vertically to the substrate, see Chapter 3 for more details.

But, what is the reason behind the very strict processing conditions? The narrow processing window can possibly be attributed to the complexity of the reaction of Ti in HCl. It was shown by Frayert and co-workers¹³⁻¹⁵ that the reaction of Ti in concentrated HCl includes six steps with three possible reaction pathways. Also, hydrogen ions resulting from the dissociation of HCl could be considered to decrease the surface energy and thus increase the film instability.¹⁶ It was shown that the activity of H⁺ ions is related to the activity of both HCl and Cl⁻ ions via:⁷

$$\frac{1}{\delta a_{HCl}} = \frac{1}{\delta a_{H^+}} + \frac{1}{\delta a_{Cl^-}}$$
[8.4]

The formation of TiO₂ in HCl was shown to proceed via the following steps:¹⁴

$$Ti+H_2O = Ti(OH) + H^+ + e^-$$
 [8.5]

$$Ti(OH) + H_2O = Ti(OH)_2 + H^+ + e^-$$
 [8.6]

$$Ti(OH)_2 + H^+ + Cl^- = [Ti(OH)Cl]^+ + H_2O + e^-$$
[8.7]

$$[Ti(OH)Cl]^{+} + OH^{-} = TiO_{2} + H_{2}O$$
[8.8]

while reaction of TiO₂ with HCl is supposed to proceed in a similar way to that in HF:

$$TiO_2 + 4H^+ + 6Cl^- = TiCl_6^{2-} + 2H_2O$$
 [8.9]

Therefore, a possible reaction pathway (mechanism) can be represented as:

$$TiO_2 + H^+ + CI^- = TiO(OH)CI$$
[8.10]

$$TiO(OH)Cl + 3H^{+} + Cl^{-} = TiCl_{2}^{2^{+}} + 2H_{2}O$$
[8.11]

$$TiCl_2^{2+} + 4Cl^{-} = TiCl_6^{2-}$$
 [8.12]

This is supported by the high stability of $TiCl_6^{2^2}$, where its free energy of formation is in the range -5.12 to -10.90 Kcal/mole depending on the type of cation.¹⁷

Now, what about the crystallinity of the fabricated nanotube arrays? To investigate the possibility of *in-situ* crystallization of the fabricated nanotube arrays, GAXRD measurements were performed, see **Figure 8.4**. The obtained GAXRD pattern shows that the fabricated material is *partially* crystalline in the anatase phase. Note that the as-anodized nanotube arrays have

anatase crystal structure, which is not in agreement with many reports in literature showing that the use of concentrated HCl ([HCl]>1.3M) usually results in the formation of rutile phase.⁴⁻⁶ However, this can be understood from the estimated crystallite size of 13 nm which is in parallel with the reported findings that anatase is more thermodynamically stable than rutile at crystallite sizes of less than 14 nm.¹⁸ The two peaks appeared at 20 values of ~ 19 and 21 could be related to non-stoichiometric titanium oxides [PDF # 00-018-1401, 00-018-1403 and 00-018-1404].¹⁹



Figure 8-4: 2° glancing angle x-ray diffraction (GAXRD) pattern of directly synthesized TiO₂ nanotube arrays sample.

Although the use of HCl as an electrolyte for Ti anodization resulted in *partially* crystalline titania nanotube arrays, no nanotube architectures were achieved at anodization potentials other than 13 V nor with HCl concentrations below 3 M which limited the nanotube length to about 300 nm. How can the tube length be increased and how can its crystallinity be improved? To this end, the effect of some additives to the HCl electrolyte on the crystallinity and tube length of the resulting arrays was investigated.

8.2 Effect of the addition of H₃PO₄

In an approach towards increasing the processing window for obtaining TiO_2 nanotube arrays in the HCl electrolyte and improving their crystallinity, the effect of the addition of 0.01-0.1 M H₃PO₄ to the HCl electrolyte was investigated. It was found that the presence of H₃PO₄ can only expand the anodization voltage up to 14 V with the 3 M HCl requirement remaining in place. Samples corroded at anodization voltages above 14 V. Samples anodized for 20 to 25 minutes at 14 V in 3 M HCl containing increasing amounts of H₃PO₄, 0.01-0.1 M, showed a corresponding change in the morphology from tubes to rods. **Figure 8.5a** shows an FESEM micrograph of a Ti sample anodized for 20 minutes at 14 V in 3M HCl containing 0.1 M H₃PO₄.



Figure 8-5: (a) Illustrative FESEM top-surface image of nano-rods/tubes obtained by anodization of Ti foil at 14 V, in 3 M HCl + 0.1 M H₃PO₄ and (b) The anodization current-time response upon anodizing a Ti foil sample at 15 V in 3 M HCl + 0.07 M H₃PO₄.

Figure 8.5b depicts the anodization current-time response upon anodizing the sample at 15 V in 3 M HCl + 0.07 M H₃PO₄. The current decayed for an initial period of 50 s reaching a steady state value, resulting in formation of barrier layer oxide. Beyond 450 s an increase in current was seen. Similar behavior is reported by Raja and co-workers¹⁶ for Ti anodized in 0.5M H₃PO₄ with incremental addition of HF to the anodization bath; with longer anodizing times perturbation of

the steady state occurs with the current starting to increase. This behavior may be attributed to localized break down of the barrier layer and possibly nucleation of secondary oxide particles.¹⁶ Raja and co-workers related the instability of the barrier layer formed during anodization of Ti to two competing forces, namely: {1} surface energy (a stabilizing force), and {2} an increase in strain energy due to re-crystallization stresses (a destabilizing force).¹⁶ No improvement in the crystallinity of the fabricated nanoarchitectures was observed. This is in line with Nakahira and co-workers who studied the formation of TiO₂ films by anodization in 0.25 M H₃PO₄ at an extremely high applied voltage (250–350 V).²⁰ The GAXRD pattern of the film showed a broad peak indicating the film was almost amorphous.²⁰

What other additives can be tested to improve the properties of the resulting nanotubes? Based on the results of Chapter 7 regarding the use of H_2O_2 to fabricate crystalline nanotubes at low temperature as well as the report of Kuraki and co-workers who showed the possibility of anatase formation upon anodizing titanium in acidic electrolyte composed of 1.5 M H_2SO_4 , 0.3 M H_3PO_4 and 0.3 M H_2O_2 .²¹ We investigated the effect of the addition of H_2O_2 to HCl electrolytes on the morphology and crystallinity of the anodically fabricated TiO₂ nanotube arrays.

8.3 Effect of the addition of H₂O₂

Hydrogen peroxide (H₂O₂) is a powerful oxidant ($E^{\circ} = 1.77 \text{ V}$) which increases the oxidation reaction rate and consequently produces a thicker oxide layer where the formation potential (U_f) mainly determines the film thickness (L):²²

$$L = d_0 + k (U_f - U_{ox})$$
[8.13]

where d_0 is the initial or native oxide thickness, k is the film formation constant= dL/dU, U_{ox} is the potential of the formed oxide which is -0.86 V for TiO₂. Hydrogen peroxide initially produces an intense yellow color with acidic Ti(IV) solution, which changes with time to green and then purple, see **Figure 8.6**.



Figure 8-6: The colors obtained upon the anodization of Ti in H_2O_2 for different time intervals, see text for details.

Samuni suggested that the reaction mechanism of Ti with H_2O_2 involves reaction between more than one H_2O_2 molecule with one Ti(IV) ion.²³ Activation energy analysis suggests that at the metal/titania interface two H_2O_2 molecules react with a Ti(IV) ion resulting in titania layer growth. Recent theoretical work by Sever and Root postulated that the energy required to bind one H_2O_2 molecule to a Ti(IV) ion is about 0.17 eV.²⁴ To understand the effect of H_2O_2 on the morphology and crystallinity of the resultant architectures, the effect of pure H_2O_2 as well as its effect in combination with HCl electrolytes were investigated.

8.3.1 Anodization in pure H₂O₂ electrolyte

Figure 8.7a,b shows FESEM micrographs of Ti samples anodized in 10 M H_2O_2 aqueous solutions for 4 hours at 60 V and 80 V, respectively. The results parallel those of Wu who reported the formation of a porous titania layer on a Ti surface within 4 hours of reaction with H_2O_2 ,²⁵ while Arabatzis and Falaras reported the fabrication of porous TiO₂ foam using H_2O_2 .²⁶



Figure 8-7: Illustrative FESEM image of titania surface achieved by Ti anodization for 4 hours using an aqueous electrolyte of 10 M H_2O_2 at (a) 60 V and (b) 80V.

Fig. 8.8 shows the current-time anodization behavior of the **Fig. 8.7b** 80 V sample. The small fluctuations in current after the current increase are similar to those observed for pitting initiation.²⁷ Haber suggests a two-electron model to describe oxide dissolution and reformation at the Ti/TiO₂ surface that may explain the porous-like structure seen in **Fig. 8.7b**:²⁸

$$2\text{TiO}_2 + \text{H}_2\text{O}_2 + 2e^- \rightarrow \text{Ti}_2\text{O}_3 + \text{H}_2\text{O} + \text{O}_2$$
 [8.14]

$$Ti_2O_3 + H_2O_2 \rightarrow 2TiO_2 + H_2O + 2e^-$$
 [8.15]



Figure 8-8: The corresponding anodization current-time response of the 80 V sample.

Figure 8.9a,b shows the GAXRD patterns obtained from samples anodized in 10M H_2O_2 at 60V and 80V, respectively. Both samples showed *partial* crystallinity in the anatse phase with the intensity of the anatase (101) peak of the 80V-sample almost double that of the 60V-sample. The (101) anatase crystallite size is also larger in case of the 80V-sample (~17 nm) than that for the 60V-sample (~14 nm). Note that, similar to the case of 3M HCl, some peaks appeared at 20 < 25 which could be related to non-stoichiometric titanium oxides [PDF # 00-018-1401, 00-018-1403 and 00-018-1404].¹⁹



Figure 8-9: 2° glancing angle x-ray diffraction (GAXRD) pattern of samples anodized in 10 M H_2O_2 at (a) 60 V and (b) 80V.

8.3.2 Anodization in HCl/H₂O₂ aqueous electrolytes

Although the use of 10M H_2O_2 led to an improvement in the crystallinity, it was not possible to achieve any tubular structure. What about the combination of HCl and H_2O_2 ? Herein the possibility of getting longer nanotube arrays and along with improving their crystallinity with the aid of H_2O_2 and HCl mixtures was investigated. Ti foil samples were anodized in aqueous solutions containing 0.5M HCl with different H_2O_2 concentrations in the range 0.1-0.5 M over the voltage range 5-25 V. For a single anodization step, it was not possible to obtain either porous structures or nanotube arrays below 8 V; a nanoporous structures started to form at 8 V and nanotube arrays at 10 V.

Figures 8.10a,b are FESEM images showing illustrative morphologies of the nanotube arrays achieved by anodization using an aqueous electrolyte of 0.5 M HCl + xM H₂O₂ at 10 V for a one hour anodization. The nanotubular morphology is starting to form in **Figure 8.10a**, while **Figure 8.10b** shows a nanotube array architecture having the morphology commonly obtained using fluoride-based electrolytes.^{29,30} Note that the 'fuzzy' layer atop the tubes is due to precipitation of a chloride layer on the sample surface.^{31,32}



Figure 8-10: Illustrative FESEM surface image of titania nanotube arrays achieved by anodization using an aqueous electrolyte of 0.5 M HCl + xM H₂O₂ at 10 V; (a) x=0.1 M and (b) x=0.4 M.

Figure 8.11a shows the corresponding anodization current-time response at 10 V, for 0.5 M HCl aqueous electrolytes containing variable H_2O_2 content. **Figure 8.11b** is an illustrative FESEM image of nanotube arrays fabricated at 20 V, one hour anodization, in the presence of 0.5 M HCl and 0.4 M H_2O_2 ; the nanotube array architecture is clearly evident. H_2O_2 concentrations above 0.4 M, or anodization voltages of 30 V or more resulted in sample corrosion.



Figure 8-11: (a) Anodization current-time response at 10 V as a function of H_2O_2 concentration and (b) FESEM image of a TiO₂ nanotube array surface achieved by Ti anodization using aqueous electrolytes of 0.5 M HCl + 0.4 M H_2O_2 at 20 V.

Figure 8.12 summarizes the increase in nanotube length for one hour anodizations as a function of H_2O_2 concentration and voltage (10 V, 20 V; 0.5 HCl).



Figure 8-12: Change in the average nanotube (array) length with H_2O_2 concentration for TiO_2 nanotubes achieved by anodization at 10 V, for one hour, in aqueous electrolytes containing 0.5M HCl and 0.1-0.5M H_2O_2 .

While it was not possible to obtain a nanotubular structure in 10M H_2O_2 , nanotubular architectures are formed using low H_2O_2 concentrations with the aid of chloride ions. This result

indicates that chloride is the essential component for nanotube formation.³¹ However H_2O_2 also has an active role that should not be neglected. Hahn and co-workers reported that the breakdown of TiO₂ in chloride containing electrolytes would require potentials of several tens of volts to occur.³² In contrast, with HCl + H₂O₂ electrolytes the results showed the possibility of formation of TiO₂ nanotube arrays at 10V suggesting a possible synergism between the H₂O₂ and chloride ions that enhanced the nanotube formation process.

Figure 8.13 shows the GAXRD pattern obtained from sample anodized in 0.5 M HCl + 0.4 M H₂O₂ at 20 V indicating *partial* crystallinity of the as-anodized nanotube arrays in the anatase phase. Note that the intensity of the anatase (101) peak is greater than that obtained for samples anodized in 3M HCl (**Fig. 8.4**) but less than that obtained for samples anodized in 10 M H₂O₂ at 80V (**Fig. 8.9b**). This can be related to some factors such as tube length (300 nm in case of 3M HCl compared to ~870 nm in here) and H₂O₂ concentration. Most interestingly is the absence of peaks at $2\theta < 25$ which might be related to the possibility that these non-stoichiometric compounds are fully oxidized to form stoichiometric anatase.



Figure 8-13: 2° glancing angle x-ray diffraction (GAXRD) pattern of nanotube array surface achieved by Ti anodization using aqueous electrolyte of 0.5 M HCl + 0.4 M H_2O_2 at 20 V.

Figure 8.14 shows illuminated-less-dark photocurrent versus voltage values for 500°C annealed nanotubular TiO₂ electrodes prepared at 10 V and 20 V anodization potentials in aqueous electrolytes containing 0.5M HCl and 0.4M H₂O₂, under AM 1.5 simulated sunlight in 1.0 M KOH. The dark current was less than 5 μ A/cm² for all samples over the displayed potential range. The AM 1.5 photocurrent values obtained are slightly better than those reported for TiO₂ nanotubes fabricated in fluoride-containing media with the longer tubes obtained at 20 V giving higher values. Note that the as-anodized photoanode fabricated at 20V shows lower current than the 10V-annealed sample.



Figure 8-14: (a) Current-voltage characteristics (light less dark currents) for the annealed TiO_2 electrodes prepared in aqueous electrolytes containing 0.5M HCl + 0.4M H₂O₂ anodized at different potentials. Also shown is response of the *partially* crystalline, as-anodized sample fabricated at 20V.

The corresponding light energy to chemical energy conversion (photoconversion) efficiencies for AM 1.5 illumination are shown in **Figure 8.15**. The photoconversion efficiency (η) was calculated using Eq. 2.13. Note that the efficiencies of the annealed samples are scaling with their length and are greater than that of the as-anodized sample. However, this low value

confirms the *partial* crystallinity nature of the as-fabricated material since totally amorphous electrodes usually show no photocurrent response.



Figure 8-15: AM 1.5 photoconversion efficiency as a function of measured potential for the asanodized as well as annealed TiO_2 electrodes prepared in aqueous solutions containing 0.5M HCl + 0.4M H₂O₂ anodized at different potentials.

With the above used aqueous electrolytes we were able to achieve *partially* crystalline TiO_2 nanotube arrays but not fully crystalline architectures. Therefore, the following question was raised: What is the potential of organic electrolytes in improving/inducing crystallinity of the anodically fabricated TiO_2 nanotube arrays? Consequently, the possibility of using a special class of organic electrolytes, polyol compounds, was investigated.

8.4 Effect of Polyols

It is well-documented that organic additives can be used to control the morphology and growth mechanisms of various nanoarchitectures.³³⁻³⁹ Preferential adsorption and the high viscosity of these additives are believed to improve the quality of the resulting films by affecting the degree of oxide dissolution at high positive potentials.³³ Among these organic additives, polyol compounds have been extensively investigated.³⁴⁻³⁹ For example, polyethylene glycol (PEG) was used as a surface modulator for WO₃ film growth³⁹ as well as colloidal Fe₃O₄ growth³⁴ helping in preferential orientation of the formed crystals. In addition, PEG was shown to enhance the film thickness,³⁵ smoothness³⁵ and porosity³⁸ as well as the formation of anatase nanocrystals in the whole TiO₂ nanostructured coating film.^{38,39} For growing TiO₂ thin films on stainless steel substrates, diethylene glycol (DEG) was shown to improve the adhesion properties of the TiO_2 thin film which could not be removed from stainless steel surface even with 1 M NaOH and concentrated HNO₃.³⁷ Based on these previous studies, the use of some polyol solvents was investigated as electrolytes during the anodization of Ti foil to fabricate TiO₂ nanotube arrays with the aim to attain room temperature *in-situ* crystallization and better morphology, which may enhance the efficiency of these architectures upon their use in solar energy conversion applications.

In this study, titanium foil samples were cleaned and anodized as described in Chapter 4 with the anodization electrolytes prepared using either ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol (TetEG) or polyethylene glycol 400 (PEG) in combination with 0.2M NH₄F, 0.05M H₂SO₄ and different percentages of water. With my interest to explore the effect of electrolyte composition, I have investigated the effect of two parameters; the electrolyte nature and different water content.

8.4.1 Effect of different polyol electrolytes

Would the nature of electrolyte used for anodizing titanium, especially its chain length, have an effect on the crystallinity and morphology of the resulting TiO_2 nanotube arrays? To answer this question, Ti foil samples were anodized in different polyol electrolytes containing 0.2M NH₄F + 0.05M H₂SO₄ + 2% H₂O at different voltages, namely 40, 60 and 80V for 20 hours. At all applied voltages (40-80V), it was not possible to detect any crystallinity for the nanotube arrays fabricated in ethylene glycol (EG) electrolytes, **Figure 8.16a**. The morphology of the nanotube arrays fabricated at 80V (2.8 µm long) is shown in **Figure 8.16b**. This is in parallel with previous reports, see Chapters 2 and 3.



Figure 8-16: (a) GAXRD pattern of TiO₂ nanotube arrays fabricated in ethylene glycol-containing electrolytes and (b) FESEM micrograph of the TiO₂ nanotube arrays obtained at 80V.

However, the nanotube arrays fabricated in diethylene glycol (DEG) at 80V (2.2µm long) showed *partial* crystallinity, with lower voltages resulting in the formation of totally amorphous architectures, **Figure 8.17a**. Note that both anatase (101) and (004) reflections were obtained, with the intensity of the 101 peak exceeding that of 004. The nanotube arrays fabricated in DEG-containing electrolytes are well-aligned with no debris observed atop their surfaces, **Figure 8.17b**.



Figure 8-17: (a) GAXRD pattern of TiO₂ nanotube arrays fabricated in diethylene glycol-containing electrolytes and (b) FESEM micrograph of the TiO₂ nanotube arrays obtained at 80V.

With the obtained *partial* crystallinity upon the use of DEG, is it possible to obtain even better crystallinity upon the use of higher molecular weight polyols? To investigate the validity of this possibility, the potential of using TEG, TetEG and PEG as electrolytes to anodize titanium was explored. The use of triethylene glycol (TEG) resulted in the formation of amorphous nanotube arrays upon anodizing at 40V and *partially* crystalline tubes at higher voltages (60 and 80V), see **Figure 8.18a**. Note that the intensity of the 101 peak increases with increasing applied voltage. However, the intensity of the anatase 004 peak decreases with increasing applied voltage. The obtained nanotube arrays (1.97µm long at 80V) were found to be compact with no debris above their surfaces, see **Figure 8.18b**.



Figure 8-18: (a) GAXRD pattern of TiO_2 nanotube arrays fabricated in tri-ethylene glycolcontaining electrolytes and (b) FESEM micrograph of the TiO_2 nanotube arrays obtained at 80V.

Almost similar trend, in terms of crystallinity, was obtained upon the use of tetraethylene glycol TetEG), **Figure 8.19a**, with the exception that the corresponding intensity of the anatase 101 peaks are higher. Also, the morphology of the nanotubes (1.7µm long at 80V) is quite similar to those obtained using TEG-based electrolytes, see **Figure 8.19b**.



Figure 8-19: (a) GAXRD pattern of TiO_2 nanotube arrays fabricated in tetra-ethylene glycolcontaining electrolytes and (b) FESEM micrograph of the TiO_2 nanotube arrays obtained at 80V.

This relative gradual improvement in crystallinity and morphology as the molecular weight of the polyol solvent increases encouraged the author to investigate even higher molecular weight polyol compounds. The nanotube arrays fabricated in polyethylene glycol 400 (PEG)-containing electrolytes showed *partial* crystallinity over the whole entire range of applied voltages (40-80V), see **Figure 8.20a**. Note that the GAXRD patterns match with the anatase patterns. This is in agreement with Djaoued and co-workers⁵⁵ and Matsuda and co-workers⁴⁰ who reported that PEG accelerates the formation of anatase nanocrystallites. The morphology of the nanotube arrays fabricated at 80V (1.05µm long) is shown in **Figure 8.20b**. Note that the pore mouths of the as-fabricated tubes were completely free of precipitate, with no need for ultrasonication.



Figure 8-20: (a) GAXRD pattern of TiO_2 nanotube arrays fabricated in polyethylene glycolcontaining electrolytes and (b) FESEM micrograph of the TiO_2 nanotube arrays obtained at 80V.

The obtained results can be summarized in **Figure 8.21**. Note that the nanotube length decreases with increasing the chain length of the polyol electrolyte, **Figure 8.21a**. This can be related to the increase in viscosity of the electrolyte as its molecular weight increases, which in turn results in slower reaction kinetics. However, on the positive side, the high viscosity of these electrolytes improved the quality of the resulting nanotube films by affecting the degree of oxide

dissolution at these high positive potentials. **Figure 8.21b** shows the change in crystallinity (in terms of anatase (101) intensity) as a function of the molecular weight of the polyol electrolytes. The intensity of the anatase (101) reflection was found to increase with increasing the molecular weight and/or applied voltage.



Figure 8-21: Effect of chain length of the polyol electrolytes on (a) the length and (b) the crystallinity of the fabricated TiO_2 nanotube arrays.

Based on the above results it appears that the chemical (e.g. hydrogen bonding^{41,42}) and physical (e.g. viscosity) properties of the solvent used play an as yet undetermined role. For example, in ethylene glycols the existence of the oxy and hydroxyl groups in the same molecule allows self association via intra- and inter-molecular hydrogen bonds.⁴¹ It was reported that PEG molecules adsorb exothermically onto TiO₂ surfaces by forming hydrogen bonds between oxygen atoms in the PEG (-CH₂-CH₂-O-) and hydroxyl groups on the TiO₂ surface.⁴³ Siffert and Li showed that the heat of adsorption of PEG on TiO₂ is about 7.5 k_BT which is of the same order as the mean value of a hydrogen bond (5-10 k_BT).⁴³

8.4.2 Effect of water content

It was shown that the amount of water added to the solvent during the fabrication of TiO_2 using various routes such as sol gel, but not anodization route, is crucial in promoting the formation of anatase phase.⁴⁴⁻⁴⁶ To explore the validity of this assumption to the anodization route and to understand the possible role of H₂O in the synthesis of anatase TiO₂ nanocrystals, the amount of H₂O added in the reaction system was systematically changed and the corresponding final products were characterized. Typical GAXRD results (in terms of the intensity of the anatase 101 peak) of the fabricated nanoarchitectures at 80V where different amounts of H₂O (0, 1, 2, 3, 6 and 10 vol. %) were added to the polyol-containing electrolytes are shown in Figure **8.22**.



Figure 8-22: Effect of water content on the crystallinity of the fabricated TiO₂ nanotube arrays in polyol-containing electrolytes at 80V.

The results demonstrated that, by changing the amount of H_2O added, the crystal structures of the products were greatly changed. When either no water or 1% H₂O was added, the XRD patterns of the resulted nanoarchitectures (in all electrolytes) showed the formation of completely amorphous surfaces. However, the GAXRD results of the products fabricated in electrolytes containing $\geq 2\%$ H₂O showed improved crystallinity (higher anatase (101) intensity) except for those architectures fabricated in EG-containing electrolytes from which fully amorphous surfaces were obtained irrespective of the amount of water added. This is in agreement with Shi and Wang who showed that increasing the amount of water in the water/ethanol mixture, used to fabricate TiO_2 , led to an increase in the percentage of the formed anatase phase.⁴⁷ Figure **8.22** also shows that the intensity of anatase (101) reflection increases with increasing molecular weight of the polyol electrolyte as well. However, the existence of amorphous regions within the crystalline regime should not be excluded under these circumstances, i.e. the formed nanoarchitectures cannot be considered fully crystalline but partially crystalline. It was supposed that by increasing the amount of H₂O the final product will completely be converted into anatase nanocrystals.⁴⁵ However, it is found that the addition of a large amount of H_2O (6 vol%) resulted in the formation of mainly amorphous materials except for those nanotubes fabricated in PEG-containing electrolytes. This is in parallel with Wang and co-workers who reported similar behavior and attributed it to the ineffective manipulation of hydrolysis and condensation process by the polyol compounds at high water content.⁴⁵ In general, it is found that the addition of large amount of water deteriorates the morphological qualities of the formed nanoarchitectures. For example, the addition of 6% H₂O to both EG and DEG resulted in the formation of low quality titania structures with ridges and debris on the nanotube surfaces, see Figure 8.23a,b. This is in parallel with Juengsuwattananon and co-workers who found that increasing the water content, during the sol- gel fabrication of TiO₂ nanocrystals, caused faster hydrolysis reaction which led to bulk precipitation instead of forming a stable sol.⁴⁸ Also, the addition of this same amount of water (6%) to TEG and TetEG-

containing electrolytes led to the formation of shorter nanotube arrays compared to those formed in same electrolytes containing less amount of water (3%), however, the quality is still almost the same, see **Figure 8.23c,d**. This could be attributed to the possibility that the oxidation potential could decrease with increase in the water content and in turn the dissolution rate of TiO_2 became higher and therefore could limit the steady state length of the nanotube.⁴⁹



Figure 8-23: FESEM images of the nanoarchitectures formed at 80V in polyol electrolytes containing 6% H₂O; (a) EG, (b) DEG, (c) TEG and (d) TetEG.

The addition of more water (10%) to the polyol-containing electrolytes resulted in the formation of discrete, totally amorphous titania nanoarchitectures, see Figure 8.24. Note that

different electrolytes (TEG and TetEG) showed somewhat different degrees of discreetness in the formed nanotube arrays.



Figure 8-24: FESEM images of the nanoarchitectures formed at 80V in polyol electrolytes containing 10% H₂O; (a) TEG and (b) TetEG.

With respect to PEG, it seems that its high molecular weight (has 400 repeating units of EG) gave it somewhat unique properties (e.g. high viscosity). The addition of 6% H₂O to the PEG-containing electrolyte resulted in the formation of longer, partially crystalline nanotubes with higher anatase (101) intensity than those obtained in same electrolytes containing 3% H₂O, see **Figures 8.22 & 8.25a**. However, the addition of 10% H₂O to PEG-containing electrolytes yielded shorter, fully amorphous nanotubes of low quality (some debris on the surface), see **Figure 8.25b**.

To investigate the limit of water content that can be added to PEG and still can retain the same compact nature of the formed nanotube arrays, titanium foil was anodized in PEG-containing electrolyte with 15% H_2O . It is clear that the formed nanotube arrays (**Figure 8.25c**) are discrete in nature and no longer being compact. Also, note that the formed nanotubes are free of debris.



Figure **8-25**: FESEM images of the nanoarchitectures formed at 80V in PEG electrolytes containing (a) 6% H₂O, (b) 10% H₂O and (c) 15% H₂O.

Figure 8.26 depicts the change in the length of the nanotubes fabricated in polyolcontaining electrolytes at 80V with the change in the water content. Upon the addition of 2% H_2O , the tube length was found to decrease as the molecular weight of the polyol electrolyte increases. This could be related to the increase in the viscosity of the electrolyte, which in turn could result in slower reaction kinetics. Almost same trend was found upon the addition of 3% H_2O with the exception that the tube length increases for each electrolyte. However, upon the addition of 6% H_2O , the nanotube length was shown to decrease compared to those obtained in same electrolytes containing less amount of water except for those nanotubes fabricated in PEGcontaining electrolytes which showed extended increase in length with increased water content. With the addition of 10% water, the length of the nanotube arrays formed in all electrolytes was found to be shorter than those obtained in electrolytes containing less water.



Figure 8-26: Effect of water content on the length of the nanotubes formed in polyol-containing electrolytes at 80V.

How could water improve the crystallinity of the anodically fabricated TiO_2 nanotube arrays in polyol electrolytes? The effect of water can be understood on the basis of the mechanistic formation of TiO_2 crystal structure. Water is the predominant source of O^{2-} ions in the anodic films especially when fabricated in organic electrolytes.⁵⁰ All TiO_2 crystal structures are built up of TiO_6^{2-} octahedra, which share corners and edges in different manners resulting in the formation of different crystalline phases, see Chapter 2 for more details. Using the two lone pairs of electrons on the oxygen, water molecules might form bridges between surface OH groups of different octahedra that share only one common vertex. Consequently, dehydration occurs and the structure of two octahedra sharing one edge is formed:⁵¹



This is followed by the placement of the third octahedron which is very important in determining whether an anatase or a rutile nucleus will be formed. This placement will depend on the nature of the reaction as well as its kinetics. For example, when SO_4^{2-} ions exist in the reaction medium, they would interact with octahedral hydroxyls by electrostatic interaction.⁵¹ Note that, in the current study, the possibility of the dissociation of SO_4^{2-} ions from the used H_2SO_4 is there. Then due to the steric effect of this bulky group, another octahedron will be favored to attack the octahedron with SO_4^{2-} along the converse direction in order to decrease the steric repulsion. Consequently, the orientation of the third octahedron will become more favored to the formation of anatase nuclei:⁵¹



8.4.3 Photoelectrochemical Properties

The photoelectrochemical properties of the as-anodized TiO_2 nanotubes fabricated in polyol electrolytes containing 3% H₂O were investigated as detailed in Chapter 4. **Table 8.1** shows the photoconversion efficiencies calculated from the measured photocurrent (Eq. 2.13) in 1 M KOH electrolyte under 1.5 AM as well as UV (320-400 nm) solar illumination (100 mW/cm², Spectra Physics Simulator, USA) with the potential scanned at a rate of 20 mV/s.

Photoanode	Nanotube	As-anodized		Thermally annealed	
	length (µm)	η% (AM 1.5)	η% (UV)	η% (AM 1.5)	η% (UV)
EG	7.121	0	0	0.21	2.05
DEG	3.765	0.025	0.31	0.20	2.20
TEG	3.241	0.025	0.35	0.23	2.25
TetEG	2.452	0.030	0.35	0.30	2.25
PEG	1.965	0.034	0.44	0.32	2.10

Table 8-1: The photoconversion efficiency (η %) of the as-fabricated and the 300⁰C-thermally annealed nanotube arrays fabricated in polyol electrolytes containing 3% H₂O.

Upon AM 1.5 illumination of the as-anodized samples, the photocurrents obtained were very low (in the microampere range) with the electrodes fabricated in EG-containing electrolytes showed almost zero current. Consequently, the calculated photoconversion efficiencies were very low. However, the fact of getting photocurrent, even if it is very minute, implies that these samples have some sort of crystallinity, especially given that the totally amorphous samples (e.g. samples fabricated in EG-containing electrolytes) showed zero current.

Is it possible to improve the crystallinity of the as-anodized electrodes via low temperature thermal annealing? Does the pre-existence of partial crystallinity help? To investigate the thermal stability and to improve the crystallinity of the fabricated nanotube arrays, the samples were annealed at 300°C for 3 hours in oxygen ambient. The 300°C was chosen for two reasons: (1) most of the polyol compounds are thermally decomposed at ~ $250^{\circ}C^{52}$ therefore, at this temperature (300°C) there should not be any polyol residuals and (2) to investigate the effect of the pre-existing partial crystallinity on improving the overall crystallinity of the material and its effect on the possibility of low temperature crystallization which in turn is expected to enhance the photoconversion efficiency of these materials. The GAXRD patterns (**Figure 8.27**) showed the formation of pure anatase phase for all annealed samples. The intensity of anatase (101) reflection was found to increase with the intensity of the pre-existing anatase peak in the asanodized samples, see **Figure 8.21b**. For example, the totally amorphous samples fabricated in EG electrolytes showed very small anatase reflection upon their annealing at 300°C. This is in agreement with the results shown at Chapter 6, see **Figure 6.2**.



Figure 8-27: GAXRD patterns of the 300^oC-thermally annealed nanotube arrays fabricated in polyol-containing electrolytes, see text.

The annealed electrodes have then been tested as photoanodes to split water under same conditions used for the as-anodized samples with better photoconversion efficiencies obtained, see **Table 8.1**. This improvement in the photoconversion efficiencies can be related to the improvement in crystallinity of the electrodes upon their thermal annealing. There is a possibility that the pre-existing anatase crystallites acted as nucleation sites (seeding layer) facilitating the nucleation and growth of more crystallites at high temperature which in turn makes the charge transfer easier. Note that the ability to fabricate such crystalline electrodes at as low as 300° C is novel. The use of this low temperature would be expected to result in very thin barrier layer which in turn would not effectively hinder the charge transfer resulting in the observed better photoconversion efficiencies. Note also that the obtained photoconversion efficiencies, especially those under UV illumination, are in great agreement with those reported for TiO₂ photoanodes annealed under higher temperatures, see Chapter 5.

To further investigate the validity of my hypothesis that the pre-existence of partial crystallinity (seeding layer) helps in crystallizing the nanotubes at as low temperature as 300° C, I have annealed the nanotube arrays fabricated at 80V in PEG-containing electrolytes at 400° C and 500° C as well, see **Figure 8.28**. The crystallinity of the annealed nanotube arrays (as indicated by the anatase (101) intensity) was found to increase with increasing the annealing temperature. Note that the intensity of anatase (101) peaks (400 CPS and 560 CPS for samples annealed at 400 $^{\circ}$ C and 500 $^{\circ}$ C, respectively) are greater than those obtained for totally amorphous samples annealed at same temperatures (280 CPS and 300 CPS), see **Figure 6.2** for comparison.



Figure 8-28: GAXRD patterns of the thermally annealed nanotube arrays fabricated at 80V in polyethylene glycol-containing electrolytes.

Furthermore, the effect of IR-annealing on the crystallinity of the as-fabricated partially crystalline nanotube arrays fabricated at 80V in PEG-containing electrolytes was investigated. **Figure 8.29** shows the GAXRD pattern of a 300° C-IR annealed sample. The intensity of the anatase 101 peak increases from ~ 86 CPS for the as-anodized sample to a value of ~ 350 CPS for the 300 $^{\circ}$ C-IR annealed sample. Note that it was not possible to crystallize totally amorphous TiO₂ samples at same temperature, see **Figure 6.10**. This confirms that the preexistence of partial crystallinity helps in crystallizing the nanotubes at low temperature.



Figure 8-29: GAXRD patterns of the as-anodized as well as the 300^oC-IR annealed nanotube arrays fabricated in polyethylene glycol-containing electrolytes.

Conclusions

The effect of electrolyte composition on the fabrication of vertically oriented, partially crystalline TiO_2 nanotube array films via potentiostatic anodization was investigated. The study showed that the formation of partially crystalline TiO_2 nanotubes depends on the electrolyte composition, applied potential as well as water content.

Arrays of partially crystalline, vertically oriented TiO₂ nanotubes with thicknesses up to 300 nm, 15 nm inner pore diameter, 10 nm wall thickness, were formed between 10 V and 13 V in 3 M HCl, with anodization durations ranging from 5 to 20 minutes. It was not possible to achieve nanotube arrays at lower or higher HCl concentrations, over a voltage span of 5 V to 60 V. The addition of a low concentration of H_3PO_4 as a buffering medium in the concentration range 0.01-0.1 M enables an increase in the anodization voltage up to 14 V. However, the resulting architecture was closer to that of rods than tubes with no observed improvement in the degree of crystallization. The addition of H_2O_2 to HCl-containing electrolytes was shown to extend the tube length up to 870 nm and improved the crystallinity of the formed architectures. The partially crystalline as-anodized samples were used as photoanodes to split water photoelectrochemically. They showed very low photoconversion efficiency (0.025%) under AM 1.5 illumination. Annealing the samples at 500^oC resulted in an improvement in the photoconversion efficiency (0.14%). This is very unique considering the fact that this is the first report on the fabrication of partially crystalline TiO₂ nanotubes in fluoride-free HCl aqueous electrolytes.

The effect of using some polyol electrolytes (diethylene, triethylene, tetraethylene and polyethylene glycols) on the crystallinity and morphology of the fabricated TiO_2 nanotube arrays was investigated. The study showed that these electrolytes along with the applied voltage can be used to induce partial crystallinity in the formed nanotube arrays. In addition, the amount of water added to these electrolytes was found to play a critical role in obtaining such partially crystalline

nanotube films. As a common feature of the nanotubes fabricated in these polyol electrolytes, the pore mouths of the as-fabricated tubes were completely free of precipitate, with no need for ultrasonication. The as-anodized nanotube arrays showed low photoconversion efficiency upon their use as photoanodes to split water photoelectrochemically indicating partial crystallinity of the tubes. Annealing the tubes at 300^oC increased the photocoversion effciency to values comparable to those usually seen when nanotubes annealed at high temperature (above 500^oC) were used.

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Chapter 9

Self-Assembled Fabrication of Vertically Oriented Ta₂O₅ Nanotube Arrays: Toward the Discovery of New Materials for Efficient Water Splitting

Besides my efforts to optimize the anodically fabricated TiO₂ nanotube arrays to enhance their performance in energy conversion applications, I have devoted some efforts in searching for new materials that might act efficiently to split water photoelectrochemically. Recently, a number of nitrides of transition metals have been found to function as photocatalysts with visible-light response.¹⁻³ Unlike other transition elements, tantalum is able to form two ionic-covalent nitridetype compounds with nitrogen; the binary nitride Ta₃N₅ and the oxy-nitride TaON,⁴ with TaON demonstrated to be responsive to excitation at wavelengths up to ca. 530nm with a suitable band gap (2.3 eV) position for overall water splitting.⁵⁻⁹ Domen and co-workers reported that TaON thin film has a very high photocatalytic activity for oxidation of water to O₂ with a quantum efficiency of 34% under visible-light irradiation.⁹ Also, Murphy and co-workers reported that the theoretical maximum possible photoconversion efficiency of TaON under AM 1.5 illumination is 9.3%¹⁰ which is very close to the 10% generally considered to be required for economic hydrogen production. It is noteworthy mentioning that all of the previous studies have been performed using thin films and/or mesoporous surfaces. Considering the unique properties of the vertically oriented nanotube array architecture as mentioned in previous chapters, the fabrication of nanotubular Ta₂O₅ structures (the starting material to fabricate TaON) of high aspect ratio has found considerable interest in the field as indicated by recent reports on the fabrication of several forms of Ta₂O₅ nanostructures such as nanoporous films,^{11,12} nanodots,¹³ nano-dimples¹⁴ and hollow spheres.¹⁵ However, the electrochemical fabrication of either Ta₂O₅ nanorod or nanotube arrays appears not yet to have been reported before this study. Therefore, could the anodization conditions be optimized to enable fabrication of such a challenging material?

In this study, pure tantalum foil (99.9% purity, 0.25 mm thick, Sigma Aldrich) was cleaned and anodized, as described in Chapter 4, in electrolytes containing concentrated HF (48%) and H_2SO_4 (98%) in the volumetric ratios 1:9 and 2:8. The effect of some additives such as H_3PO_4 (0.05-0.1M), ethylene glycol (5-10 vol.%) and dimethyl sulfoxide (5-10 vol.%) were also investigated.

With stirred mixtures of concentrated HF and H_2SO_4 it was possible to achieve nanodimpled tantala surfaces, pore diameters 40-55 nm, over the voltage range 10 V to 20 V. **Figure 9.1a** shows an illustrative FESEM image of Ta surfaces anodized at 15 V for 10 min in an aqueous electrolyte of HF + H_2SO_4 in the volumetric ratio 2:8. Close-packed hexagonal spacing of the pores is achieved, with the pore diameter increasing from \approx 40 nm to 55 nm with increasing HF concentration (1:9 to 2:8 ratio). It is necessary to stir the electrolyte during anodization to obtain a patterned surface, otherwise a smooth surface is obtained.¹⁴ In an approach analogous to that reported by Allam and co-workers,¹⁶ the effect of the addition of H₃PO₄ as a buffering medium in the concentration range 0.05-0.1 M was investigated, by which the formation of nanowire/nanorod arrays up to 1300 nm in length was observed. **Figure 9.1b** shows a nanowire/rod bundle, from a mechanically fractured sample, obtained using a 1:9 vol. ratio of HF + H₂SO₄ with 0.1M H₃PO₄ at 15V.



Figure 9-1: Illustrative FESEM micrograph of tantala film topology obtained upon anodizing Ta in: (a) a stirred aqueous electrolyte containing $HF + H_2SO_4$ (2:8 vol. ratio, 15 V) (b) $HF + H_2SO_4$ (1:9) + 0.1M H_3PO_4 (15 V, cross sectional view of mechanically fractured sample) independently of electrolyte stirring.

The as-anodized fabricated nanorod arrays are amorphous, subsequently crystallized by a high temperature anneal. **Figure 9.2** shows the XRD of a sample annealed at 400°C for 3 hours in oxygen with an up/down ramp rate of 1°C/minute, with the peaks indicating formation of Ta_2O_5 .



Figure 9-2: 2° glancing angle x-ray diffraction (GAXRD) pattern of sample fabricated in HF + H_2SO_4 (1:9) + 0.1M H_3PO_4 after annealing at 400°C for 3 hours in oxygen (up/down ramp rate of 1°C/minute).

Based on previous efforts using polar organic electrolytes for Ti anodization, ¹⁷⁻²⁰ the effect of adding relatively low concentrations of either ethylene glycol (EG) or dimethyl sulfoxide (DMSO) to aqueous electrolytes containing mixtures of HF and H₂SO₄ was investigated. Tantala nanotube arrays were achieved in electrolytes containing concentrated HF and H₂SO₄ in the volumetric ratio 1:9 in the presence of 5-10 vol. % of either EG or DMSO over the voltage range 10 V to 20 V. Anodization of Ta foil at 10, 12 and 15 V in electrolytes containing HF, H₂SO₄ and 5% DMSO for 20 min results in the formation of vertically-oriented nanotube arrays of lengths 2.3 μ m, 7.5 μ m and 11.1 μ m, respectively. **Figure 9.3a** is a FESEM image of a mechanically fractured nanotube array sample obtained at 15 V. Anodization at 20 V, even for durations as short as a few minutes, results in tantalum oxide nanotube array membrane formation, see **Fig. 9.3b**; these membranes, dried in nitrogen, remain flat.



Figure 9-3: Illustrative FESEM images of surfaces obtained upon anodizing Ta in aqueous electrolytes containing $HF + H_2SO_4$ (1:9) + 5% dimethyl sulfoxide at: (a) 15V sample mechanically fractured for viewing, and (b) Schematic illustration of the growth and detachment of the tantala nanotube array membrane from the Ta substrate.

Figures 9.4a,b and 9.5a show cross-sectional and back-side images of a tantala nanotube array membrane. Without disturbing their flatness, the initially amorphous membranes were crystallized via a 300°C 1 h anneal in a pure oxygen environment, with glancing angle X-ray diffraction patterns (GAXRD) of a resulting sample shown in **Figure 9.5b**.



Figure 9-4: (a) Cross sectional FESEM image of 20 V free standing membrane and (b) 20 V, top surface of resulting self-standing membrane.



Figure 9-5: (a) bottom of nanotube array membrane obtained at 20 V, and (b) 2° glancing angle x-ray diffraction (GAXRD) pattern of a membrane sample annealed at 300°C for 1 hour in oxygen (ramp rate 1°C/min).

Figure 9.6a-c shows well-developed nanorod/nanotube arrays, with thicknesses up to $5.1 \mu m$, obtained by anodizing tantalum in aqueous electrolytes containing 1:9 HF+H₂SO₄ and 5 vol.% EG for 20 min at, respectively, 10 V, 12 V and 15 V.



Figure 9-6: FESEM image of tantala surfaces achieved using an electrolyte containing HF + H_2SO_4 (1:9) + 5 vol% ethylene glycol at: (a) 10 V, (b) 12 V, and (c) 15 V.

Note that the resulting architectures at 10 and 12 V (**Fig. 9.6a,b**) seem closer to that of rods than tubes. However, inspection of the structures obtained at 15 V shows that the surface, although coated with a thin layer of precipitate debris, has characteristic openings on the surface indicating nanotubular morphology. Anodization at 20 V for durations of 25 min or longer resulted in the detachment of the formed Ta oxide nanotube arrays in membrane form.²¹

The thickness of the nanotube/nanorod films are found to increase with increasing anodization voltage; **Fig. 9.7a** shows the length of the resulting nanotubes as a function of anodization potential using electrolytes of either HF + H₂SO₄ (1:9) + 5% EG, or HF + H₂SO₄ (1:9) + 5% DMSO, with an anodization period of 20 min. Using the described one-step synthesis route Ta₂O₅ nanotube membranes up to \approx 19 µm in length have been achieved. The anodization current-time response of samples anodized in electrolytes containing either EG or DMSO, **Fig. 9.7b**, shows a characteristic shape including the classic dip–rise–gradual fall seen when nanotube arrays are achieved via anodization of Ti in aqueous HCl¹⁶ or HF²² solutions.



Figure 9-7: (a) Variation of nanotube length as a function of anodization voltage for samples fabricated in the presence of ethylene glycol (EG) and dimethyl sulfoxide (DMSO). (b) Anodization current-time response of Ta samples anodized in different electrolytes, either HF + H_2SO_4 (1:9) + 5% EG, or HF + H_2SO_4 (1:9) + 5% DMSO. Anodization time in all cases is 20 min.

Similar to Ti, initially a compact oxide layer is formed through hydrolysis of tantalum:

$$2 \text{ Ta} + 5 \text{ H}_2\text{O} \leftrightarrow \text{Ta}_2\text{O}_5 + 10 \text{ H}^+ + 10 \text{ e}^- \qquad \text{E}^\circ \approx 0.75 \text{ V}_{\text{NHE}}$$
 [9.1]

This oxide layer leads to a dramatic decrease in the anodization current due to its poor electrical conductivity. Note that the current decreased drastically (**Fig. 9.7b**) in a few seconds from an initial value of about 450 mA to about 50 mA in EG containing electrolytes and 100 mA in DMSO containing electrolytes. After that, Ta_2O_5 starts to dissolve forming pores, leading to the observed slight increase in current with time. Under sufficient applied voltage magnitude the electric field will be strong enough to migrate the tantalum ions leaving behind voids in the interpore areas which in turn will separate one pore from one another leading to the formation of discrete tubes oriented vertically to the substrate.

Per detachment of the anodic film, the author believes that this may be associated with fluoride ions incorporated into the anodic film. It was shown, during anodization of tantalum, that the inward mobility of fluoride ions is almost twice that of O^{2-} ions, ²³ leading to the formation of a thin layer of TaF₅ that separates the tantalum substrate from the growing anodic oxide film. This fluoride layer was shown to weaken the adherence of the resultant anodic film.²³

Conclusions

The formation of various Ta_2O_5 nanoarchitectures via potentiostatic anodization of Ta in aqueous electrolytes containing HF and H₂SO₄ along with low concentrations of either ethylene glycol (EG) or dimethyl sulfoxide (DMSO) is well documented. This study showed that the formation of Ta_2O_5 structures depends on the applied potential as well as the electrolyte composition. Nano-dimpled tantala surfaces, pore diameters 40-55 nm, were obtained upon anodizing Ta at 10-20 V in stirred electrolytes containing mixtures of HF (48%) and H₂SO₄ (98%) in the volumetric ratios 1:9 and 2:8, with the pore diameter increasing with the amount of HF in the mixture. The addition of H₃PO₄ as a buffering medium in the concentration range 0.05-0.1 M enables the fabrication of Ta_2O_5 nanorods up to 1300 nm in length. High aspect ratio vertically oriented, Ta_2O_5 nanotube array films and membranes were obtained upon the addition of 5-10 vol% of either EG or DMSO to electrolyte mixture containing HF and H_2SO_4 (1:9). Upon anodizing Ta in aqueous electrolytes containing 5% EG, the resulting architectures at 10 V and 12 V are closer to that of rods than tubes. However, anodization at higher voltages, e.g. 15 V, resulted in nanotube formation. The addition of 5% DMSO to the HF and H_2SO_4 (1:9) electrolyte enables fabrication of high aspect ratio nanotube arrays at anodization potentials ranging from 10 V to 20 V, with the length of the nanotubes increasing with potential. Self-standing, mechanically robust nanotubular membranes up to 19 µm in thickness are obtained at anodization voltages of 20 V. Stirring of the electrolyte was found to have no effect on nanotube array formation. On the contrary, stirring was found to lead to faster detachment of the formed nanotube membranes at shorter lengths.

Considering the great utility of the vertically oriented nanotube array architecture in many applications, the subject calls for more systematic studies at various concentrations of HF and H_2SO_4 in the presence of other organic additives at different anodization potentials to gain more insight into the prevailing mechanisms. This will be one task of the future work plans. Also,

testing the material as a photoanode to split water photoelectrochemically and modifying its band gap, especially with nitrogen doping, will be another future task but left to another student.

It is important to mention here that, besides the expected promising performance of this material (after being converted to TaON) as a photocatalyst to split water, this material shows a good performance upon use as a template to enhance osseointegration, see Appendix C.

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Plans for Future Work

The presented work in this dissertation on anodically fabricated TiO_2 nanotube arrays has shown that doping and/or controlling the crystallinity of the material would improve its performance as a photoanode to split water photoelectrochemically. More research and measurements are necessary in order to quantify these improvements and to understand the mechanisms of the findings shown in the previous chapters. Therefore, this section will provide some suggestions for work that could be done in order to complement and extend the work presented in this dissertation.

1. Mixed-Oxide Nanotube Arrays

Chapter 5 showed that *in-situ* doping of TiO_2 nanotube arrays enhanced its optical and photoelectrochemical properties. However, controlling the amount of dopant is still a challenge which needs more investigations. The author believes that anodizing an alloy foil of Ti with the desired dopant with different concentration will result in the fabrication of mixed oxide nanotube arrays which is expected to enhance the energy harvesting capability of the resultant architectures. For example, based on the results of Chapter 5 which showed that W doping greatly enhanced the photoelectrochemical properties of TiO_2 , it is possible to start with anodizing Ti-W alloys which contain different concentrations of W, then we can estimate the threshold W concentration that will lead to the optimum desired efficiency. Same concept can be done with many other binary alloy systems such as Ti-V, Ti-Mn, etc.

2. In-situ Doping and Crystallization Simultaneously

Based on the efforts reported in Chapter 5 towards the *in-situ* doping of TiO_2 and the crystallization efforts reported in Chapters 6-8, further work should be conducted to investigate the possibility of achieving both *in-situ* doping and crystallization in a single inclusive step.

3. Fabrication of Stable p-type Photocathode

Another future task will be devoted towards fabricating stable p-type semiconductor cathodes with the aim to achieve a self-biased p-n junction, a so called photoelectrochemical diode, for solar water-splitting. The formation of p-Cu₂O nanotube/nanowire arrays could be investigated. Also, Cu foils that contain different amounts of Ni could be used to fabricate p-type semiconductor cathodes. The author's preliminary results of fabricating some Cu-oxide nanoarchitectures by anodization are shown in **Figure 1** below.



Figure 1: (a,b,c) FESEM of the nanoarchitectures obtained upon anodizing Cu foil in aqueous electrolytes and (b) 2° glancing angle x-ray diffraction (GAXRD) pattern of sample a after annealing at 300°C for 1 hour in oxygen (ramp rate 1°C/min).

Appendix A

Some Basic Fundamental Aspects of Semiconductors

According to the band theory of solids,¹ the valence band (E_{ν}) is the highest energy band in a semiconductor that becomes fully occupied by electrons as the temperature falls towards 0 K with the next energy band, above the valence band, referred to as the *conduction band* (E_c) . The energy gap between the valence band and the conduction band is known as the bandgap (E_{e}) . Semiconductors have a small bandgap $(0.2 - 3.5 \text{ eV})^{1}$ that allows optical and thermal excitations of valence band electrons (usually bound to the atoms in the solid) to the conduction band. Upon excitation, electrons promoted to the conduction band leave behind empty states in the valence band known as *holes* which act essentially as positive charges. In conducting materials, such as metals, the valence and conduction bands overlap.¹ Insulating materials have a very wide bandgap that is too large for any valence electrons to be thermally excited into the conduction band. In this regards, two kinds of semiconductors can be distinguished: *direct* and *indirect* bandgap semiconductors,¹ see Figure 1. In case of *direct* bandgap semiconductors, the bottom of the conduction band and the top of the valence band occur at the same position in wave vector momentum k space (k = 0).² The absorption of a photon, with an energy greater than or equal to the bandgap energy will generate an electron-hole pair. The electron is excited to the conduction band, leaving a hole in the valence band. This is known as the direct or optical transition. However, in *indirect* bandgap semiconductors, the bottom of the conduction band is shifted in k space (by k_c) and no longer matches up with the top of the valence band.⁵ The indirect transition involves both a photon (to excite an electron to the conduction band) and a phonon (average lattice vibration), to move the electron across k space.¹



Figure 1: Schematic diagrams of the *direct* and *indirect* bandgap transition processes where E is the energy and k is the wavevector.¹

In reality, crystal lattices deviate from ideal atomic structures and possess defects which influence various physical properties of the material; notably the electrical conductivity.² *Intrinsic* semiconductors have a negligible number of impurities, while *extrinsic* semiconductors have impurities that "donate" electrons to the conduction band, or "accept" electrons from the valence band.¹ Usually intrinsic semiconductors are intentionally "doped" with foreign impurities to produce an extrinsic semiconductor for use in specific applications. Donor or acceptor energy levels are formed just below the conduction band edge or just above the valence band edge, respectively. Donor impurities result in *n-type* conductivity, where conduction is dominated by electrons, the negative charge carriers.¹ Alternatively, acceptor impurities result in *p-type* conductivity, where conduction is dominated by holes, the positive charge carriers.¹

Another very important terminology in the semiconductor science is the *Fermi function* which describes the probability $f(E-E_F)$ that a given available energy state will be occupied at a given temperature T (K):³

$$f(E - E_f) = \left[1 + \exp\left(\frac{E - E_f}{kT}\right)\right]^{-1}$$
[1]

where E is the energy, E_F is the Fermi level and k is Boltzmann's constant. The basic assumption of this function dictates that, at ordinary temperatures, most of the levels up to the Fermi level (E_F) are filled and relatively few electrons have energies above the Fermi level. Note that the *Fermi level* is the energy at which the probability of an energy level being occupied by an electron equals one-half. It is also known to be equivalent to the electrochemical potential of the electron in a material.⁴ Based on the fact that the Fermi level is on the order of electron volts (e.g., 7 eV for copper), whereas the thermal energy (k_BT) is only about 0.026 eV at 300K, the Fermi function at ordinary temperatures is essentially 1 up to the Fermi level, and rapidly approaches zero above it.⁵

Figure 2 shows the implications of the Fermi function for the electrical conductivity of a semiconductor. According to the band theory of solids, there is a gap between the Fermi level and the conduction band of the semiconductor. At higher temperatures, a larger fraction of the electrons can bridge this gap and participate in electrical conduction.



Figure 2: The implications of the Fermi function for the electrical conductivity of a semiconductor.¹

The population depends upon the product of the Fermi function and the electron density of states, see **Figure 3**. So in the gap there are no electrons because the density of states is zero.¹ In the conduction band at 0K, there are no electrons even though there are plenty of available states, but the Fermi function is zero. At high temperatures, both the density of states and the Fermi function have finite values in the conduction band, so there is a finite conducting population. The population of conduction electrons for a semiconductor is given by:⁵

$$N_{CB} = AT^{3/2} e^{\left(\frac{-E_s}{2kT}\right)}$$
[2]

where
$$A = \frac{2^{5/2} (m\pi k)^{3/2}}{h^3} = 4.83 \times 10^{21} electrons / m^3 K^{3/2}$$



Figure 3: The population of conduction electrons for a semiconductor.¹

In semiconductors, the Fermi level lies within the bandgap being around the mid-point between E_c and E_v in case of intrinsic semiconductors. However, in case of an n-type semiconductor, the impurity ions produce a donor level E_D just below the empty conduction band and in turn E_F is shifted towards E_c and is often between the E_D and E_c , consequently the Fermi energy will be shifted towards the conduction band edge,³ see Figure 4.



Figure 4: Electronic energy diagrams of intrinsic, doped n-type and p-type semiconductors.⁴

Metal-oxide semiconductor materials are generally of much lower purity than traditional semiconductors and often possess *lattice defects* (e. g. vacancies and interstitials) that can act as either donors or acceptors as well as *electronic defects*, such as extra electrons from dopants.² Note that electron and local lattice distortion created by the charge carrier are electrically active and can introduce charge carriers into mid-bandgap energy levels.²

Although Metal-oxide semiconductors cannot be considered as pure intrinsic semiconductors, the intrinsic carrier density (n_i) was shown to be highly temperature dependent with the existence of a high temperature range where the concentration of intrinsic charge carriers exceeds that of the extrinsic carriers, consequently the electrical properties of the semiconductor become independent of the impurities within the material and the semiconductor exhibits intrinsic behavior.¹ On contrary, at lower temperatures, the conductivity is dominated by impurity conduction mechanisms resulting from the largely temperature-independent extrinsic defects.²

For oxides such as titania, that have transition metal ions with incompletely filled 3d shells, conduction can be achieved through the introduction of vacancies or impurity ions into the lattice.⁶ The change in valency as a result of the introduction of a dopant is compensated by a neighboring parent metal ion. For example, the incorporation of a higher valence cation (W^{6+}) into the TiO₂ will decrease its work function and enhance the electron density via the following defect-site reaction:⁷

$$WO_3 \leftrightarrow W_{Ti} + 2O_0^{X} + \frac{1}{2}O_{2(g)} + 2e^{-1}$$
[3]

The metal ion that has undergone a valency change as a result of the dopant (to retain charge neutrality) is referred to as a donor center, or more specifically as a majority center or a minority center depending on valence change.⁶

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Appendix B

Incident Photon to Charge Carrier Efficiency (IPCE)

The IPCE provides a measure of the efficiency of conversion of incident photons on the photoelectrochemical solar cell to the photocurrent flowing between the working and counter electrodes.^{1,2} An IPCE of 100% means the generation of one photoelectron for each incident photon. However, there are some losses associated with the reflection of incident photons, their imperfect absorption by the semiconductor material and recombination of charge carriers within the semiconductor before reaching the electrolyte.¹⁻⁴

Quantum Yield = Number of carriers (n) / Number of photons (N)

$$\phi = \frac{en}{eN} = \frac{en/s}{eN/s} = \frac{I(amp)}{eN/s} = \frac{I(amp)/cm^2}{\frac{eN}{s}/cm^2}$$
[1]

Incident Power

$$P = Nhv$$

$$P\left(\frac{Watt}{cm^{2}}\right)or\left(\frac{Joules}{\sec cm^{2}}\right) = Nh\frac{c}{\lambda}$$

$$P\left(\frac{Joules}{s.cm^{2}}\right) = \left(\frac{N}{s.cm^{2}}\right)\left(6.62 \times 10^{-34} Js\right) \times \frac{3 \times 10^{8} m/s}{\lambda(nm) \times 10^{-9} m}$$

$$\left(\frac{N}{s.cm^{2}}\right) = \frac{P\left(\frac{J}{s.cm^{2}} or \frac{W}{cm^{2}}\right) \times \lambda(nm)}{(6.62 \times 10^{-17}) \times 3}$$

$$\left(\frac{N}{s.cm^{2}}\right) = \frac{Power\left(\frac{W}{cm^{2}}\right) \times \lambda(nm) \times 10^{17}}{19.86}$$
[2]

Substituting the value of (N/s.cm²) in Eq. 1

$$\phi = \frac{I_{sc}(amp/cm^{2}) \times 19.86}{e \times P\left(\frac{W}{cm^{2}}\right) \times \lambda(nm) \times 10^{17}} = \frac{I_{sc}(amp/cm^{2}) \times 19.86}{1.6 \times 10^{-19} \times P\left(\frac{W}{cm^{2}}\right) \times \lambda(nm) \times 10^{17}}$$

$$\phi = \frac{I_{sc}(amp/cm^{2}) \times 19.86}{P\left(\frac{W}{cm^{2}}\right) \times \lambda(nm) \times 1.6 \times 0^{-2}} = \frac{I_{sc}(amp/cm^{2})}{P\left(\frac{W}{cm^{2}}\right)} \times \frac{1240}{\lambda(nm)}$$

$$\phi\% = IPCE\% = \frac{I_{sc}(amp/cm^{2})}{P\left(\frac{W}{cm^{2}}\right)} \times \frac{1240}{\lambda(nm)} \times 100$$
[3]

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