Titania Nanostructures for Optoelectronics Applications

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A dissertation submitted to

The Faculty of
the College of Science of
Northeastern University
in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

April, 2015

Dissertation directed by
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Acknowledgments

It is my pleasure to express the deepest appreciation to my committee members: Prof. Swastik Kar, Prof. Nathan Israeloff and Prof. Christiaan Richter for being on my committee and for their thoughtful questions and valuable comments.

None of this dissertation would be possible without the guidance and help from Prof. Latika Menon, my academic advisor. She is an outstanding mentor, not only in the sense of her extensive knowledge and experiences that guided me throughout the research, but also with her passion, enthusiasm, wisdom, and diligence that will continue benefiting me in the future.

I owe special thanks to Dr. Eugen Panaitescu, who helped me in almost every possible detail from the beginning to the end of this research with incredible patience. From brainstorming new ideas and planning experiments, to conducting experiments and data analysis, he is always available to give me invaluable advice and encourage me to overcome the difficulties.

I would also like to thank Fangze Liu, who helped me with important assistance, inquiries and discussion, and Helen VanBenschoten, who provided facility support in the fabrication of solar cell.

I want to thank the department of Physics at Northeastern University for accepting me in the doctoral program and providing financial support.

Finally, I would like to dedicate this dissertation to my family, especially my husband and parents, for their endless support, understanding, encouragement and love.
Abstract of Dissertation

Titanium dioxide (titania) nanotubular structure discovered in 2001 have been attracting extensive interest due to their widely applications in photocatalysis, catalysis and solar cells. The final products of titania nanotube (TiNT) arrays can be synthesized in three forms. One is in form of ordered arrays attached to original Ti substrate, another one is in form of free-standing arrays and the last form is white powders. In this dissertation, we review the development history of these three types of TiNT arrays and introduce the fabrication process of TiNTs products in detail including morphology characterization, fabrication parameter study and optimization of synthesis condition.

Since titania is a semiconductor with large band gap (3.2 eV), the large bandgap leads to only UV light absorption, which constitutes less than 5% of the whole solar spectrum. In order to efficiently harvest solar energy for the solar cells made of titania, several methods depositing TiNT arrays with metal oxides to improve the light harvesting are presented in this dissertation. A comprehensive study of forced hydrolysis method is carried out and investigated.

Preliminary devices are built up in DSSCs concept based on the hybrid structure of TiO$_2$/Fe$_2$O$_3$. Some important parameters, such as open circuit voltage ($V_{OC}$), short circuit current ($I_{SC}$), and fill factor (FF) are evaluated. Optical properties of the samples with the hybrid architecture are studied to achieve an optimal performance in DSSCs-type solar cells.
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Chapter 1: Introduction

1.1 Motivation

With increasing demand for clean energy resources, there is a need to design better optoelectronics with cost-effective and environment-friendly materials for applications related to solar cells or electronic devices transmitting light information. One potential material showing promising properties for such applications is titanium dioxide.

All crystal forms of titanium dioxide are n-type, wide-bandgap semiconductors ($E_g \approx 3 \text{ eV}$), and the suitable band-edge position further enables its potential in solar energy and environmental applications. Abundance, non-toxicity, stable physical and chemical properties, and good photocatalytic properties enhance titanium dioxide’s competitive advantage among similar materials (Si, ZnO). Titanium dioxide is widely used in dye-sensitized solar cell (DSSC), water-splitting, water and air purification, biomedical coating, and sensor applications.

In 1999, the first demonstration of fabricated nanostructure surfaces (pores) on titanium dioxide by electrochemical anodization of Ti-based alloy in an acidic, fluoride-base electrolyte triggered intense investigations in this material. Anodization is a cheap, simple and mass-production method, which can produce very uniform titania nanotube arrays over a large area with effectively controlled morphologies. Most applications listed above depend on the light absorption capability of titanium dioxide. Improvement of light absorption properties of titanium dioxide can be achieved by
optimizing the morphology of nanotubes and by combining titanium dioxide nanotube arrays with narrow bandgap metal oxides (copper oxide and iron oxide) which will enhance absorption in the visible range.

Successful utilization of titanium dioxide nanotubes for optoelectronics applications requires detailed studies on formation mechanism, fabrication optimization, structure modification and device design. For that, we use various characterization techniques in this dissertation, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy, energy dispersive spectrum (EDS), and reflectance spectroscopy.

1.2 Overview

The dissertation first describes titanium dioxide nanotube arrays fabrication by electrochemical anodization, with special focus on the anodization optimization for production of nanotubes with controlled tube dimensions and large yield. To optimize the light absorption of titanium dioxide nanotubes, several deposition methods to attach metal oxide nanoparticles onto the nanotubes have been studied, and a complete investigation has been carried out on optical and photoelectric properties of the hybrid samples. The final goal of the dissertation is to design a device based on novel, low-cost, durable and environment-friendly hybrid structure of TiO$_2$ nanotubes/metal oxides for solar energy applications.

Chapter 2 introduces background information on titanium dioxide for applications in the fields of pigment, photocatalysis and DSSC. A literature review about the
development of titanium dioxide nanotubes including the fabrication history and the theoretical study in formation mechanism is also provided.

Chapter 3 describes experiments to study the anodization parameters affecting the fabrication of titanium dioxide nanotube arrays for optimized morphology and for enhanced and rapid yield of titanium dioxide nanotube powders. In order to enhance the visible light harvesting of titanium dioxide nanotubes, nanotube arrays are deposited with a metal oxide absorber layer (copper oxide or iron oxide) by using thermal evaporation method, electrochemical method and conventional co-precipitation method. Relative evaluations on those deposition methods are provided based on the experimental results.

Chapter 4 describes attachment of iron oxide nanoparticles on titanium dioxide by forced hydrolysis of FeCl$_3$ solution followed by heat treatment. The deposition process is described in detail, and a comprehensive investigation is provided on the hybrid structure of TiNTs/Fe$_2$O$_3$. The morphology and crystalline structure of TiO$_2$/Fe$_2$O$_3$ composite are analyzed using scanning electron microscope (SEM), X-ray diffraction (XRD), energy dispersive spectrum (EDS) and transmission electron microscope (TEM).

Chapter 5 discusses the optical properties of TiNTs synthesized under different conditions, with various annealing temperatures and annealing times, and coated with metal oxides with varying thickness, etc. The work on TiNTs decorated with different amounts of iron oxide is described in detail. Preliminary devices based on DSSC-type solar cell concept using TiO$_2$/Fe$_2$O$_3$ have been fabricated. Photovoltaic property of those
devices with different anode contacts and with different morphologies of TiNTs is investigated. Primary solar cell parameters, such as $V_{OC}$, $I_{SC}$ and $FF$, are evaluated.

Possible improvement methods for better performance are provided.

Chapter 6 summarizes the work done in dissertation and proposes future directions of research for this project.
Chapter 2: Introduction of TiNTs

2.1 Background – Applications of Titanium Dioxide

Titanium dioxide, an n-type semiconductor with a wide band gap, is one of the most widely investigated semiconductors. Bulk TiO$_2$ in nature is known to have three main crystalline forms: anatase, rutile and brookite. It has attracted great interest due to its good physical and chemical properties, such as high optical transmittance [1], high refractive index [2], chemical stability and high photoactivity, and also due to its applications in various fields of photocatalysis, solar cell, gas sensing, biomedical and catalysis [3].

2.1.1 Pigment

Titanium dioxide has been most widely used as white pigment in paint industry since 1929 because of its brightness and high refractive index (3.87 for rutile and 2.5-3 for anatase TiO$_2$) [4]. Titanium dioxide of micro particle size has great light-scattering properties for visible light, so the color of small particle size powders turns to be opaque and white. It is employed as colorant in variety of products that require white opacity and brightness, such as paints, coatings, plastics and rubber, paper, printing inks, ceramics, cosmetics, food and toothpastes. Nano-sized titanium dioxide due to its large effective surface area is transparent and more sensitive to ultraviolet light, which allows it to be used as an effectively protective ingredient (physical UV absorber) for sunscreens. Overall, in our society, titanium dioxide is used predominantly for consumer applications
that require white color and UV screening. Total global demand was approximately 5.31 million tons of pigmented TiO$_2$ in 2010, and the demand is expected to increase in the future years [5].

2.1.2 Photocatalysis applications

Photocatalytic activity is the ability of a material to generate electron-hole pairs as a result of exposure to solar irradiation. The resulting photogenerated electrons and holes migrate to the surface reaction sites and cause redox reactions similar to electrolysis. The materials involved in the photocatalytic reactions are semiconductors that have a band structure in which the conduction band and valence band are separated by a suitable gap. Among several metal oxide semiconductors, such as WO$_3$, SrTiO$_3$, ZnO and ZnS, TiO$_2$ has been shown to be the most useful photocatalyst for numerous uses in environmental applications due to its biological and chemical inertness, resistance to photocorrosion and chemical corrosion [4], [6], [7]. Three main photocatalysis applications, water splitting organic compound decomposition and inactivation of bacteria, are discussed in the next sections.

2.1.2.1 Hydrogen generation from water splitting,

Water splitting attracts particular interest since it only involves inexpensive and inexhaustible water, light radiation (photon) and photocatalyst. The first report on light-induced water splitting was published from Fujishima and Honda in 1972 [8]. In their experiment, n-type TiO$_2$ worked as anode and Pt served as cathode, and no electric
power was applied. For overall water splitting process, in the presence of illumination on TiO$_2$, water molecules are reduced by photogenerated electrons to produce hydrogen at the Pt electrode and are oxidized by photogenerated holes to produce oxygen at the TiO$_2$ electrode. The first successful discovery of water splitting on TiO$_2$ surfaces to produce hydrogen triggered worldwide research activities on this material. Early results in 1980s of several researchers revealed that Pt/TiO$_2$ powders system cannot evolve hydrogen and oxygen in stoichiometric ratio, which should be 2 [9]–[12]. Furthermore, they found that the efficiency of H$_2$ and O$_2$ evolution by decomposition of H$_2$O could be improved by using the system of Pt-TiO$_2$ powders in aqueous NaOH solution or under NaOH coating conditions and in addition of alkali carbonates, which were reported by Sato et al. and Onishi et al. [13]–[15].

The two main phases of titanium dioxide used as photocatalysts are anatase and rutile. However, they only absorb ultraviolet light due to the wide band gap (3.2 eV for anatase and 3.0 eV for rutile). Visible-light driven photocatalysts based on TiO$_2$ could be achieved (1) by doping with transition metals, such as Ni$^{2+}$/Nb$^{5+}$, Cr$^{3+}$/Sb$^{5+}$ and Rn$^{3+}$/Sb$^{5+}$, as reported by Kudo et al. [16], [17] where the co-doped TiO$_2$ system was sensitive to visible light and active for oxygen evolution from an aqueous silver nitrate solution; (2) by loading with various metal complex and dyes [18]–[21], in which hydrogen evolution was observed in this TiO$_2$ system by visible light irradiation.

Since the discovery of nanotubular structure of titanium dioxide in 2001, number of studies have been done on the photoelectrochemical generation of hydrogen by using
TiNTs. Bard et al. [22] showed that nanotubular structure indeed enhanced the photocatalytic activity of TiO$_2$ in water splitting by maximizing solar energy harvesting. Grimes et al. [23]–[25] demonstrated that photoconversion efficiency or photocleavage of water could be significantly improved by optimizing structural and morphological parameters, such as wall thickness, length and crystallization of TiNTs. Beside structural optimization, many researchers achieved high hydrogen evolution rate by using TiNTs in modified forms, such as carbon doped TiNTs [22], [26], Ir and Co ionized TiNTs [27], and narrow band gap metal oxide deposited nanotubes [28].

2.1.2.2 Decomposition of undesired hazardous compounds

Since the photocatalytic property of titanium dioxide was discovered by Fujishima and Honda, titanium dioxide has been known as a strong oxidizing material, which could be very useful in decomposition of unwanted organic compounds [29]–[31]. The mechanism for degradation of organic pollutants is similar to that of water splitting. In aqueous solution with titanium dioxide dispersion, electron-hole pairs in titanium dioxide are excited under exposure to a light source (photons), migrate to the surface area and react with the absorbed organic molecules [3]. Finally, the unwanted organic compounds are decomposed into carbon dioxide and water, which are harmless to the environment. The first clear recognition and implementation of semiconductor photocatalysis for the removal of hazardous organic contaminants came in 1983 from David Ollis and his coworkers’ [32], [33], where halogenated hydrocarbon contaminants were destroyed by using TiO$_2$ as photocatalyst. From subsequent reports, it has been
shown that over 200 kinds of organic pollutants could be decomposed by sensitizing TiO$_2$ [7], [34]. Mills & Morris [35] showed that photocatalytic activity of TiO$_2$ was related more to the specific surface area than the crystal phase of TiO$_2$. TiO$_2$ also has been used as photocatalysts for conversion of toxic inorganic substrates to harmless or less toxic byproducts [4].

2.1.2.3 Photodestruction of cancer cells, bacteria and viruses

TiO$_2$ has also been used as photocatalyst in antimicrobial applications. Under the irradiation of UV light, the generation of electrons at conduction band and holes at valence band in TiO$_2$ produce ‘OH radical, superoxide radical ‘O$_2^-$, singlet oxygen $^1$O$_2$, peroxide radical ‘OOH and hydrogen peroxide H$_2$O$_2$ [36]–[38]. These reactive oxidation species result in physical damage to the membrane of cells, leading to cell death [39]. The UV-light induced photo-destruction of bacteria using semiconductor photocatalysts is described in Figure 1.

![Diagram of TiO$_2$ Nanotubes and their interaction with UV light](image)
Figure 1. Schematic representation of the photocatalytic bacterial disinfection [40].

One of the earliest works with regards to the application of semiconductor photocatalysis as a method for disinfection was first reported by Matsunaga et al. [41]. They discovered that microbial cells, such as Lactobacillus acidophilus, Saccharomyces cerevisiae and Escherichia coli (E. coli) were completely killed in presence of TiO$_2$/Pt particles under UV light after 60 minutes. Visible light active titanium dioxide photocatalysts were achieved by non-metal doping, such as nitrogen (N), carbon (C) and sulphur (S) doping [42]–[44]. Superior photocatalytic activities of such N-doped [45], [46], C-doped [47], S-doped [48] and N, S co-doped [49], [50] TiO$_2$ were observed on inactivation of E.coli under visible light irradiation. Recent work with titania nanotubes performed by our group[40], using E.coli and Staphylococcus aureus (S. aureus) as the target microorganisms, revealed excellent antibacterial properties in comparison to commercial Evonic Degussa P25 under 24 hours of UV exposure. Specifically, 97.53% of E. coli and 99.94% of S. aureus were destroyed after 24 hours, while Degussa lost its antimicrobial properties after 1-6 hours. We demonstrated that the architecture, surface and physicochemical properties of TiO$_2$ nanotubes along with specific experimental conditions of the biological investigation, play a significant role in the disinfection activity [40].
2.1.3 DSSCs

The main photovoltaics (PVs) application of TiO$_2$ is in DSSC. DSSC is one of the most promising candidates for solar cell, and it has been extensively investigated. DSSC has attracted a lot of attention because of its simple structure, easy fabrication, low production cost and moderate (~10%) energy conversion efficiency [51]. Typical DSSC consists of a wide band n-type semiconductor working as electron conductor coated with dye and a liquid electrolyte, and two transparent conductive electrodes, which are often a conductive oxide on glass, such as Fluorine doped tin oxide (FTO) conductive glass. Photovoltaic effect in DSSC happens at the interface between semiconductor and dye. The electrons in dye are excited by illumination, and transport to conduction band of the wide band semiconductor. TiO$_2$ is so far the most used as the wide band semiconductor due to its good physical and chemical property. The electrons pass through the external load and transport back to the counter electrode, which is in contact with the liquid electrolyte. Dye is regenerated by those electrons from the liquid electrolyte. The principle of DSSC is shown in Figure 2 [52].
Figure 2. Principle of operation and energy level schematic of a DSSC. Photoexcitation of the sensitizer (S) is followed by electron injection into the conduction band of the mesoporous oxide semiconductor. The dye molecule is regenerated by the redox system, which itself is regenerated at the counter electrode by electrons passing through the load. All potentials are referred to the standard calomel electrode (SCE) [52].

Since low light absorption of a dye monolayer limits the light harvesting, DSSC based on single surface structure typically possesses low efficiency below 1%. The high-efficiency DSSC with conversion efficiency of the order of 7.1% was first reported by O’Regan and Grätzel in 1991 [53]. The breakthrough idea in this new architecture was that they used mesoporous membrane-type films made of nanoparticulate paste instead of thin film. In further studies, nanotubular structure was also used for efficient light harvesting. An overall efficiency of almost 7% was reported for DSSC based on TiNT arrays with length of several micrometers [54]. In order to solve the sealing
problem caused by liquid electrolytes, solid p-type semiconductors interpenetrating the nanocrystalline TiO₂ structure were considered instead of liquid electrolytes [55], [56].

2.2 Background – TiNTs synthesis by electrochemical anodization

The successful discovery of carbon nanotubes by Iijima in 1991 [57] has stimulated intense interest in the synthesis of nanoarchitecture of other substances and chemical compounds due to their unique properties, such as high active surface-to-volume ratios and quantum size effects. In the case of TiO₂, nanotube arrays have been found to enhance the photocatalytic activity of TiO₂ in water splitting by maximizing solar energy harvesting [22]. TiNT arrays could be fabricated by various methods including nanoporous alumina template methods [58]–[61], sol-gel methods (organo-gelators templates) [62], [63], seeded growth methods [64] and hydrothermal methods [65], [66]. Among all those fabrication routes, the cheapest, simplest and easiest to scale method is electrochemical anodization, which can produce very uniform TiNT arrays in a large area and with controlled dimensions.

2.2.1 TiNTs in form of ordered arrays attached to original Ti substrate

The first discovery of fabricating nanostructure surfaces (pores) on titanium dioxide by electrochemical anodization of Ti-based alloy in an acidic, fluoride-base electrolyte was reported by Zwilling and co-workers in 1999 [67], [68]. They found that the nanoporous structure only formed when sufficient HF was added to the electrolyte mixture. In 2001, Gong and co-worker achieved well-aligned and highly uniform TiNT
arrays by anodizing titanium foil in an aqueous solution containing dilute HF (0.5wt %) acid [69] with constant anodization voltage with an approximately average tube diameter of 60 nm and tube length of 250 nm. In 2003, Grimes et al. obtained TiNT arrays with maximum length of approximately 500 nm by using 0.5% hydrofluoric acid electrolyte with a time-dependent linearly varying anodization voltage [70]. The limitation of the nanotubes length is due to the fact that the oxidation rate, which contributes to the nanotubes wall formation at the bottom, is balanced out by the chemical dissolution at the top of the nanotubes. In subsequent work, it was found out that longer nanotube arrays up to micrometers were produced in acidic fluoride electrolyte with a higher pH, which was reported by Cai et al [71], and in neutral fluoride solution, which was reported by Schmuki et al [72], [73]. The first generation nanotube arrays growing in aqueous dilute HF electrolytes and the second generation nanotube arrays growing in buffered neutral electrolytes are tightly attached to the original Ti substrate.

2.2.2 TiNTs in form of free-standing arrays

Third generation nanotubes are fabricated in non-aqueous fluorine based electrolytes in combination with a variety of organic polar organic electrolytes including dimethyl sulfoxide, formamide, ethylene glycol and N-methylformamide [74]. The lower oxygen content in the polar organic electrolytes compared with aqueous electrolytes reduces the oxidation rate which results in slower rate of formation of nanotubes. On the other hand, the chemical dissolution at the top of the nanotubes [75] occurs at an even slower rate, the overall result being longer tube formation. Schmuki group and Grimes
group achieved TiNT arrays of 7 μm long in glycerol electrolytes [73], TiNTs up to 70 μm in formamide and/or N-methylformamide solution [74], TiNTs up to 100 μm in dimethyl sulfoxide electrolyte [74], [76], and longest TiNTs up to 1000 μm in ethylene glycol solution [77]. Nanotube arrays longer than several tens of microns in length are mechanically robust enough that they can be easily peeled off from the Ti substrate and form a transparent free-standing membranes [77], [78].

2.2.3 TiNTs in form of powders

The common ingredient in the previous electrolytes for formation of titanium dioxide nanotubes arrays by electrochemical anodization is fluoride ions. The hypothesis was that fluoride ions is an indispensable ingredient to produce TiNT arrays by anodization because only fluorine has the ability to “dissolve” titanium dioxide and form the complex TiF$_6^{2-}$ in solution [79], [80]. This hypothesis was disproved in 2007 by Richter and co-workers, who first reported a successful fabrication of high aspect ratio TiNT arrays in chloride ion containing electrolytes instead of fluorine based electrolytes [81].

Compared with traditional fluorine based electrolytes, chlorine based electrolytes have several important advantages. Firstly, it represents a less hazardous alternative to the highly toxic hydrofluoric acid. Secondly, it shows significant increase in growth rate. Nanotubes with a length up to 50 μm can be achieved within 5 minutes in chlorine based electrolytes, while it takes up to 70 hours to obtain 67 μm long nanotubes in fluorine based electrolytes [82]. Those nanotubes are significantly thinner with diameter of about
20 nm and with wall thickness of about 4 nm. Thirdly, it creates a new form of TiNT arrays with macroscopic morphology in the form of white powders which are nanotubes bundles made up of tightly packed collection of individual nanotubes.

2.2.4 Formation mechanism of TiNTs by electrochemical anodization

TiNTs formation involves two basic processes. One is anodic growth of compact titanium oxide layer on Ti metal surface (electrochemical oxide formation) and the other is chemical dissolution of titanium oxide barrier to form nanotubular structure. These two procedures are described below.

Anodic oxidation procedure:

In the electrolytes, water undergoes auto-ionization and water molecules break into protons and hydroxyls according to Equation 1:

$$H_2O \rightarrow H^+ + OH^- \quad \text{Equation 1}$$

The protons and hydroxyls are consumed at anode and cathode respectively. Ti foil is oxidized by hydroxyls into titanium oxide at anode (see Equation 2) and protons receive electrons at cathode to generate hydrogen (see Equation 3):

$$\text{Ti (s)} + 2\text{OH}^- (aq) \rightarrow \text{TiO}_2(s) + 2\text{H}^+ (aq) + 4\text{e}^- \quad \text{Equation 2}$$

$$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad \text{Equation 3}$$

The overall oxidation procedure is expressed in Equation 4:

$$\text{Ti(s)} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 2\text{H}_2 \quad \text{Equation 4}$$
All the reactions listed above are the key primary reactions happening at anode and cathode. There are some secondary reactions during the anodic oxidation process resulting in the evolution of oxygen (and fluorine or chlorine) at the anode.

Chemical dissolution:

The nanotubular structure forms by chemical dissolution of titanium oxide in the form of soluble fluoride complexes by the following reaction (Equation 5 and Equation 6), which is widely reported by most authors [71], [72], [80], [83]–[85].

\[
Ti^{4+} + 6F^- \rightarrow TiF_6^{2-} \quad \text{Equation 5}
\]

\[
TiO_2(s) + 6F^- + 4H^+ \rightarrow TiF_6^{2-}(aq) + H_2O \quad \text{Equation 6}
\]

This process reduces the thickness of oxide barrier layer at the nanotubes bottom, and keeps the electrochemical oxide formation process active.

The overall formation process of TiNTs is concluded in four stages [86], and the relative illustration is shown in Figure 3. In the first stage, a compact titanium oxide layer grows on the surface of Ti sheet due to interaction of the metal with OH⁻ (Equation 2). In the second stage, metal ion (Ti⁴⁺) will be ejected from the metal/oxide interface and move towards the oxide/electrolyte interface under the action of an electric field. In the third stage, field-enhanced dissolution occurs at the nanotubes bottom (Equation 5). In the fourth stage, due to the presence of F⁻ ions, chemical dissolution of titanium oxide also takes place during anodization (Equation 6).
Figure 3. Schematic diagram of the evolution of nanotubes arrays at constant anodization voltage: (a) oxide layer formation, (b) pit formation on the oxide layer, (c) growth of the pit into scallop shaped pores, (d) metallic part between the pores undergoes oxidation and field assisted dissolution, and (e) fully developed nanotubes arrays with a corresponding top view [86].

TiNTs grow as a result of competition between electrochemical oxide formation and chemical dissolution. Once electrochemical oxidation rate is faster than chemical dissolution, the increased oxide barrier layer will slow down the electrochemical etching until the chemical dissolution process catches up. Length of nanotubes reaches the maximum when the electrochemical etching and the chemical dissolution reach equilibrium.
2.2.5 Annealing treatment

TiNT arrays fabricated by electrochemical anodization of Ti in fluoride or chloride containing electrolytes are amorphous. Crystalline titanium dioxide with high electrical conductivity is required in electrical and photoelectric applications. Most solar energy applications, especially photocatalysis, are based on anatase phase due to the good photocatalytic properties compared with rutile and brookite phases [87]. Amorphous titanium dioxide nanotube arrays can be converted to crystalline nanostructure by heat treatment, namely thermal annealing [88]. Grimes group [89] reported that anatase phase appeared at temperature near 280°C, the onset of transformation from anatase to rutile was observed at 430°C and nanotubular structure was stable up to approximately 580°C. Schmuki group [90] reported that annealing condition including time and temperature had a large impact on the solid-state conductivity of TiO₂ nanotubes due to crystallization of amorphous titanium dioxide, and anatase tubes showed considerably lower resistance than rutile containing tubes. Of course, in addition of temperature and time, the crystal phase will be affected by heating rate, annealing gas, annealing environment (dry or humid) and other factors. Generally speaking, anatase phase can be obtained by annealing at temperature between 350°C and 450°C.
Chapter 3: Synthesis of titania nanotubes in diverse forms

3.1 Anodization setup

All the titanium dioxide nanotubes samples are synthesized by electrochemical DC anodization of Ti foils (Sigma-Aldrich, 0.127mm, 99.7% purity). The general procedure consists of six steps.

1. Design the size of samples. Ti foil is cut into small pieces with a size of 3 cm×2 cm.

2. Clean before anodization. Ti foil is ultrasonically degreased in isopropanol alcohol (Alfa Aesar, ACS, Liquid, 99.5% min) for at least 30 minutes. Then, Ti foil is rinsed with isopropanol alcohol (IPA) and dried in air.

3. Load Ti foil. The clean Ti foil is treated as working electrode and a platinum mesh works as counter electrode. Two electrodes are separated by a distance of 3 cm.

4. Anodization. The voltage is applied across the electrodes and the Ti foil with an area of 2 cm×2 cm is immersed in the electrolyte for anodization. During anodization process, numerous bubbles are generated on the surface of platinum mesh because of the evolution of hydrogen at the cathode. Bubbles are also noticed on the surface of titanium foil due to oxygen and halide gas evolution.
5. Unload sample. The pre-anodized sample is removed and then the applied voltage is turned off.

6. Clean after anodization. Sample is rinsed with deionized (DI) water and IPA, and then is ultrasonically cleaned for about 30 minutes with IPA to remove the residue on the surface of sample. Finally, sample is rinsed with IPA and dried by compressed air.

Constant potential is provided by a computer-assisted Agilent 6811B power supply shown in Figure 4 (Agilent Technologies, Santa Clara, CA), which is also used to monitor the external current with the aid of a LabVIEW program. The typical curve for current vs. time during anodization is recorded in Figure 5. The initial increase of current is due to the onset of anodization process. As the oxide layer on the surface of Ti foil becomes thicker and thicker, current starts to decrease until reaches a relative stabilization corresponding to the continuous tubes formation.

![Power supply](image)

**Figure 4.** Power supply (Agilent 6811B) interfaced with a computer to apply voltage or current (DC or AC) and record the same.
Figure 5. Typical curve of current vs. time during anodization process.

The two-electrode anodization setup is shown in Figure 6. The desired electrolytes are selected to produce different kinds of products. (1) To produce TiNTs in form of ordered arrays attached to original Ti substrate, we use 100 ml aqueous solution with 0.5 wt % hydrofluoric acid (HF) (Alfa Aesar, Liquid, 99.99% (metals basis), 40% min) or 100 ml ethylene glycol (Alfa Aesar, 99%) based solution with 0.3 wt % ammonium fluoride (Alfa Aesar, crystalline, ACS, 98.0% min); (2) To produce TiNTs in form of free-standing arrays, we use 200 ml ethylene glycol based solution with 0.05 M potassium fluoride (Sigma-Aldrich, purum p.a., ≥ 99.0% (F)); (3) To produce TiNTs in
form of powders, we use 200 ml aqueous solution with 0.1 M-0.5 M ammonium chloride (Alfa Aesar, Granular, 99.5%, min) in combination of hydrochloric acid.

Figure 6. Photograph showing a two-electrode anodization setup we use in our lab to synthesize TiNTs. Different solutions are used to produce different products.

3.2 Fabrication

As mentioned in section 2.2 that there are three types of TiNTs products and they are TiNTs in form of ordered arrays attached to original Ti substrate, in form of free-standing arrays and in form of powders.

3.2.1 Morphology characterization for short and long TiNTs

TiNT arrays, attached to original Ti substrate, can be obtained in both aqueous HF solutions (first generation) and organic-based electrolytes (third generation). Different
dimensions of nanotubes are observed for the two different chemical electrolytes as shown in Figure 7 and Figure 8.

Figure 7. SEM images for TiNTs anodized at 20 V for 1 hour in 100 ml aqueous solution with 0.5wt % hydrofluoric acid. (a) Top view of nanotubes. (b) Side view of nanotubes.

The sample shown in Figure 7 was made in 100 ml aqueous solution with 0.5wt % hydrofluoric acid. Ti foil was anodized at 20 V for 1 hour. The diameter of the nanotubes was around 100 nm, which can be seen in Figure 7 (a), and the length of TiNTs was about 400 nm shown in Figure 7 (b). The length of this kind of TiNTs (first generation - referred from now on as short nanotubes) is always less than 500 nm, as mentioned in section 2.2.1.
Figure 8. SEM images for TiNTs anodized at 60 V for 2 hours in 100 ml ethylene glycol based solution with 0.3wt% ammonium fluoride. (a) Top view of nanotubes. (b) Side view of nanotubes.

The sample shown in Figure 8 was made in 100 ml ethylene glycol (95v%) based solution with 0.3wt% ammonium fluoride. The Ti foil was anodized at 60 V for 2 hours. The diameter of the nanotubes was also around 100 nm (see Figure 8 (a)) and the length of TiNTs was quite long over 10 μm (see Figure 8 (b)). This kind of TiNTs (third generation) made in organic solution containing fluoride salt with constant anodization voltage easily grow up to lengths of the order of tens of micrometers (referred from now on as long nanotubes).

Besides the dimensions of these two kinds of TiNTs, it is also noticed that the morphologies are different. The short nanotubes are comparatively more compact than long nanotubes, while the long nanotubes are more uniform with regards to diameter and periodic arrangement when compared with short nanotubes. In addition, two different samples could be distinguished by naked eye. The long nanotubes sample has a dark, matte surface (Figure 9 (b)) when compared with the original Ti metal surface (Figure 9 (a)).
In Figure 9 (c), short nanotubes sample presents a slightly shiny, greenish layer on the sample surface. The color is directly related to the thickness of the oxide layer or the length of the titania nanotubes.

Figure 9. (a) Blank Ti foil. (b) Long nanotubes sample after anodization in ethylene glycol solution for 3 hours. (c) Short nanotubes sample after anodization in HF electrolyte for 1 hour.

3.2.2 Key anodization parameters

Key anodization parameters, such as anodization voltage, anodization time, water content in electrolyte and Ti foil thickness, play an important role in the properties of formed titania nanotubes. In this section, some examples are provided to help understand how the anodization parameters affect the dimensions of final products, like diameter and length.
3.2.2.1 Anodization voltage

Based on reported information [69], [71] average diameter of nanotubes is affected by the anodization voltage. An independent investigation has been carried out on the effect of the anodization voltage on nanotubes diameter. TiNT arrays were made in an ethylene glycol based electrolyte containing 5v % H$_2$O and 0.3wt % NH$_4$F with a voltage ranging from 30 V to 60 V, resulting in average diameter ranging from 50 nm to 90 nm, as shown in Figure 10. The result is in line with reported information that nanotubes diameter increases with increasing anodization voltage. Figure 11 shows a linear relationship between nanotubes diameter and anodization voltage.
Figure 10. SEM images for titanium dioxide nanotubes arrays anodized in ethylene glycol electrolyte for 1 hour at (a) 30V, (b) 45V and (c) 60V.
Figure 11. A plot of diameter of titanium dioxide nanotubes made by DC anodization vs. applied voltage. A linear relationship is found between nanotubes diameter and anodization voltage.

3.2.2.2 Anodization time

The effect of anodization time on the nanotubes length has been investigated. Length of the nanotubes is a critical dimension affecting electric [90], optical [91] and photoelectrolysis properties [25] of TiNTs. Our results are consistent with that obtained by Grimes group [92] that length of nanotubes fabricated by anodization increases as the anodization time increases. TiNT arrays made at 60 V in an ethylene glycol based
electrolyte containing 1v % H₂O and 0.05 M KF with an anodization duration ranging from 4 hours to 18 hours, range in length from 18 μm to 71 μm, as shown in Figure 12 and Figure 13.
Figure 12. SEM images for titanium dioxide nanotubes arrays anodized in ethylene glycol electrolyte at 60 V for (a) 4 hours, (b) 6 hours and (c) 18 hours.
Figure 13. A plot of length of titanium dioxide nanotubes made by DC anodization vs. anodization time.

3.2.2.3 Water content in the electrolyte

Besides anodization voltage and time, water content in electrolyte also affects the dimension of nanotubes. A related investigation was carried out by using dimethyl sulfoxide electrolytes [76]. We studied the relationship between water content and length of nanotubes by using ethylene glycol solution with water content ranging from 2% to 20%. The SEM images of nanotubes samples synthesized in ethylene glycol solution with various water content is shown in Figure 14. Figure 15 summarizes the length of the
nanotube arrays obtained by DC anodization at 60 V for 1 hour as a function of water content in ethylene glycol solution. It shows that length decreases from over 10μm to 3μm as water content increases from 2% to 10%. Water content below 2% results in facile detachment of the TiNTs from the substrate when sample dries (as shown in Figure 17), and no nanotubes form above 20% water content. This result could be explained in that the presence of water in the electrolyte is directly related to the chemical dissolution rate.

Figure 14. SEM images for the samples, which were synthesized at 60 V for 1 hour in ethylene glycol solution with (a) 2% water content, (b) 5% water content, (c) 10% content and (d) 20% content.
Figure 15. Variation of nanotubes length obtained from an ethylene glycol solution containing different DI water content.

3.2.2.4 Ti foil thickness

The thickness of original Ti foil is usually not considered to be a factor affecting the formation of TiNT arrays, but it does affect the growth rate of the nanotubes during the anodization process. Two kinds of Ti foils with different thicknesses were used in the following experiments. Figure 16 indicates that growth rate of nanotubes is accelerated by the increase in thickness of Ti substrate. The length of sample with thin Ti substrate are much shorter than that with thick Ti substrate during the same anodization time (18 hours), and even the thin sample anodized for a longer time (7 hours) is still shorter than the thick sample (6 hours).
Figure 16. A plot of nanotubes length vs. anodization time for two samples fabricated in ethylene glycol solution containing 1% KF by using 0.25 mm thick Ti foil (black dots) and 0.127 mm thick Ti foil (red dots). It shows nanotubes growth rate is directly dependent on the thickness of original Ti foil.

3.2.3 Free-standing TiNT arrays

As mentioned in section 2.2.2, the final products of TiNT arrays can be produced in form of free-standing arrays, also called flakes. The nanotube arrays longer than several tens of microns in length are mechanically robust enough so that they can be easily peeled off from the Ti substrate and form transparent membranes made of free-standing TiNT arrays as shown in Figure 17.
Figure 17. The photograph of product of titania free-standing arrays. The membranes made of TiNT arrays can be easily peeled off from the Ti substrate.

Long-length oriented TiNT arrays have been attracting significant interest and have been widely employed in DSSC applications replacing the mesoporous membrane type film made of nanoparticulate paste. Besides the high effective surface area, the one-dimensional nature and transparency of the nanotubes aids in trapping light, and provides a directed traveling path for electrons avoiding charge carrier recombination at the grain boundaries and the loss during the long diffusion paths through the random TiO$_2$ nanoparticle network. In addition to the DSSC consisting of TiNTs attached to Ti substrate, DSSC can be fabricated from titania membranes peeled off from Ti substrate, and attached to transparent conductive oxide (TCO), like fluorine doped tin oxide (FTO) conductive glass or indium tin oxide (ITO) conductive glass. Such DSSC consisting of
titania membranes attached to TCO is illuminated on the front-side (anode), which improves the light harvesting efficiency and shows enhanced performance [93]–[95].

After anodization, the TiNT arrays are ultrasonically cleaned with IPA and DI water. The compressive stress between the barrier layer (TiO$_2$) and metal interface (Ti) facilitates detachment from the underlying Ti substrate. The as-peeled titania membrane is very flat when it is wet, while it curls significantly and even fractures into small pieces when it is dried after removal from liquid due to surface tension forces [77] as shown in Figure 18. Such curled membrane are not suitable for use in front-side illumination type DSSC applications.

![Figure 18. As-peeled TiNTs membrane ultrasonically cleaned with IPA and DI water after electrochemical anodization in fluoride solution at 60 V for 24 h.](image)

In recent investigations, detachment of high quality, large area titania membranes is achieved by various methods, such as two-step anodization [93], [95]–[97], high voltage pulse [98], reduction of anodization voltage [99] and critical point drying method [78].
The obtained free-standing titania membranes are transparent, comparatively flat in large area, and are thus suitable for use in front-side illuminated DSSC applications.

The following section describes two-step anodization method in detail.

Experimental procedure:

1. TiNT layers with a thickness of about 20 μm are obtained by a first anodization step as described previously in 100 ml 95v% ethylene glycol based solution with 0.05 M potassium fluoride at 60 V for 6 hours.

2. As-anodized sample is ultrasonically cleaned with IPA for 30 minutes and dried with compressed air.

3. The anodized sample is then annealed in a furnace at 450°C for 2 hours. Amorphous titania is converted to crystalline titania.

4. To detach the TiNT membranes, a second anodization step is performed in the same solution under the same anodization conditions as in the first step.

5. The sample is rinsed with DI water to remove the chemical residue on the surface.

6. Afterwards, the second-step anodized sample is soaked in 10% hydrogen peroxide (Alfa Aesar, Liquid, ACS, 29-32% w/w, aq. Soln. stab) solution at room temperature for a few hours facilitating the detachment from the underlying Ti substrate.

TiNT layers forming during the second anodization step are still amorphous and therefore undergo preferential chemical dissolution in the H₂O₂ solution so that the
previously annealed TiNT layers formed by the first anodization step are lifted off as free-standing membranes, as shown in Figure 19. In Figure 19 (a), the TiNTs membrane is flat and sits in a Petri dish next to the Ti substrate, on which the amorphous thin titania layer (from second anodization step) is still attached. Figure 19 (b) is a comparison photograph between curled membrane and flat membrane.

![Figure 19](image)

**Figure 19.** (a) As-peeled free-standing TiNTs membrane obtained by second anodization method. (b) Comparison photograph for curled membrane and flat membrane.

### 3.2.4 TiNT powders

As introduced in previous section, TiNT arrays can be fabricated in fluorine ion-free electrolytes. TiNTs produced in chlorine electrolytes have a quite different macroscopic morphology than those in fluorine electrolytes. They are in form of white powders. Based on reported method of fabrication in chlorine based electrolytes [81], [100], [101], we investigated effective synthesis of large quantity of TiNT powders, the aim being to find the optimal condition for fast synthesis of the powders. The content in
this section investigates the influence of various anodization parameters such as chloride ions concentration, anodization voltage, and solution pH on the yield of the TiNT powders.

Since the reaction in chlorine-based anodization is more intense than that in fluorine based anodization, the thickness of Ti foil is much more important in this experiment. Three Ti foils with thickness of 0.032 mm, 0.127 mm and 0.89 mm were anodized at 16 V in a standard solution of 0.2 M chloride ions with pH around 2.6 for up to 2 hours. The result is shown in Figure 20, revealing that the original Ti foil thickness plays an important role. For thinner foils the tube formation is very rapid at the liquid surface. Thus for the same anodization conditions the 0.032 mm thick foil fell into the solution after 17 minutes, and the 0.127 mm after 38 minutes, stopping the anodization process. It turns out 0.89 mm thick Ti foil has the suitable thickness for this investigation and this type of foil was used throughout the rest of the study.
Figure 20. Ti foil thickness study. It turns out 0.89 mm thick Ti foil is the suitable thickness for this investigation.

The experiment is designed in the following way:

1. Design the size of samples. Ti foil is cut into small pieces with a size of 4 cm×3 cm.

2. Anodization. The nanotubes are produced by anodization of titanium foil for up to 2 hours in chloride-ions containing solution. TiNT arrays in form of white powders are suspended in solution or precipitate at the bottom of beaker during anodization process (see Figure 21).

Figure 21. Anodization process for formation of titanium dioxide nanotube arrays in chlorine-based electrolytes.

3. Wash and dry. After anodization, the white precipitate is collected from the solution, washed in IPA by centrifuge and finally dried on hot plate. SEM is
used to image the nanotubes, both for the powders and those remaining on the samples (see Figure 22).

Figure 22. SEM images of powder grains consisting of nanotube bundles several microns in size (top left). Top view of one of the grains (top right). Higher magnification images showing side (bottom left) and top (bottom right) views of few microns long and about 20 nm diameter nanotubes, tightly bound into microscopic sized bundles.

4. Annealing. TiNT powders are annealed for one hour at 300°C with both heating and cooling rate of 1°C/min in order to crystallize.
Figure 23. XRD spectrum for nanotube powders before and after annealing. Anatase peaks come out after annealing.

XRD is employed to confirm crystallinity of the samples (see Figure 23). The XRD spectrum reveals that after annealing the amorphous TiNT powders crystallize into anatase (the dotted vertical lines represent the anatase reference lines taken from PDF #21-1272).

Eight anodization conditions with different combinations of chloride ion concentration (0.1 M-0.5 M), pH (1.88 and 2.60) and voltage (12 V-20 V) are tested, and the corresponding information and results are shown in Table 1.
Table 1. Experimental conditions for eight samples and corresponding results.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Cl\textsuperscript{-} concentration</th>
<th>Solution pH</th>
<th>Voltage (V)</th>
<th>Powder yield (g/hrs)</th>
<th>Titanium mass loss (g/hrs)</th>
<th>Ti to TiO\textsubscript{2} conversion efficiency (%)</th>
<th>I\textsubscript{ave} (mA/cm\textsuperscript{2})</th>
<th>I\textsubscript{stddev} (mA/cm\textsuperscript{2})</th>
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<td>0.631</td>
<td>53.5</td>
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<td>6.4</td>
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<td>1.88</td>
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<td>0.161</td>
<td>70.6</td>
<td>16</td>
<td>0.5</td>
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<tr>
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<td>16</td>
<td>0.100</td>
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<td>36.7</td>
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</tr>
<tr>
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<td>2.6</td>
<td>16</td>
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<td>12.5</td>
<td>1</td>
</tr>
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<tr>
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<td>2.6</td>
<td>20</td>
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<td>0.224</td>
<td>67.1</td>
<td>22.5</td>
<td>3.3</td>
</tr>
<tr>
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<td>0.2</td>
<td>2.6</td>
<td>12</td>
<td>0.080</td>
<td>0.074</td>
<td>64.8</td>
<td>7.1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

During the study we quantify the efficiency of titanium to titanium oxide molar ratio conversion, as \( \varepsilon = \frac{\Delta m_{\text{Ti}}}{m_{\text{powder}}} \cdot \frac{M_{\text{TiO}_2}}{M_{\text{Ti}}} \times 100\% \), where \( \Delta m_{\text{Ti}} \) is the mass difference of Ti foil before and after anodization, \( m_{\text{powder}} \) is the mass of final powder synthesized, and \( M_{\text{TiO}_2} \) and \( M_{\text{Ti}} \) are the molar masses of titanium oxide (80) and titanium (48) respectively (see Table 1).

However, due to the loss of powders during repeated washing and centrifuging, losses are bigger in percentage when the initial mass is smaller, thus we cannot draw pertinent conclusions out of these calculations. Better powder recovery methods are
envisioned for the future, and the 60-70% conversion efficiency that we already obtained is encouraging.

By analyzing the relationship between powder yield and current density, we find that powder yield is always proportional to the current density. So current density could be an alternative way to determine the optimal condition for fast synthesis of TiNT powders.

It is clear that the samples with high chloride ions concentration (0.5 M) have high current density. But the reactions for those samples with 0.5 M chloride ions are strong and lead to unwanted high solution temperature. Therefore, even though more power could be produced using 0.5 M chloride ion concentration, this is not an optimal condition. The comparison between current density among samples is shown in Figure 24.
Figure 24. Current density as a function of time comparison between each pair of pH values, chloride ions concentration and anodization voltages.
From Table 1 and Figure 24, it can be easily seen that the yield of titania powders increases with chloride ions concentration, with the anodization voltage, and with the solution acidity (decreasing pH). However, one must keep a balance between the increasing powder production rate and the corresponding increase in the anodization current. High current values (as is the case for both trials involving 0.5 M concentration of Cl⁻ - Sample 1 and Sample 6) caused the solution to heat quickly, and the anodization was stopped in both cases long before the desired 2 hours due to safety concerns. For the lab scale experiment (12 cm² samples in 250 ml solution), we identify concentrations in the range of 0.1-0.2 M, pH below 2 and a voltage of around 16 V to be the optimal conditions for the fast synthesis of TiNTs powders.

3.3 Deposit TiNTs with metal oxides

As mentioned in Chapter 2, titanium dioxide is widely used in solar energy applications. The single largest obstacle for titania in solar energy applications is the large band gap. TiO₂ exists in three crystalline phases, namely rutile (EBG = 3.05 eV), anatase (EBG = 3.23 eV) and brookite (EBG = 3.26 eV) (see Figure 25). Due to the large bandgap, it only absorbs UV light, which constitutes less than 5% of the whole solar spectrum. In order to broaden the light absorption to visible light region, we are modifying TiNTs by depositing narrow band gap metal oxides such as iron oxide and copper oxide. In this section, some successful fabrication routes for metal oxide deposition onto nanotubes are presented, and their advantages and disadvantages are discussed.
Figure 25. Band positions of several semiconductors in contact with aqueous electrolyte at pH 1. The lower edge of the conduction band (red colour) and upper edge of the valence band (green colour) are presented along with the band gap in electron volts. The energy scale is indicated in electron volts using either the normal hydrogen electrode (NHE) or the vacuum level as a reference. Note that the ordinate presents internal and not free energy. The free energy of an electron–hole pair is smaller than the band gap energy due to the translational entropy of the electrons and holes in the conduction and valence band, respectively. On the right side the standard potentials of several redox couples are presented against the standard hydrogen electrode potential [102].
3.3.1 Thermal evaporation method

Thermal evaporation technique is a pure physical method to deposit desired metal on the target. The principle is simple and straight-forward. The schematic diagram of thermal evaporator is given in Figure 26.

![Schematic diagram of thermal evaporator.]

**Figure 26. Schematic diagram of thermal evaporator.**

The general procedure is summarized in six steps.

1. Place the target on substrates. In this work, we place the titanium dioxide nanotubes onto the substrates with open end of the nanotubes facing down onto the material holder.

2. Load desired metal. Load copper or iron metal shots on the material holder.

3. Vacuum the space. Place glass bell jar to close the vacuum chamber and start the vacuum pump.
4. Heating. When internal pressure decreases to a certain value ($< 10^{-5}$ torr), turn on the power supply and slowly increase the current. The temperature of material holder can be controlled by the current.

5. Deposition. The metal in the holder melts when the temperature is high enough. The current is further increased and deposition begins when metal starts to evaporate.

6. Cooling. After deposition for desired time, the current is decreased slowly, pumping is stopped and the power supply is turned off. Take out the target when the whole system has cooled down.

The amount of metal deposited on the target could be controlled by several parameters, such as deposition time, metal evaporation rate and initial amount of metal. Figure 27 shows the samples deposited with Cu for 2 minutes (left) and for 10 minutes (right). As may be noted, for 2-minute deposition sample, the amount of Cu deposited on nanotubes is too low to coat the entire surface of nanotubes. For 10-minute deposition sample, the amount of Cu deposited on nanotubes is too high resulting in clogging of the nanotubes.
Figure 27. SEM images for samples deposited with Cu for 2 minutes (left) and 10 minutes (right).

Typical SEM images of successfully deposited metal are shown in Figure 28. Thermal evaporation method is conducted to deposit titanium dioxide nanotube arrays with both Cu (two images on top in Figure 28) and Fe (two images at bottom in Figure 28). The top views reveal that the nanotubes are not clogged by the metal particles, and the side views indicate external walls of the nanotubes are coated by metal particles hundreds of nanometers deep.

Figure 28. SEM images of TiNTs on which Cu (top) and Fe (bottom) are deposited by thermal evaporation.
The samples are analyzed by means of XRD as shown in Figure 29. The peaks from anatase in XRD are found at 25.28°, 48.05°, 53.89° and 55.06°, corresponding to (101), (200), (105) and (211) planes of anatase (PDF #21-1272), respectively. The peaks from Cu in XRD are found at 43.30°, 50.43° and 74.13°, corresponding to the (111), (200), and (220) planes of Cu (PDF #04-0836), respectively. The peaks from Fe in XRD are found at 44.67°, 65.02° and 82.33°, corresponding to the (110), (200), and (211) planes of Fe (PDF #06-0696), respectively. Thus XRD spectra confirm that after annealing, the amorphous TiNTs crystallize into anatase. Cu/Fe could also be detected after deposition and it can be subsequently converted to metal oxide by heat treatment.
Figure 29. The XRD Spectra for samples deposited with Cu (top) and Fe (bottom).
In conclusion, thermal evaporation method for attaching metal onto TiNTs is very simple (no chemicals required) and nanotubes surface coating is uniform. But the preparation process including vacuum and heating and cooling is time consuming, so the whole process usually takes several hours. Since the internal pressure and the initial amount of metal shot are hard to control for every deposition, the final deposition result is not consistent across different samples. The penetration depth is also limited to less than 1 µm, making them unsuitable for photovoltaic applications.

### 3.3.2 Electrochemical method

Another common method used to attach desired material on target substrate is electrochemical deposition [103]–[105].

Based on reports [106], [107], experiments have been conducted to deposit nanotubes with Cu$_2$O in a modified electrolyte by means of two-electrode electrochemical deposition.

The general procedure and optimal deposition conditions are summarized as follows:

1. Prepare TiNTs samples by anodization of Ti in fluorine based solution. For better deposition TiNTs samples are annealed to increase the electrical conductivity. Tube dimensions used in this study are 2.2 µm in length and 70 nm in diameter.

2. Prepare Cu ions source solution. First, prepare 100 ml solution of 0.3 M CuSO$_4$ (Alfa Aesar, Crystalline, ACS, 98.0-102.0%) + 1.5 M Citric acid (Alfa Aesar,
Crystalline, anhydrous, ACS, 99.5+% + 5 M NaOH (Fisher Scientific, flakes).

Second, additional NaOH is added in initial solution to adjust pH to 11.

3. Set the temperature of the electrodeposition. Temperature of solution is set to 50°C during deposition process.

4. Load sample. Place nanotubes sample on cathode electrode, and place Pt mesh on anode electrode. Cu²⁺ is reduced to Cu⁺ by receiving electrons at cathode.

5. Deposition. A pulsed voltage with pulse-to-relaxation ratio of 0.25 s to 0.75 s is provided, and deposition is conducted under 2 V bias for about 5 minutes.

SEM images of successful sample are shown in Figure 30. Top view image (left) reveals the size of grains is around 50 nm, which is comparable to the nanotubes dimension (~ 70 nm), and some grains aggregate together to form large blocks on top of nanotubes which may result in clogging. Cross-section view image (right) indicates that deposition occurs both inside and outside nanotubes.

Figure 30. SEM images of TiNTs on which Cu₂O is deposited by electrochemical deposition for 5 minutes.
Cu₂O is confirmed by XRD investigation, as shown in Figure 31. XRD spectrum reveals that Ti signal comes from substrate, anatase signals are from the annealed sample, and the deposited grains are Cu₂O. The peaks from Cu₂O in XRD are found at 36.5°, 42.5°, 61.5° and 73.5°, corresponding to the (111), (200), (110) and (311) planes of Cu₂O (PDF #65-3288), respectively.

![XRD Spectrum](attachment:image.png)

**Figure 31.** The XRD Spectrum for sample deposited with Cu₂O by electrochemical deposition.

An alternative AC-DC combined electrodeposition method is used to deposit iron, at room temperature. AC voltage is used to reduce the barrier layer underlying the TiNTs layer by forming pores in the barrier. DC voltage is then applied for deposition. The
general deposition process is similar to electrodeposition of Cu$_2$O, though there are some differences:

1. TiNT sample is placed at cathode electrode, and Pt mesh is placed at anode electrode.

2. Aqueous electrolyte is prepared by introducing 10g FeSO$_4$ (Alfa Aesar, ACS, 99+%) and 2.5g H$_3$BO$_3$ (Alfa Aesar, +8 Mesh Granular, Metal basis, 99.99%) into 250 ml DI water.

3. First, AC voltage is provided with frequency at 250 Hz for 30 seconds at 25 V, 15 V, 10 V, 7 V and 4 V, respectively. Second, DC voltages is provided for 30 seconds at 2 V and 1 V, respectively.

4. Ultrasonically clean the samples after electrodeposition.

The samples are observed under SEM. Figure 32 reveals that the electrochemical method for depositing Fe is not as good as that for depositing Cu$_2$O. Fe grains are too large and hence many of them do not penetrate into nanotubes, and most large grains remain on top of tubes. There are few small Fe grains in the nanotubes, as labeled by the red circles in Figure 32 (right).
Figure 32. SEM images of TiNTs on which Fe is deposited by AC and DC combined electrochemical deposition.

Fe grains are converted to iron oxide, hematite, by post heat treatment, in which the deposited samples are annealed at 350°C for 2 hours. The morphology of the grains observed under SEM changes from cubic shape to spherical shape as shown in Figure 33.

Figure 33. SEM images of electrochemical deposited samples before (left) and after (right) annealing.

The crystalline structure is characterized by X-ray diffractometer. XRD spectrum in Figure 34 confirms that after annealing, Fe (cubic grains) is successfully converted into hematite (spherical grains).
Figure 34. XRD spectrum indicates Fe is oxidized into Fe$_2$O$_3$ after annealing.

In conclusion, electrochemical method for depositing TiNTs with metal or metal oxide nanoparticles is relatively simple and fast (usually a few minutes) when compared with thermal evaporation method. The grains obtained in electrodeposition are large. In Cu$_2$O case, grains are over 50 nm, and nanotubes are filled up by those Cu$_2$O grains. In Fe case, most grains are larger than diameter of nanotubes, preventing their penetration into nanotubes resulting in clogged tubes.

3.3.3 Conventional co-precipitation method

Conventional co-precipitation method is widely used to produce nanoparticles, for example, gold nanoparticles previously synthesized on TiNTs in our lab [108]. For iron
oxide nanoparticles, the basic recipe is that iron oxide nanoparticles are obtained by mixture of solution of ferrous chloride (FeCl\(_2\)) and ferric chloride (FeCl\(_3\)) in molar ratio of 1:2 and solution of ammonium hydroxide (NH\(_4\)OH) or sodium hydroxide (NaOH) [109]–[111].

First, we tried to attach iron oxide nanoparticles on titanium dioxide nanotubes in one step by soaking nanotubes samples in the iron oxide nanoparticles containing solution, but it turns out very few iron oxide nanoparticles attached on to the nanotubes. The method was then modified slightly to a two-step deposition. Using this method, we successfully deposited TiNTs with iron oxide nanoparticles.

The two-step deposition procedure is summarized as follows.

1. Prepare TiNTs samples by anodization of Ti in fluorine based solution. Long TiNTs samples are used in this experiment and are annealed before deposition.
2. Introduce Fe ions into nanotubes. TiNTs samples are soaked in solution of FeCl\(_2\)+FeCl\(_3\) in molar ratio of 1:2 (0.64 M FeCl\(_2\)·xH\(_2\)O, Alfa Aesar, reagent, 99%+1.28 M FeCl\(_3\)·6H\(_2\)O, Sigma-Aldrich, ACS, reagent, 97%) for 4 hours on hot plate with surface temperature at about 110°C. High temperature helps to accelerate the penetration of Fe ions into the nanotubes. Samples are taken out of FeCl\(_2\)+FeCl\(_3\) solution, and dried with compressed air or dried in vacuum chamber.
3. Soak samples in NH\(_4\)OH solution. TiNTs samples are soaked in 5 M NH\(_4\)OH (Alfa Aesar, Liquid, ACS, 28.0-30.0% NH\(_3\)) solution for 4 hours at room
temperature. At the end of the process iron oxide nanoparticles form on surface of nanotubes.

The morphology and structure of some successful samples are characterized by using SEM and XRD. Figure 35 shows the images of nanotubes deposited with iron oxide nanoparticles. Iron oxide nanoparticles are small in size (~10 nm-20 nm) when compared with dimension of nanotubes (diameter ~70 nm). The top view image reveals that the small size allows the iron oxide nanoparticles to penetrate into the TiNTs without clogging. Coating on external wall surface of nanotubes with nanoparticles is relatively uniform in as observed in side view image.

**Figure 35.** SEM images of TiNTs deposited with iron oxide nanoparticles by co-precipitation method.

In Figure 36, the peaks from Fe$_3$O$_4$ in XRD are found at 37° corresponding to the (311) planes of Fe$_3$O$_4$ (PDF #26-1136). It is confirmed that the nanoparticles are Fe$_3$O$_4$. The weak peak of Fe$_3$O$_4$ may be due to the small nanosize of the particles and the strong intensity from anatase and Ti signals.
In conclusion, conventional co-precipitation method for attaching iron oxide nanoparticles onto TiNTs is simple (no external power supply required). The size of nanoparticles (10 nm-20 nm) are much smaller than that of grains (>50 nm) obtained in electrodeposition. Good coating is observed on both internal and external surface of TiNTs in most regions. Since the formation of iron oxide nanoparticles is very rapid when the samples are immersed in NH₄OH solution, concentration of NH₄OH is dissipated significantly during the reaction of Fe₃O₄ nanoparticle formation leading to difference in concentration in certain region. Overall, Fe₃O₄ coating on TiNTs by
co-precipitation deposition is uniform in certain region, but it is not homogeneous over the sample area.

3.3.4 Summary

In order to enhance the light harvesting property of titanium dioxide in visible region, depositing TiNTs samples with metals and metal oxides has been conducted by using thermal evaporation deposition, electrochemical deposition and conventional co-precipitation deposition. Some successful samples are obtained, and the morphologies and structures are investigated by using SEM and XRD. A brief summary is presented in Table 2.

<table>
<thead>
<tr>
<th></th>
<th>Reproducibility and control over deposition</th>
<th>Uniform coating</th>
<th>Non-Pore/tube clogging</th>
<th>Fast deposition</th>
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<tbody>
<tr>
<td><strong>Thermal evaporation</strong></td>
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<td><strong>Electrochemical method</strong></td>
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<td><strong>Conventional Co-precipitation</strong></td>
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Table 2. A summary of advantages and disadvantages of thermal evaporation method, electrochemical method and conventional co-precipitation method.

The comparison table indicates a good deposition method should have four factors (a) the successful results should be reproducible and well-controlled. (b) Coating on
nanotubes should be uniform and homogeneous over entire surface of samples. (c) The metal or metal oxide particles deposited on TiNTs should be small enough to penetrate inside the nanotubes without clogging. (d) The deposition process should be simple, scalable and fast. In the Chapter four, a modified deposition method will be discussed, namely forced hydrolysis, which satisfies all four criteria.
Chapter 4: Integration of TiNTs with iron oxide by forced hydrolysis method

4.1 Hydrolysis concept

Hydrolysis is a chemical process in which a salt reacts with water. In the presence of water, the salt is cleaved into two parts, and deprotonation of water happens at the same time. One fragment of parent molecule gains a hydrogen ion ($H^+$) from the water, and the remaining group of parent molecule gains the hydroxyl group ($OH^-$). Hydrolysis is a precipitation process to produce homogenous, fine and well-dispersed solid particles with nanoscale size by using simple chemicals. Formation of the particles occurs by nucleation and growth. Nucleation of solid particles occurs once the concentration of the particular particle reaches a critical saturation. Subsequent growth in size is due to the continuous diffusion of solute onto the nuclei formed initially. In some cases in which the hydrolysis cannot occur under normal condition, some catalysts, such as strong acids and bases, should be added to speed up the reaction with water. Temperature is also an important alternative way to accelerate hydrolysis.

4.2 Forced hydrolysis of FeCl$_3$ solution

Forced hydrolysis of aqueous FeCl$_3$ solution is a simple and fast way to synthesize ferric hydrous oxide particles. This method has been investigated widely since the original work of Matijevic and Scheiner, and the mechanisms of iron oxide particles formation at elevated temperature has been discussed in many papers [112]–[116].
Rochelle and Udo described the possible reaction in aqueous FeCl$_3$ solution in the following way [117]. Iron (III) chloride (FeCl$_3$·6H$_2$O) is used as precursor to provide iron source. In the present of water, FeCl$_3$·6H$_2$O dissociates to form hexa-aquo ion (See Equation 7),

$$FeCl_3 + 6H_2O \rightarrow Fe(H_2O)_6^{3+} + 3Cl^-$$

Equation 7

The electropositive cation induces the H$_2$O ligands to act as acids and, except at very low pH, hydrolysis, i.e. deprotonation of these ligands, takes place. The process is stepwise with ultimately all six ligands being deprotonated. Complete hydrolysis corresponds to formation of an iron (III) oxide (See Equation 8) or oxide hydroxide (See Equation 9),

$$2Fe(H_2O)_6^{3+} \rightarrow Fe_2O_3 + 6H^+ + 9H_2O$$

Equation 8

$$Fe(H_2O)_6^{3+} \rightarrow FeOOH + 3H^+ + 4H_2O$$

Equation 9

In general, akaganeite, $\beta$-FeOOH, forms first in the FeCl$_3$ solution, and $\alpha$-Fe$_2$O$_3$ is obtained by prolonged aging time, elevated temperature, or post heat treatment [118]. The morphology and size of the particles depend on a lot of variables, such as ferric salt concentration, solution pH, time and temperature.

4.3 Method

4.3.1 Forced hydrolysis setup

The experiment can be operated under normal laboratory conditions. No complicated chemicals and no special conditions, such as very high temperature and high
pressure, vacuum space, clean room are required [119]. It only involves single chemical (FeCl$_3$·6H$_2$O) and simple equipment (hot plate) as shown in Figure 37.

![Figure 37. Schematic diagram of setup for TiNTs deposition by forced hydrolysis of FeCl$_3$ solution.](image)

The production can be easily scaled up and it is favorable for industrial manufacturing due to the low cost fabrication.

### 4.3.2 Role of Initial temperature in FeOOH nanoparticle attachment

FeOOH nanoparticles attachment to TiNTs was first achieved by Yu et al [120]. This process involved soaking the nanotubes in FeCl$_3$ at 80°C for 12 hours, and resulted in 60 nm long FeOOH nanospindles attached onto samples. The main deficiency of this method is that the long FeOOH nanospindles restrict the dimension of titanium dioxide nanotubes that can be used. The nanotubes with smaller diameter than 60 nm, will not allow the FeOOH nanospindles to grow inside. Another deficiency of this method is the deposition time.

In order to find a solution to address the issues mentioned, two experiments have been performed and the results are shown in Figure 38. In Figure 38 (a), nanotubes
sample was soaked in FeCl₃ solution at room temperature, and was then heated to 75°C. In Figure 38 (b), nanotubes sample was immersed after the solution temperature reached 75°C. Both samples were soaked for 30 minutes. It is clear that the sample in Figure 38 (a) is coated by numerous nanoparticles, but no particles attach to the sample in Figure 38 (b). The mechanisms of FeOOH nanoparticle attachment in these two cases can thus be concluded as follows. In case (a), nucleation of FeOOH nanoparticles occurs on the surface of nanotubes and the particles grow in size. In case (b), nucleation of FeOOH nanoparticles occurs in solution, and when the tubes are immersed afterwards, the already-formed nanoparticles will not attach to the nanotubes. By comparing these two cases, we conclude that the initial temperature plays an important role in attachment.

Figure 38. SEM images for two TiNTs samples, which were soaked in the same solution for 30 minutes. (a) The nanotubes sample was immersed in solution at room temperature and then transferred to hot plate. (b) The nanotubes sample was immersed in solution when the temperature reached 75°C.
4.3.3 Standard Experimental procedure for FeOOH nanoparticles attachment to titanium dioxide nanotubes (TiNTs/FeOOH)

In this section, we describe a standard attachment procedure for a modified forced hydrolysis method, which is much faster and produces FeOOH nanoparticles in controllable small size. The modified deposition method is general for all nanotubes dimensions due to the small size of FeOOH nanoparticles. Detailed information about nanoparticle size and loading percentage will be discussed in next section.

The standard procedure consists of five steps as follows:

1. Long titanium dioxide nanotubes samples with length of about 2.2 μm and diameter of about 70 nm are produced by DC anodization. The nanotubes arrays are still attached to the original titanium foil substrate.

2. 20 mM fresh FeCl₃ solution is prepared by introducing 0.16 g of FeCl₃·6H₂O (Sigma-Aldrich, ACS, reagent, 97%) in 30 ml DI water under the magnetic stirring, and a clear light yellowish solution forms. The solution is transferred into a Petri dish.

3. The as-prepared long nanotubes samples are soaked immediately in the fresh solution at room temperature (20℃), and the Petri dish is covered.

4. Finally, the Petri dish is placed on the hot plate with surface temperature of 150℃. As temperature in solution increases, color of the solution starts to change within 5 minutes from light yellowish to deep orange and then to brownish, as shown in Figure 39.
Figure 39. Color of FeCl₃ solution (a) before and (b) after heating for 30 minutes.

Color change during heating indicates that FeOOH nanoparticles form in the solution. With increase in time, color changes from light to dark due to the increasing density of formed nanoparticles in the solution.

5. After soaking, nanotubes samples are taken out, rinsed in DI water, ultrasonically cleaned to remove the extra residues and then dried by compressed air. Color change of the samples indicates that FeOOH nanoparticles are successfully attached to TiNTs. As shown in Figure 40, deeper color on samples is observed for longer soaking time.
Figure 40. Color of samples soaked in FeCl₃ solution during heating for (a) 5 minutes (b) 15 minutes and (c) 30 minutes. The samples are present before (top) and after (bottom) annealing.

4.4 Morphology and architecture of TiO₂/FeOOH composite

The SEM images in Figure 41 show overall morphologies of TiO₂/FeOOH hybrid combination. As shown in Figure 41 (a), the typical as-prepared blank TiO₂ nanotubes are self-oriented in one direction, with length of 2.2 μm and inner diameter of 70 nm. Figure 41 (b) shows the morphology of the sample after only 5 minutes of soaking. FeOOH nanoparticles can form in very short time and coat the TiO₂ nanotubes, uniformly attaching both on the inside and outside of nanotube walls. A decrease in inner diameter of TiO₂ nanotubes is observed as shown in Figure 41 (c), as more FeOOH nanoparticles load onto the 15 mins-soaking sample. The TiO₂ nanotubes start to fill up
with FeOOH nanoparticles after 30 minutes of soaking, as shown in Figure 41 (d). Time of forced hydrolysis of FeCl₃ solution is thus a good parameter to control the loading of FeOOH particles on the TiO₂ nanotubes. Since the solution temperature has a relationship with the soaking time, the solution temperature determines the nanoparticle growth rate, as will be discussed in the next section.

Figure 41. SEM images of titanium oxide nanotubes: (a) blank sample, and deposited with iron hydrous oxide nanoparticles for (b) 5 minutes (c) 15 minutes and (d) 30 minutes respectively. All scale bars are 100 nm.

4.5 Size measurements of FeOOH nanoparticles

The size of the deposited FeOOH nanoparticles depends on the soaking time as displayed in Figure 42. Figure 42 (a)-(c) show that FeOOH nanoparticles grow in size
and the morphology of the nanoparticles change from round grain to rod shape as the soaking time increases. The range of the average diameter for the nanoparticles varies from 6 nm for 5 minutes soaking to 14.73 nm for 30 minutes soaking as shown in Figure 42 (d)-(f). The size distribution is somewhat wide due to the relatively short soaking time. Narrower size distribution of the particles can be achieved for longer soaking time [113].
Figure 42. SEM images of iron oxide nanoparticles attached to TiNTs for different soaking times: (a) 5 minutes (b) 15 minutes and (c) 30 minutes, and the corresponding size distribution of the particles (d–f). Scale bar is 100 nanometers for all SEM images; histograms are constructed based on at least 52 particles measurements for all plots.

FeOOH nanoparticles growth rate is estimated by analyzing the relationship between time and temperature. Figure 43 (a) shows the relationship between FeOOH nanoparticle size and soaking time. The slope of the curve represents the growth rate. The growth rate is very slow at the beginning when FeOOH nanoparticles start to form at around 5 minutes, and then growth rate increases at 15 minutes, and finally at 30 minutes, the growth rate increases significantly. By analyzing the relationship between time and temperature, we determined that the change in growth rate is partially affected by the temperature. Figure 42 (b) shows that within first 5 minutes, the FeCl₃ solution temperature increases from room temperature to 65°C corresponding to the slow growth rate. At 15 minutes, the temperature reaches around 70°C corresponding to the intermediate growth rate. At 30 minutes, the temperature reaches the maximum 75°C corresponding to the fast growth rate. Matijevic and Scheiner demonstrated that small changes in temperature and soaking time can produce large changes in particle size and morphology [112].
Figure 43. (a) The average size of iron oxide nanoparticles and (b) temperature is dependent on soaking time. The two plots indicate temperature affects the particles growth rate.

4.6 Loading estimate

Nanoparticle loading can be estimated from measurement of wall thickness as shown in Figure 44. The bare nanotubes wall thickness is about 8.78 nm (Figure 44 (a)). The wall thickness of decorated nanotubes increases from about 13 nm to 30 nm as soaking time increases from 5 minutes to 30 minutes, as shown in Figure 44 (b)-(d). This implies that more FeOOH nanoparticles are attached to TiNTs with longer soaking time.
Figure 44. Wall thickness distribution of the TiNTs.

Bare TiNT: $t=8.78 \pm 2.16\text{nm}$
5mins: $t=13.11 \pm 2.45\text{nm}$
15mins: $t=16.05 \pm 4.43\text{nm}$
30mins: $t=30.43 \pm 5.28\text{nm}$
Accurate loading estimation could be obtained from energy dispersive spectra (EDS) of TiNTs samples after annealing treatment, where FeOOH is converted into Fe$_2$O$_3$ and amorphous TiO$_2$ is converted into anatase. This will be discussed in section 4.8.

4.7 Post annealing treatment

As-deposited TiNTs samples are annealed in the tubular furnace at 350°C overnight (about 17 hours) with heating and cooling rate of 1°C/min. Both amorphous titanium dioxide and FeOOH nanoparticles are converted to crystalline anatase and Fe$_2$O$_3$ by post annealing treatment [121]. The crystallization to anatase leads to a significant increase in conductivity. The annealing temperature is set to 350°C, because it is found that when annealing temperature is higher than 450°C, the formations of other two TiO$_2$ phase Rutile and Brookite are observed, which has a comparatively low conductivity. The long time annealing for 17 hours is adopted since the resistance of the TiO$_2$ nanotubes decreases with prolonged annealing [90]. The optimized post heat treatment is significant for the use of this TiO$_2$/Fe$_2$O$_3$ composite in electrical and photoelectric applications.

Crystallographic structure of Fe$_2$O$_3$, which are collected from reaction solution is studied using both Raman spectrum and XRD spectrum as shown in Figure 45. In Figure 45 (a), the main intensity peak from Fe$_2$O$_3$ in Raman [122] are 225 (strong), 247 (weak), 299 (strong), 412 (strong), 497 (weak), 613 (medium) cm$^{-1}$, as displayed on the Raman plot. In Figure 45 (b), the peaks from hematite in XRD are found at 24.22°, 33.38° and 35.78°, corresponding to the (012), (104), and (110) planes of hematite (PDF #33-0664), respectively. The peaks are slightly shifted, most likely due to slightly different cell
parameters of the nanosized particles. Both plots confirm that $\beta$-FeOOH is transformed to $\alpha$-Fe$_2$O$_3$ after annealing treatment.

Figure 45. (a) Raman spectrum and (b) XRD spectrum of Fe$_2$O$_3$ nanoparticles deposited on silicon substrate after annealing the samples at 350°C for 17 hours. H(hkl) is the reference peaks for hematite.
Structure and composition of the hybrid TiO$_2$/Fe$_2$O$_3$ are characterized by using TEM. Figure 46 displays the TEM images for two different samples. (a) One was soaked in FeCl$_3$ solution for 5 minutes; (b) One was soaked for 30 minutes. Both samples were annealed at 350°C for 17 hours in O$_2$ after deposition. The top two TEM images in Figure 46 illustrate the increase in loading and increase in size of the nanoparticles with increasing soaking time. The remaining two HRTEM images and two SAED images in Figure 46 exhibit crystalline fringes and electron diffraction patterns for anatase and hematite. In Figure 46 (a), only anatase lattice fringes are observed and no hematite fringes are detected. This is possibly due to the small amounts of hematite particles. In Figure 46 (b), the lattice fringe of 0.256 nm shown in HRTEM image corresponds to the (110) plane of hematite. H(113) is also found in SAED image confirming that the iron oxide nanoparticles crystallize as α-Fe$_2$O$_3$. 
Figure 46. TEM (top), HRTEM (bottom) and SAED (insets) images for two different samples of titanium dioxide nanotubes deposited with iron oxide nanoparticles. (a) The sample was soaked for 5 minutes; (b) The sample was soaked for 30 minutes. The interplanar distance of α-Fe₂O₃ is d=0.256 nm, corresponding to the (110) plane of hematite (PDF #33-0664), and the interplanar distance of anatase is d=0.351 nm corresponding to the (101) plane (PDF#21-1272).
4.8 Loading of Fe$_2$O$_3$ nanoparticles on TiNTs

4.8.1 Dependence on deposition time

In order to quantitatively analyze the loading information of iron oxide nanoparticles on TiNTs, we use energy dispersive spectrum to estimate the elements quantities in the samples. Energy dispersive mapping can provide further information on the uniformity of the iron oxide nanoparticles distribution on the TiNTs samples surface.

In this investigation, we prepared a new batch of samples, which were anodized in 99v% Ethylene Glycol based solution at 60 V for 16 hour in the form of free-standing membranes with the length of about 50 μm. Elemental data analysis from EDS should be more accurate when performed on free-standing membranes peeled off from Ti substrate, thus eliminating the additional Ti signal from the substrate. Iron oxide nanoparticles were attached onto nanotubes membranes by forced hydrolysis method using the standard process as described in section 4.3.3. Three kinds of samples deposited with iron oxide for 10 minutes, 20 minutes and 30 minutes were used in this study.

The results are shown in Figure 47 and Figure 48. As expected, Fe element (green dots in Figure 47) distributes uniformly along the nanotubes, all the way to the bottom in all the samples, mimicking the Ti and O elemental mapping (blue and red dots in Figure 47). It confirms that the forced hydrolysis method works successfully on free-standing nanotubes membranes. The purple regions indicate the sections that were selected for detailed elemental intensity calculations along the longitudinal direction from the bottom of the nanotubes to the top. Figure 47 shows the amount of each element as a function of
distance from the bottom of the nanotube. As may be noted the amount fluctuates along
the distance, even for Ti and O which are expected to be distributed uniformly over the
entire tube length. The average amount of Ti slightly decreases as the distance increases.
This may be attributed to the fact the wall thickness is greater at the bottom of the tube
than at the top. In the case of iron, the average amount increases slightly with increasing
distance from the bottom. This may be explained as arising due to the fact that as iron
oxide nanoparticles diffuse from the top of nanotubes, less and less nanoparticles are
able to reach the bottom. Also as the wall is thicker at the bottom, there is less area
available for iron oxide attachment. However, the slopes of the linear approximations are
very small. Thus within the limits of experimental error we can conclude that iron oxide
nanoparticles are distributed uniformly over the entire surface area of the samples.
Figure 47. Elemental map for TiNTs samples deposited with iron oxide nanoparticles for (a) 10 minutes, (b) 20 minutes and (c) 30 minutes showing the presence of Ti (blue dots), O (red dots), Fe (green dots), corresponding SEM images (top) and plots of elements distribution vs. distance (bottom).
Accurate loading information as function of deposition time is obtained from energy dispersive spectra as shown in Figure 48. From the Fe to Ti ratio calculations we find that the loading of iron oxide onto nanotubes increases as the soaking time increases. Fe loading percentage increases from 4.03% for 10 minutes soaking and reaches 16.53% after 30 minutes soaking. The relationship between Fe loading and the soaking time and the equation for the best-fit are indicated on the plots of Fe percentage vs. soaking time in Figure 48.

**Figure 48.** Energy dispersive spectra (EDS) of titanium oxide nanotube membranes deposited with iron oxide nanoparticles for 10, 20 and 30 minutes respectively. The ratio of Ti to Fe is shown in atom percentage in the insets. A large C presence is detected most probably from the supporting carbon tape.
4.8.2 Dependence on structure and orientation of titania samples

Dependence of iron oxide nanoparticles loading on the structure of titania samples is investigated for nanoparticle anatase powders, ground free-standing membranes and intact free-standing membranes. Grinding of the membranes results in a powder consisting of randomly oriented nanotube bundles as opposed to the parallel-aligned nanotubes in the intact membranes. The vertically aligned and randomly oriented TiNT arrays were produced with the same length of about 50 μm. The control sample of titania nanoparticle powders (average particle size 21 nm) were purchased from Solaronix. All samples were deposited at the same deposition condition in 60 ml FeCl₃ solution for 20 minutes. The loading information is estimated by EDS (shown in Figure 49) and the results are expressed in ratio of Fe to Ti as shown in Table 3.
Figure 49. Energy dispersive spectra (EDS) of titania samples with various structures: powders, randomly oriented arrays and vertically aligned arrays attached with iron oxide nanoparticles.
<table>
<thead>
<tr>
<th>Ratio of Fe to Ti</th>
<th>Anatase powders</th>
<th>Randomly oriented TiNTs</th>
<th>Vertically aligned TiNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5:10</td>
<td>1:10</td>
<td>3:10</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3. Dependence of iron oxide loading on the structure of titania samples, which were made of powders, randomly oriented nanotubes arrays and vertically aligned nanotube arrays.**

As expected, attachment of iron oxide nanoparticles depends on the structure of titania samples. The nanotubular structure gains more iron oxide than the nanoparticulate structure because of the higher effective surface area available for deposition. The vertically aligned nanotube arrays offer the maximum surface area for nanoparticles attachment due to their alignment along the vertical axis favoring gravitation-driven diffusion of nanoparticle inside the tubes. The ratio of Fe to Ti in vertically aligned nanotubes sample (3:10) is six times that of powders sample (0.5:10). For this reason, vertically aligned TiNT arrays are more suitable for PV applications such as DSSCs when compared with the mesoporous membrane type film made of nanoparticulate paste.
Chapter 5: Optical properties and photovoltaic properties

5.1 Optical properties

Many applications of titanium dioxide, like photocatalysis and DSSC, are dependent on its optical properties, especially absorption property. In this section, we discuss some aspects that affect absorbance of TiNT arrays. Absorbance is calculated from UV-VIS-NIR diffuse reflectance measurements, which are recorded by a high-resolution spectrometer (Ocean Optics Spectra Suite: HR 4000 CG-UV-NIR) and a combined deuterium and a tungsten-halogen lamp (Hamamatsu L10290).

5.1.1 Influence of annealing condition

Absorption ability of TiNT arrays in visible light region could be improved by annealing samples for longer time and at higher temperature. The optical property can be directly explained by band gap, since light with energy above the band gap will have sufficient energy to excite an electron into the conduction band from the valence band. Consequently the light will be absorbed. The decrease in optical band gap of anatase could be achieved by annealing, which can be explained as a result of the change in nanotubes layer density, the higher crystallinity and increase in grain size [123], [124]. We prepared samples by annealing them under different conditions. The average crystallite size of samples is estimated by using the full width at half maximum (FWHM) of the intense (101) diffraction peak of anatase according to Scherer equation (Equation 10). The corresponding parameters and results are displayed in Table 4.
\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  

Equation 10

where \( D \) is the crystallite size in nm, \( \lambda \) is wavelength of X-Ray (0.1540 nm), \( \theta \) is the Bragg angle, and \( \beta \) is the FWHM in radians.

<table>
<thead>
<tr>
<th>2θ (°)</th>
<th>θ (°)</th>
<th>cosθ</th>
<th>FWHM (°)</th>
<th>FWHM Radian</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.38</td>
<td>12.69</td>
<td>0.97557</td>
<td>0.33276</td>
<td>0.005808</td>
<td>24.46</td>
</tr>
<tr>
<td>25.06</td>
<td>12.53</td>
<td>0.97618</td>
<td>0.29820</td>
<td>0.005205</td>
<td>27.28</td>
</tr>
<tr>
<td>25.34</td>
<td>12.67</td>
<td>0.97656</td>
<td>0.27566</td>
<td>0.004811</td>
<td>29.53</td>
</tr>
<tr>
<td>25.38</td>
<td>12.69</td>
<td>0.97557</td>
<td>0.27146</td>
<td>0.004738</td>
<td>29.99</td>
</tr>
</tbody>
</table>

Table 4. The average grain size of the annealed samples is evaluated using the full width at half maximum (FWHM) of the intense (101) diffraction peak of anatase according to Scherer equation.

The estimated crystallite size of the sample annealed at 350°C for 2 hours is 24.46 nm, which is smallest among all the annealed samples. The estimated crystallite size of the sample annealed at 450°C for 17 hours is 29.99 nm, which is the largest. Throughout the investigation of the relationship between annealing conditions and optical property of anatase, we find that annealing at 450°C for 17 hours would be optimal for solar energy harvesting applications. All the samples used in section 5.2 were annealed under these optimal annealing conditions.

5.1.2 Optical properties of TiNTs coated with metal oxide

Titanium dioxide is a semiconductor with wide band gap of 3.05 eV-3.26 eV. The large bandgap leads to its inherent optical property that it absorbs only in the UV range,
which constitutes less than 5% of the whole solar spectrum. Light harvesting can be enhanced by integrating with metal oxides like iron oxide and copper oxide. Methods to synthesize TiNTs in modified form by depositing narrow band gap metal oxides are discussed in Chapter 3 and 4. In the present section, optical properties of the hybrid structure of TiNTs decorated with metal oxide nanoparticles are investigated.

5.1.2.1 Ordered TiNTs attached to Ti substrate

All the samples employed in this experiment are in form of ordered arrays with a length of about 2.2 μm, which are still attached to original Ti substrate. Figure 50 shows the absorbance spectra of TiNTs in modified form with (c) copper oxide nanoparticles deposited by electrochemical method and (d) iron oxide nanoparticles deposited by conventional co-precipitation method, and the corresponding morphologies of the hybrid structures. Figure 50 (a) shows that titania nanotubes are partially filled up with copper oxide. Figure 50 (b) shows titania nanotubes are decorated with iron oxide nanoparticles of small size. High visible light absorption ability has been observed in the absorbance spectra seen in Figure 50 (c) and (d). The visible light absorbance of the copper oxide sample (Figure 50 (c)) is better when compared with the iron oxide sample (Figure 50 (d)). This might be due to better filling of nanotubes with copper oxide than with iron oxide. In both cases, the visible light absorption is enhanced by the addition of the metal oxide.
Figure 50. SEM images showing the morphologies of TiNTs coated with (a) Cu$_2$O by electrochemical method and (b) Fe$_3$O$_4$ by conventional co-precipitation method. The corresponding absorbance spectra are presented in (c) and (d) respectively.

Additional experiments were performed to investigate the dependence of absorbance of the hybrid structure on the amount of iron loading. We prepared samples by forced hydrolysis method which provides uniform, controlled iron oxide coating on the nanotube arrays as discussed in Chapter 4. Three samples with different iron oxide loading were prepared. As estimated by EDS spectra shown in Figure 51, the ratios of Fe to Ti in the three samples are (a) 3:10, (b) 4:10 and (c) 12:10, respectively. It should be
noted, that part of the Ti signals may come from the underlying Ti substrate, so the ratio of Fe to Ti in the nanotubes will be higher.
Figure 51. Energy dispersive spectra of samples loaded with different amount of iron oxides. Three samples were prepared by forced hydrolysis method. The ratio of Ti to Fe is shown in atom percentage in the insets.

The effect of iron oxide incorporation on the light absorbance characteristic of the three samples is measured by absorbance in UV-NIR range as shown in Figure 52. The absorbance in visible light region is increasing with iron oxide loading. The bare TiNTs absorbs no visible light because of the wide band gap. As expected, an increase in relative absorbance in the visible light ranging from 380 nm to 600 nm has been observed for all the TiO$_2$/Fe$_2$O$_3$ composite samples with respect to the bare TiO$_2$ nanotubes.

However, decreasing absorbance in UV region is observed for the samples with increasing iron oxide loading. This can be attributed to the shadowing effect due to the dense coverage of iron oxide nanoparticles on the surface of nanotubes which inhibits UV light absorption [103].
Figure 52. The absorbance characteristic in UV-NIR range for TiO$_2$/Fe$_2$O$_3$ hybrid structure samples with different amount of iron oxide prepared by forced hydrolysis method. The relative absorbance spectra are calculated from diffuse reflectance spectroscopy measurements. (The absorbance peak in NIR region comes from the original lamp spectrum)

5.1.2.2 Free-standing TiNT arrays

Additional experiment were performed on TiNTs in form of free-standing membranes. In Figure 53 (a) The TiNTs samples were attached with iron oxide nanoparticles by forced hydrolysis methods for 5, 7, 10, 20 and 30 minutes. After
deposition, the membranes with thickness of 50 \( \mu \text{m} \) were peeled off from the underlying Ti substrate. They are then ground and made into pastes, which were then transferred onto conductive glass for subsequent PV measurements as will be discussed in a later section. Absorbance results for such samples are shown in Figure 53 (a).

![Absorbance results for such samples are shown in Figure 53 (a).](image-url)
Figure 53. The absorbance characteristic in UV-NIR range for (a) randomly oriented TiO$_2$/Fe$_2$O$_3$ hybrid structure samples and (b) vertically aligned TiO$_2$/Fe$_2$O$_3$ hybrid structure samples with various deposition time prepared by forced hydrolysis method. The relative absorbance spectra are calculated from diffuse reflectance spectroscopy measurements. (The absorbance peak in NIR region comes from the original lamp spectrum)

Compared with Figure 52, absorption peaks in visible light region for all the samples in Figure 53 (a) are comparatively low. This is possibly due to the small amounts of hematite particles with respect to the thick titania layer. The ratio of Fe to Ti in the samples with 10, 20 and 30 minutes deposition are calculated to be only 0.4:10, 1:10 and 2:10 respectively with only lower ratios estimated for the 5 and 7 minutes deposition samples. The overall trend of curves shown in Figure 53 (a) indicates that higher absorbance in visible light range is obtained for the samples with higher iron oxide content. The absorbance in the visible region is found to be almost independent of iron oxide deposition time as shown in Figure 53 (b). Here the samples were made up of vertically aligned TiNTs. The peak at around 570 nm corresponds to the hematite band gap (2.2 eV). Even for short deposition time, around 5 mins, the absorbance is found to increase significantly in the visible region. This is an interesting result indicating that the vertically aligned samples have the potential to achieve desirable optical properties even at low levels of iron oxide loading.
5.1.3 Comparison with dye-sensitized nanotubes

Many different dyes have been employed and explored for sensitization of anatase [125] in the Gratzel DSSC design, among which a ruthenium-based dye, commercially known as N3, has become the most efficient and widely used [126].

In order to compare the visible light absorbance of metal oxide nanoparticles vis-à-vis the standard N3 dye molecules, dye-sensitized TiNTs samples were prepared and their optical properties have been studied.

The sequence of steps to prepare dye-sensitized nanotubes is as follows:

1. Prepare TiNTs samples in 100 ml 95v% ethylene glycol based solution with 0.05 M potassium fluoride at 60 V for 16 hours (for randomly oriented TiNTs) or for 6 hours (for vertically aligned TiNTs). The TiNTs layer has a thickness of 50 μm, which could be peeled off from the Ti substrate easily (for randomly oriented TiNTs) or has a thickness of 20 μm (for vertically aligned TiNTs).

2. Grind the 50 μm flakes into fine powders to obtain randomly oriented TiNTs. Distribute the randomly oriented TiNTs and vertically aligned TiNTs into three groups.

3. The first group is blank nanotubes which is the reference group. The second group is attached with dye molecules by soaking nanotube powders in 0.0003 M dye solution overnight. The third group is deposited with Fe₂O₃ by forced hydrolysis method.
The absorbances in UV-NIR range were measured as indicated in Figure 54. In both cases, bare TiNTs have poor absorbance in visible light, as observed in the previous experiments. The titania nanotubes attached with dye molecules (red line) shows a high absorbance in visible light range as expected. By comparing the red curve and blue curve in Figure 54, we find sample attached with dye and the sample deposited with Fe₂O₃ have similar optical properties, especially in vertically aligned TiNTs case. In other words, monolayer of Fe₂O₃ works similar to dye molecules. These results are encouraging. Thus a new concept in low cost solar cells could be envisioned wherein earth-abundant oxides could easily replace expensive dye molecules [127].
Figure 54. The absorbance characteristic in UV-NIR range for (a) randomly oriented and (b) for vertically aligned TiNTs/Fe$_2$O$_3$ (blue line) compared with randomly oriented dye-sensitized TiNTs (red line).
5.2 Photovoltaic properties

A preliminary device was made in DSSC-type configuration which was described in section 2.2.3. The schematic design of preliminary device is shown in Figure 55. Like traditional DSSC, the new device is built up in sandwich structure, in which TiNT arrays work as electron conductor and liquid electrolyte is used to assist the electrons in transporting. However, instead of dye (red dots in typical DSSC), iron oxide (thin yellow layer in preliminary device) is employed as light absorber layer in the new device.

Figure 55. Design of preliminary device made of TiNTs with iron oxide nanoparticles as absorber layer. The overall architecture of new device is similar to that of the typical DSSC.

Figure 56 shows the principle of operation for such a device. The left figure shows...
the energy band diagram for TiO$_2$ and iron oxide in separation in dark. Once they contact each other, the Fermi energy level should be in equilibrium when they reach the thermal equilibrium (middle figure). The electrons in iron oxide are excited by illumination, and transport to conduction band of TiO$_2$ (right figure). The electrons pass through the external circuit and return back to the counter electrode, which is in contact with the liquid electrolyte. Absorber layer is regenerated by those electrons from the liquid electrolyte.

![Energy Band Diagram](image)

**Figure 56.** Principle of operation and energy level scheme of the preliminary device. Photoexcitation of the iron oxide absorber layer is followed by electron injection into the conduction band of the titanium oxide semiconductor. The absorber is regenerated by the liquid electrolyte, which itself is regenerated at the counter electrode by electrons passing through the load.

We fabricated devices in three types: (1) original underlying Ti substrate is used as anode contact for the device using ordered TiNT arrays, or transparent conductive oxide glass is used as anode contact for the device using (2) pastes consisting of randomly
oriented TiNT bundles and (3) free-standing TiNT membranes. To evaluate the photovoltaic performance, the current-voltage characteristic of the device is measured under simulated AM 1.5 illumination provided by a solar simulator (Oriel instrument 68805, 68705 and 66055) applying an external bias to the device and measuring the generated photocurrent with a Keithley model 2400 digital source meter. The PV properties as measured for each of these configurations are reported below.

**5.2.1 Ti as anode contact**

The device is made in the following steps:

1. Long titanium dioxide nanotubes samples with length of about 2.2 μm and diameter of about 70 nm are synthesized in 95% ethylene glycol for 3 hours by DC anodization. The nanotube arrays remain attached to the original titanium substrate.

2. FeOOH layer is attached on nanotubes by soaking the nanotubes samples in 20 mM fresh FeCl₃ solution on hot plate with surface temperature of 150°C.

3. Fe₂O₃ layer and crystalline anatase nanotubes are obtained by annealing treatment after deposition.

4. TiNTs samples with iron oxide layer are sandwiched with a Pt-coated FTO glass counter-electrode using a polymer spacer (Surlyn, Dupont). Electrolyte (PMII) is introduced into the space between the sandwiched electrodes.

Photovoltaic properties are measured by means of I-V plots and transient response time. I-V behavior is measured in both dark and light with illumination on the cathode
side of the device. Preliminary results such as open circuit voltage, short circuit current, fill factor and response time are presented in Figure 57.

Figure 57. I-V plot (left) and transient response (right) for the preliminary device with Ti foil as anode contact. The titania layer is about 2.2 μm long. The large short circuit current observed in dark might be due to the background light and it seems to be comparable because of the low light photocurrent.

For this device, open circuit voltage is 0.185 V, short circuit current is 22.9 μA/cm², and fill factor is 0.44. The short circuit current observed in dark might be due to the background light. The response time (light-on and light-off) is more than 3 minutes. Low photocurrent and long response time may be attributed to the charge carrier recombination and the loss during the penetration through titanium oxide barrier layer below the arrays before they reach the Ti anode.
5.2.2 Conductive glass as anode contact and titania layer made of randomly oriented nanotubes arrays paste

First, TiNTs/ Fe₂O₃ samples are prepared as follows:

1. TiNTs flake samples with length of about 50 μm are synthesized in 99% ethylene glycol for 16 hours by DC anodization. The nanotube membranes will be peeled off in the later step.

2. FeOOH layer is attached on nanotubes by soaking the nanotubes flake samples in 20 mM fresh FeCl₃ solution on hot plate with surface temperature of 150°C.

3. The titania nanotube membranes with iron oxide layer are peeled off from the Ti substrate after deposition and are ground into fine powders.

4. A paste is made out of the powders by introducing 2 g Polyethylene glycol (PEG) (20,000 Alfa Aesar) and 6 g TiNT fine powders in the mixture of 0.2 ml 2.4-Pentanediine (Aldrich), 0.2 ml Triton-X (Alfa Aesar) and 5 ml DI H₂O.

5. Conductive glass is ultrasonically cleaned with IPA for 30 minutes followed by rinsing with DI water, ethanol and acetone.

6. A TiO₂ compact layer is deposited on the glass substrate by aerosol spray pyrolysis at 450°C. A commercial titanium diisopropoxide bis(acetylacetonate) solution (75% in 2-propanol, Sigma-Aldrich) is diluted in ethanol (1:39, volume ratio) [128].
7. TiCl$_4$ treatment. Immerse conductive glass in 0.1 M TiCl$_4$ (Alfa Aesar, Liquid, 99.0%, min) (89 ml H$_2$O + 1 ml TiCl$_4$) in open chamber for 60 min followed by rinsing with DI water after TiCl$_4$ treatment.

8. Dry glass substrate at 450°C for 20 minutes with both up rate and down rate of 20°C/min.

9. The paste prepared in step 4 is transferred onto a conductive glass electrode using a standard doctor-blade technique.

10. Anneal the paste in two steps: first at 180°C for 1 hour with an up rate of 5°C/min in order to evaporate the organic chemicals, then anneal at 450°C for 17 hours with an up rate of 1°C/min to firmly adhere the titania paste to the conductive glass [93].

11. The device is finally sealed with a Pt coated FTO conductive glass counter electrode using a polymer spacer (Surlyn, Dupont). Electrolyte (PMII) is introduced into the space between the sandwiched devices.

I-V plots and transient response spectra are shown in Figure 58, and the related preliminary parameters of the samples are shown in Table 5.
Figure 58. I-V plot (left) and transient response (right) for the preliminary device with conductive glass as anode contact. The titania paste is made of randomly oriented nanotube powders attached with iron oxide nanoparticles for (a) 5 minutes, (b) 7 minutes and (c) 10 minutes. The paste is annealed in two steps.
Table 5. PV parameters for the devices made of randomly oriented TiNTs, such as open circuit voltage, short circuit current and fill factor.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Voc (V)</th>
<th>Isc (μA/cm$^2$)</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-mins sample</td>
<td>0.53</td>
<td>15</td>
<td>0.38</td>
</tr>
<tr>
<td>7-mins sample</td>
<td>0.52</td>
<td>25</td>
<td>0.28</td>
</tr>
<tr>
<td>10-mins sample</td>
<td>0.62</td>
<td>66</td>
<td>0.40</td>
</tr>
</tbody>
</table>

As expected, the photocurrent increases with increasing iron oxide loading consistent with improved visible light absorption observed in optical measurements (see Figure 58 and Figure 59). As deposition time increases from 5 minutes to 10 minutes, the photocurrent increases from 15 μA/cm$^2$ to 66 μA/cm$^2$.

All samples have been found to respond to light immediately when light is turned on and off. It takes a few seconds (up to 22 second for 10-mins deposited sample) to reach stable values. Increased current and reduced response time (< 0.2 s) in these samples can be attributed to elimination of barrier layer resulting in better mechanical and electrical contact between TiNTs paste and conductive glass.
Figure 59. Short circuit current of devices as a function of deposition time. The devices are made of randomly oriented TiNTs attached with iron oxide nanoparticles by soaking in FeCl$_3$ solution for various time. The titania paste is annealed in two steps.

**5.2.3 Conductive glass as anode contact and titania layer made of vertically aligned nanotube arrays**

Here, we employ vertically aligned titania membranes as light absorber layer instead of randomly oriented titania arrays paste. The procedure for making this kind of device is described as follows.

1. TiNTs flake samples with length of about 20 μm are synthesized in 99% ethylene glycol for 6 hours by DC anodization.
2. Titania membranes are detached from Ti foil substrate using two-step anodization method.

3. FeOOH layer is attached on nanotubes by soaking the detached nanotube membranes in 20 mM fresh FeCl₃ solution for varying times on hot plate with surface temperature of 150°C.

4. The titania nanotube membranes with iron oxide layer are cleaned in DI water.

5. Conductive glass is ultrasonically cleaned with IPA for 30 minutes followed by rinsing with DI water, ethanol and acetone.

6. A TiO₂ compact layer is deposited on the glass substrates by aerosol spray pyrolysis at 450°C. A commercial titanium diisopropoxide bis(acetylacetonate) solution (75% in 2-propanol, Sigma-Aldrich) is diluted in ethanol (1:39, volume ratio).

7. TiCl₄ treatment. Immerse sample in 0.1 M TiCl₄ (Alfa Aesar, Liquid, 99.0%, min) (89 ml H₂O + 1 ml TiCl₄) in open chamber for 60 min followed by rinsing with DI water after TiCl₄ treatment.

8. Dry glass substrate at 450°C for 20 minutes with both up rate and down rate of 20°C/min.

9. A titania nanopowder viscous paste is prepared by introducing 0.03 g titania nanopowder (Sigma-Aldrich, ~21 nm particle size, ≥99.5%, trace metals basis, Aerioxide P25) in the mixture of 3 μl acetic acid (Alfa Aesar, glacial, ACS,
99.7+%) and 97 μl DI H₂O [94]. Finally, apply the titania nanopowder viscous paste on conductive glass substrates.

10. Transfer vertically aligned free-standing TiNT membranes from step 4 on titania viscous paste layer immediately when the paste is wet.

11. Anneal the titania membranes on transparent conductive glass at 180°C for 1 hour with temperature up rate of 5°C/min to evaporate the organic chemicals followed by annealing at 450°C for 17 hours with up rate of 1°C/min to firmly adhere the vertically aligned TiNT membranes to the conductive glass.

12. The working electrode is sandwiched together with a Pt coated fluorine-doped glass counter electrode using a polymer spacer (Surlyn, Dupont). Electrolyte (PMII) is introduced into the space between the sandwiched devices.

I-V plots are measured in both dark and light as shown in Figure 60, corresponding parameters as shown in Table 6. For this type of devices, open circuit voltages are almost constant of around 0.6 V, approaching the theoretical limit of 0.8 V. The best short circuit current is 260 μA/cm², which is 4 to 5 times better than random oriented TiNTs as shown in Table 5. Also good response time (< 0.2 s) (light-on and light-off) is consistent with previous devices, which are not shown here since we already solved this problem.

The increase in short circuit current can be attributed to the full utilization of the one-dimensional nature and transparent property of nanotube arrays which can help to trap light and provide a directed traveling path for electrons.
Figure 60. I-V plots for the devices with conductive glass as anode contact. The vertically aligned titania membranes are deposited with iron oxide for 5-30 minutes and annealed in two steps.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Voc (V)</th>
<th>Isc (μA/cm²)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-mins sample</td>
<td>0.54</td>
<td>43.3</td>
<td>0.56</td>
<td>0.013</td>
</tr>
<tr>
<td>7-mins sample</td>
<td>0.61</td>
<td>109</td>
<td>0.61</td>
<td>0.040</td>
</tr>
<tr>
<td>10-mins sample</td>
<td>0.64</td>
<td>183</td>
<td>0.57</td>
<td>0.067</td>
</tr>
<tr>
<td>15-mins sample</td>
<td>0.62</td>
<td>228</td>
<td>0.51</td>
<td>0.072</td>
</tr>
<tr>
<td>30-mins sample</td>
<td>0.58</td>
<td>260</td>
<td>0.50</td>
<td>0.075</td>
</tr>
</tbody>
</table>

*Table 6. PV parameters for the devices made of vertically aligned TiNTs, such as open circuit voltage, short circuit current, fill factor and efficiency.*
Dependence of short circuit current and efficiency of this type of devices on deposition time are plotted as shown in Figure 61. The short circuit current steadily increases with deposition time, which is consistent with what we obtained in section 5.2.2. Both current and efficiency seem to reach plateau at around 30 min. However, there is still potential to improve the performance of this type of device: (1) employ thinner layer of titania membranes (< 20 μm) to reduce the resistance in titania layer; (2) optimize titania nanopowder viscous paste to firmly attach TiNT membranes to conductive glass; (3) deposit nanotube membranes with more iron oxide to harvest solar energy.

Figure 61. Short circuit current and efficiency of devices as a function of deposition time. The devices are made of randomly oriented TiNTs attached with iron oxide nanoparticles by soaking in FeCl₃ solution for various time.
5.2.4 Comparison of photovoltaic properties

Based on the above results it is interesting to compare the PV properties for the Fe₂O₃ integrated TiNT samples (both randomly oriented TiNTs and vertically aligned) vs. dye-sensitized devices.

First, we make a comparison as a function of TiNTs orientation, that is, randomly oriented TiNTs vs. vertically aligned TiNTs for both iron oxide as well as dye molecule absorbers. IV plots and important PV parameters are displayed in Figure 62 and Table 7. For both sets of samples, (with iron oxide absorbers or dye molecules), vertically aligned TiNTs are found to perform better than randomly oriented TiNTs. The efficiency of the best vertically aligned TiNTs device is about five to eight times better than that of randomly oriented TiNTs for both types of absorbers.

![Graphs showing comparison of photovoltaic properties based on TiNTs orientation](image)

**Figure 62.** Comparison of photovoltaic properties based on TiNTs orientation (Randomly oriented TiNTs vs. vertically aligned TiNTs). Dye-sensitized devices were prepared for reference.
We also noted that for the vertically aligned TiNTs, dye sensitized devices are found to perform better than iron oxide attached TiNT devices. The results are shown in Figure 63 and Table 8. The dye-sensitized samples perform about 10 times better than Fe₂O₃ (0.9% vs 0.075%). This may be attributed to the fact that although iron oxide works as well as dye as far as its optical behavior is concerned, the high electrical resistance of iron oxide results in lower current. The low current may also originate from the standard electrolyte (PMII) that was used. While this electrolyte is optimized for dye, it is not optimized for iron oxide absorber. Use of other electrolytes that are optimized for iron oxide could improve the performance further. Indeed this is warranted from the fact that when we compare the performance of dye-sensitized TiNTs versus commercial titania nanoparticle-based DSSCs (Gratzel design), our devices outperform the DSSC cells by a factor of 2 (see Figure 64 and Table 9).
Figure 63. Comparison of photovoltaic properties based on absorber (Fe₂O₃ vs. dye).

<table>
<thead>
<tr>
<th>Vertically aligned TiNTs electrode</th>
<th>$V_{OC}$ (V)</th>
<th>$I_{SC}$ (mA/cm²)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>0.58</td>
<td>0.26</td>
<td>0.50</td>
<td>0.075</td>
</tr>
<tr>
<td>Dye</td>
<td>0.77</td>
<td>2.13</td>
<td>0.55</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Table 8. The performance parameters of the devices in Figure 63.

Thus in conclusion, our results indicate the strong potential for vertically aligned high-aspect ratio TiNT structures for use in moderately efficient solar cells. Our results also show the strong potential for the use of thin layers of iron oxide absorbers for efficient solar energy harvesting. Replacement of dye molecules with iron oxide will not
only be a low-cost alternative to expensive dye molecules, it will also use a sustainable
and environment-friendly material.

Figure 64. Comparison of photovoltaic properties based on configuration
(vertically aligned TiNTs vs. Degussa anatase).

<table>
<thead>
<tr>
<th>TiO₂ electrode+dye</th>
<th>Voc (V)</th>
<th>Isc (mA/cm²)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertically aligned TiNTs</td>
<td>0.77</td>
<td>2.13</td>
<td>0.55</td>
<td>0.90</td>
</tr>
<tr>
<td>Degussa</td>
<td>0.78</td>
<td>1.05</td>
<td>0.54</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Table 9. The performance parameters of the devices in Figure 64.
Chapter 6: Conclusion and Future work

In this dissertation, we investigated the optical and photovoltaic properties of titanium dioxide and modified titanium dioxide for PV applications.

We synthesized TiNT arrays in three different forms using electrochemical anodization: powders, nanotubes attached to titanium foil and free-standing nanotube membranes. We found the optimal synthesis parameters to achieve a fast yield of TiNT powders: Cl\textsuperscript{-} concentration of 0.1-0.2 M, pH below 2, and DC voltage of 16V. Morphology control of attached TiNTs and detachment of free-standing membranes have also been investigated. Tube diameter is mainly controlled by the anodization voltage, while the length is controlled by anodization time and by the water content in the electrolyte solution. Water content plays a major role also in the strength of the physical contact between the nanotubes and the underlying Ti substrate. The higher the water content, the stronger the attachment of the nanotubes to the substrate; water content below 2% results in facile detachment of the TiNTs from the substrate, while water content above 20% does not result in nanotubes formation. The quality of the free standing membranes has been improved by employing a double-anodization method, resulting in flat, robust, non-curling TiNT flakes.

In order to extend the spectral response of titania from the UV region into the visible range, many different methods (thermal evaporation, electrochemical deposition and co-precipitation) for integration of TiNTs with metal oxides such as copper oxide and iron oxide have been investigated. We demonstrated a new deposition method based
on forced hydrolysis of FeCl$_3$ solution followed by post annealing treatment which is proved to be by far the best synthesis route for uniform decoration of TiNTs with iron oxide (hematite) nanoparticles. For such hybrid TiO$_2$/Fe$_2$O$_3$ structures, the size and loading of the nanoparticles could be easily controlled by tailoring synthesis parameters such as the soaking time and temperature.

The optical properties measurements of such hybrid structures revealed an increase in the absorbance in the visible range from 380 to 600 nm. This behavior is similar to that demonstrated by the widely used Ruthenium-based dye molecules in Gratzel-type solar cells. Low-cost, earth-abundant metal oxide absorbers can be employed in place of expensive dyes in PV applications.

Preliminary devices based on DSSC-type solar cell concept using TiO$_2$/Fe$_2$O$_3$ have been fabricated, and some promising results PV properties were obtained. Vertically aligned TiNTs perform better than commercial anatase. Open circuit voltage of about 0.6 V indicates very good band alignment of the iron oxide with anatase titania, approaching the theoretical limit of open circuit voltages typically measured for standard titania based DSSCs. Measured short circuit current density values up to 0.26 mA/cm$^2$ with an efficiency of 0.075% have been obtained. These values are somewhat about ten times lower when compared with commercial DSSCs, wherein $I_{SC}$ values in the range of 1-10 mA/cm$^2$ have been measured. One reason for the low performance in our cells is due to high internal resistance arising from the insulating iron oxide and the poor electrical contact between titania and conductive glass. Further optimization in iron oxide
deposition, choice of electrolyte, cell packaging and electrolyte sealing can lead to currents as high as 2 mA/cm² resulting in overall efficiency of 1% or higher. Response times below 0.2 s have been observed for some of best performing samples, pointing to possible future applications in photodetecting devices.

These results can be further improved in new types of device concepts such as Metal-Insulator-Semiconductor. These devices would employ iron oxide absorbers in direct contact with metal back contacts for improved hole conductivity by tunneling through the thin insulating layer. Further optimization of the forced hydrolysis method for better control of the thickness and uniformity of the iron oxide absorber layers will also result in higher short circuit currents. Employment of different hybrid structures such as TiO₂/Cu₂O can also result in better performance in terms of V_{OC} (better band alignment) and I_{SC} in future devices.
References


S. Kobayashi, N. Hamasaki, M. Suzuki, M. Kimura, H. Shirai, and K. Hanabusa, “Preparation of Helical Transition-Metal Oxide Tubes Using Organogelators as


Application number: PCT/US2014/016027