Optical, Electrical and Catalytic Properties Of Titania Nanotubes

A dissertation presented

By

Mohamed AbdElmoula

Submitted in partial fulfillment Of the requirements for the degree of Doctor of Philosophy In the field of Physics

In the Graduate School of Arts and Sciences Northeastern University Boston, Massachusetts

August 2011
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ABSTRACT OF DISSERTATION

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ABSTRACT

In past decades revolutionary developments took place in many aspects of science. One of the leading developments is in the field of material science where there is great interest in developing new materials for various applications. Massive number of applications will change the entire life of mankind on earth and in space. Nanomaterials science is considered the pioneer in this new era.

Titania nanotube is considered a very important material due to its promising applications in many fields ranging from energy harvesting to sensors and photocatalytic applications. Electrochemical anodization method is used to fabricate titania nanotube arrays, this method is preferred than other methods for many reasons, for example it has good degree of controlling tube length, tube diameter and tube wall thickness. In addition to controlling tube parameter this method provides a scalable, easy and cheap technique for future industrial applications. My work in this thesis is focused on this kind of nanotubes arrays. In this dissertation we will provide an introduction to fabrication of titania nanotube arrays. We will provide an overview about the reported methods of fabrication and the advantage of each method. Also we will describe some anticipated application and the challenges to make these nanotubes functional and efficient.

Secondly, we will carry out a comprehensive study of the electrical transport of a single titania nanotube, where we have been able to study for the first time the electrical transport properties of a single titania nanotube using E-beam Lithography technique. Also we will explore parameters that affect these transport properties such as annealing conditions and the morphology of the nanotube. We will describe a study of the optical
properties of free standing titania nanotube arrays, where we will investigate the transmission, reflection and absorption of electromagnetic spectrum from 300nm to 1000nm (which cover the infrared, visible light and ultra violet region). This study is done both qualitatively and quantitatively using integrating sphere spectrometry. Finally, we will carry out a study of catalytic properties of modified titania nanotube arrays where the modification is done by controlled attachment of gold nanoparticles to the surface of the titania nanotube arrays. These gold nanoparticles when supported by titanium oxide surface works as a very good catalyst for CO oxidation reaction at room temperature and lower.
DEDICATION

I dedicate this thesis

To those who sacrificed their lives for the freedom and dignity of Egypt

The martyrs of the January 25-2011 revolution
ACKNOWLEDGMENTS

The work done in this dissertation is not solely my own effort. Many people helped me to get this work done, and I would like to express my deepest gratitude for all of them. First, I would like to thank my advisor, Prof. Latika Menon, for her constant support, direction, guidance, patience and wise mentoring. I would like to thank my committee members: I thank Prof. Donald Heiman, for his help with the optical measurements and consultations. I thank Prof. Jeffrey Sokoloff, for his fruitful discussion and consultations. I thank Prof. Swastik Kar for his important guidance and discussion in the electrical transport properties section, also for his directions in the optical properties section. I would like to thank Prof. Laura Lewis, for her very important directions and support; I would like to thank Prof Ronald Willey, for his help with conducting the catalytic measurements. I would like to thank my Lab mates: I thank Eugene Panaitescu for his help throughout the dissertation work; Pegah Hosseinpour for her important inquiries and discussion; Dalmau Reig-i-Plessis for his help and discussions; Ragen McAdoo for this help in the catalytic measurements. I would like to thank my classmates for their help during the first two years of the PhD program. I would like to thank staff of Kostas research center at Northeastern University for their help and training on many fabrication instruments: I thank Richard DeVito for his valuable advice and guidance; and Scott McNamara and David McKee for their training and help. I would like to thank CHN users for their help, especially Praba Selvarsah for his outstanding help and valuable advice. I also thank Didier F. Casse, Cihan Yilmaz and Peter Ryan for their help. I would like to thank my teachers in the Physics department, Cairo University, Egypt for their
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Chapter-1

Introduction

1.1 Motivation

1.2 Thesis outline
1.1. Motivation

The study of nanoscale systems has been ongoing for decades, but recent breakthroughs in high resolution imaging techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and scanning tunneling microscopy (STM) have enabled researchers to see and work with materials smaller than anything ever researched before. In addition, the evolution of modern computing and electronics to ever smaller transistors, microchips, and devices has fueled a booming industrial search for new materials and their novel applications. Additionally, the recent decoding of the human genome has led medical researchers to seek nano-sized particles that can interact with the DNA itself to cure diseases. And, medical researchers are actively seeking to develop new nanomedicines that can interact only locally with tumors and diseases without affecting other cells in the body. They have demonstrated that one way to do this is with drug-coated nanoparticles controlled by magnetic fields. Indeed, the nanoscale scientific revolution has hardly just begun, and there are many important and exciting basic physical properties that must be understood and many scientific challenges that must be overcome before nanomaterials can be applied to the world's problems.

One of the major challenges with nanoscale materials is that the fabrication technique is expensive and time consuming, and it is difficult to control nanoscale materials parameters to a high degree. In order to fulfill the basic requirements for industrial applications, nanoscale materials must be able to be manufactured on a large scale at a
low cost and with a good degree of control. One way to do this is by using the bottom-up
technique of chemical self-assembly. Here, constituent materials assemble themselves by
acting as building blocks under the influence of some external stimulus such as an
electric field.

However, very little research has been done on the basic physics of such methods, either
on the fabrication of the materials or on the basic physical properties of bottom-up
synthesized materials themselves. The boom in nanoscale science gives us a fantastic
opportunity to explore the many fascinating and bizarre physical properties of nanoscale
materials. These properties include electron transport that does not obey normal 3-
dimensional laws, but rather acts as a 1- or 2-dimensional quantum system, and optical
properties that are unlike any in macroscopic bulk materials due to the unique ordering of
nanostructure of the bottom-up synthesized materials.

A cheap, simple, and reliable way to fabricate nanostructures is by utilizing the
electrochemical anodization method. It is a well-known technique for fabricating many
nanomaterials. These materials include highly ordered titania nanotube arrays, a highly
ordered nonporous Alumina. These arrays are formed by electrochemical anodization of
titanium foils and have demonstrated some remarkable properties that have successfully
given a potential for a large number of diverse applications, including solar cells,
hydrogen sensors, water splitting, biofiltration membranes and catalytic applications.
There is extensive work in the field to enhance and control the fabrication of these
nanotube arrays, but very little work done to explore its physical properties in greater detail and how to relate these properties to the fabrication routes. Here, we focus on the electrical transport properties and the optical properties. Many potential applications depend on the transport properties of titania nanotube. The assumption that the electrical transport properties is the same when compared with the bulk titania needs to be investigated. Also, when we take into account that fabricated titania nanotube arrays form in the amorphous phase and require thermal annealing in order to transform them into crystalline nanotubes, the result is a polycrystalline nanotube array. It crystallizes in Anatase phase when annealed at temperature around 400 C and at higher temperature it crystallizes in Rutile phase.

Due to polycrystallinity, geometrical nanostructure and impurities from the fabrication process, we expect to have a difference in the electrical transport properties of these titania nanotubes from the bulk titania crystals. Another aspect that needs to be investigated is the dependence of electrical transport properties on the annealing conditions and its response and sensitivity to different gases.

Many potential applications also depend on the propagation and absorption of light by the titania nanotube arrays. There is extensive work done to enhance the absorption of solar spectrum and to shift the absorption to the visible light range. This can be achieved by lowering the band gap of the Anatase phase from 3.2 eV, which lies in the ultraviolet range, to smaller values in the visible light range. Some work has been done to
investigate the behavior of light propagation and reflection from titania nanotube arrays, especially for long (greater than 10 microns) nanotube arrays where many research groups are competing to increase the nanotube length to several hundred of microns or more.

The high aspect ratio of titania nanotube arrays provides a very large surface area. This property when combined with the semiconductor nature of titania gives rise to new kinds of applications, where surface area really matters. One of these applications is catalysis. We were intrigued by the very large surface titania nanotubes can provide, until we found an article in Science journal published 1998 [213], where Gold nanoparticles when supported on titania thin film surface showed an extraordinary catalytic property for CO oxidation reaction at temperatures below 24 C. We were motivated to use the titania nanotube arrays as support for gold nanoparticles to make this process more efficient. The goal was to come up with a method to make controlled attachment of gold nanoparticles on titania nanotubes possible.
1.2. Thesis outline

In the past section we presented the main reasons that motivated me to carry out this piece of work. It is important to provide an outline for this dissertation in a more preliminary way, so as to make the structure of my dissertation more understandable as one project. The purpose of the Outline here is to emphasize the logical order of the dissertation and to make the reader able to see the big picture before going to the technical and experimental details in each investigation.

The general goal of this dissertation is to present a full view of some physical properties of the newly discovered anodic titania nanotubes; these physical properties have been chosen based on its huge importance to both industrial applications aspect and scientific values aspect. Due to the time constraint for the PhD program, one cannot cover all the important physical properties in experimental investigations. For this reason, it has been restricted to the electrical transport, optical and catalytic properties of titania nanotubes.

In chapter 1, the various motivations that fueled me to conduct these investigations and the dissertation outline is presented.

Chapter 2 covers the background of titania nanotube arrays; in this background coverage, we will give a brief survey about titanium dioxide as a material and its proprieties, and then we will move to Titanium dioxide nanotube and its discovery, where we will mention the fabrication techniques and how to control the titania nanotube
parameters through fabrication. The potential applications are discussed in the last section of that chapter.

**Chapter 3** will be about the electrical transport properties of titania nanotube, where we will start with the motivation to study the electrical transport properties. Then we will discuss the proposed method for carrying out this investigation, which employs E-beam lithography technique for having gold contacts on a single titania nanotube sample, and its main advantage compared to other methods. Also we will mention all the technical challenges we had to overcome, for example, a major problem was the effect of thermal stress on the gold electrodes across the nanotube. We will address this problem in more detail and successful solutions for all these problems will be described. Investigating the Current (I) versus Voltage (V) behavior of single titania nanotube is the main objective of this study. For successful samples we will present the results of the IV curve for an amorphous single titania nanotube and for a thermally-annealed titania nanotube. And for the annealed nanotube, we will investigate the different annealing conditions, annealing temperature and various annealing gases, where we expect to demonstrate a variation of the IV behavior for different annealing gases and to enhance the current by increasing the final annealing temperature. Finally we will report the annealing conditions that will provide optimum electrical transport properties in titania nanotube.

**Chapter 4** concerns the optical properties of free standing titania nanotube arrays. It has been demonstrated that titania nanotubes can form free standing arrays under certain
fabrication conditions. In this regard we carried out a systematic investigation of the optical properties of this structure. In this chapter we will start with the motivation for studying the optical properties. Then we will mention the specific fabrication condition and the technique to obtain free standing titania nanotube arrays. We will mention the proposed methods for carrying out this investigation, starting with normal light incidence measurements, where we will measure the reflectance and transmittance from the two sides of the sample, open tube side and closed tube side, also known as top side and bottom side, where these measurements will provide qualitative results. In order to get quantitative results, especially to calculate the absolute absorbance of the titania nanotube arrays, we need to use integrating sphere spectrometer. By repeating those investigations for samples with different nanotube parameter, i.e. tube length and tube diameter, we will be able to have a final conclusion about the reflectance, transmittance and absorbance of light in the titania nanotube arrays.

Chapter 5 concerns the catalytic properties of titania nanotube arrays. In this chapter we will mention the details of catalytic behavior of titania nanotube arrays when decorated with gold nanoparticles. This catalytic behavior found to enhance the carbon monoxide oxidation reaction at temperate below 0°C. In the first part of this chapter, we will focus on the technical problems regarding attachment of gold nanoparticle on titania nanotube arrays. We were able to find a new technique for controlled attachment of gold nanoparticles with diameters ranging from 2 nm to 15 nm. Then we will mention the investigations we did to study the conversion of carbon monoxide to carbon dioxide with
the aid of gold decorated titania nanotube arrays to demonstrate the functionality of these samples in carrying out this reaction at room temperature.
Chapter-2

Background on Titania nanotubes

Outline

2.1. Titanium Dioxide (Titania)

2.2. Titanium Dioxide Nanotubes
2.1. Titanium Dioxide (Titania)

2.1.1. Titanium and Titanium Dioxide

Titanium is a transition metal with a silver color as shown in figure (1). It is the ninth most abundant element found in earth’s crust (Table 1) [1] and the seventh-most abundant metal. This is an important consideration for a material that is being proposed for use in wide-scale energy production. In addition to be relatively abundant as a metal, titanium has two useful properties: corrosion resistance and the highest strength-to-weight ratio of any metal.

![Titanium metal in nature and after flattening to form a foil of titanium](image)

Table (1) Element abundance on earth crest [1]

<table>
<thead>
<tr>
<th>Element</th>
<th>Abundance percent by weight</th>
<th>Abundance parts per million by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>46.1%</td>
<td>461,000</td>
</tr>
<tr>
<td>Silicon</td>
<td>28.2%</td>
<td>282,000</td>
</tr>
<tr>
<td>Aluminum</td>
<td>8.23%</td>
<td>82,300</td>
</tr>
<tr>
<td>Iron</td>
<td>5.63%</td>
<td>56,300</td>
</tr>
<tr>
<td>Calcium</td>
<td>4.15%</td>
<td>41,500</td>
</tr>
<tr>
<td>Sodium</td>
<td>2.36%</td>
<td>23,600</td>
</tr>
<tr>
<td>Magnesium</td>
<td>2.33%</td>
<td>23,300</td>
</tr>
<tr>
<td>Potassium</td>
<td>2.09%</td>
<td>20,900</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.565%</td>
<td>5,650</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.14%</td>
<td>1,400</td>
</tr>
</tbody>
</table>
Titanium is always bonded to other elements in nature, and it is widely distributed and occurs primarily in the minerals anatase, brookite, ilmenite, perovskite, Rutile, titanite, as well in many iron ores [4]. When titanium bonds only with oxygen it forms the titanium oxide compound. From all the listed minerals, only anatase, Brookite and Rutile are pure titanium oxide compounds. In their natural abundance each mineral has certain color and luster, but when grinded, all these minerals will turn into a white powder of titanium dioxide as shown in figure (2). In fact, titanium dioxide powder is “too” white to the extent that in some industrial applications it is known as “the whitest white.”
Figure (2) a- This image represents a single crystal of Anatase mineral with its black color found in nature [5]. b- This image represents a Rutile mineral with its black color found in nature [6]. c- This image represents a Brookite mineral with its red color found in nature [7]. d- This image represents titanium dioxide powder with its white color [8].

Now we will give a brief review on the properties of these titanium dioxide compounds as found in nature. We will only mention the main properties that will serve the dissertation purpose without verbosity.

2.1.2. Titanium Dioxide phases (Anatase, Brookite and Rutile)

TiO$_2$ forms in the three different structures, each containing its own similar, but different structural and optical properties. The most abundant and most extensively studied is the Rutile phase. The other two polymorphs are anatase and Brookite. Anatase is the most commonly-used form in laboratory research and is the least abundant of all three forms, while the Brookite phase, until recently, was less researched in detail. All have been studied for their photocatalytic and Photo-electrochemical applications. When found in nature the difference in these three crystal structures can be attributed to various pressures and heats applied from rock formations in the Earth. At lower temperatures the anatase and Brookite phases are more stable, but both will revert to the Rutile phase when subjected to high temperatures. Although Rutile is the most abundant of the three phases, many quarries and mines containing only the anatase or Brookite form exist.
The crystal structure of Anatase and Rutile is tetragonal; while the Brookite has an orthorhombic structure as shown in figure (3). Away from the crystal structure many physical properties of the Anatase and Rutile phases are listed in table (2). Since Brookite is less studied and does not play a considerable role in many of the titanium oxide applications, we will focus only on the Anatase and Rutile phases.

Figure (3) Geometrical illustration of the crystal structure of Anatase, Rutile and Brookite
<table>
<thead>
<tr>
<th>Property</th>
<th>Anatase</th>
<th>Rutile</th>
<th>Brookite</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
<td>Orthorhombic</td>
<td>[9, 10]</td>
</tr>
<tr>
<td>Atoms per unit cell</td>
<td>4</td>
<td>2</td>
<td>8</td>
<td>[10, 11, 12]</td>
</tr>
<tr>
<td>Lattice parameters</td>
<td>a= 0.3785 nm</td>
<td>a= 0.4594 nm</td>
<td>a= 0.9184 nm</td>
<td>[10, 11, 12]</td>
</tr>
<tr>
<td></td>
<td>c = 0.9514 nm</td>
<td>c=0.29589 nm</td>
<td>b=0.5448 nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c=0.5145 nm</td>
<td></td>
</tr>
<tr>
<td>Unit cell Volume (nm(^3))</td>
<td>0.1363</td>
<td>0.0624</td>
<td>0.2575</td>
<td></td>
</tr>
<tr>
<td>Density (Kg m(^{-3}))</td>
<td>3894</td>
<td>4250</td>
<td>4120</td>
<td>[10, 11, 12]</td>
</tr>
<tr>
<td>Index of refraction</td>
<td>2.54, 2.49</td>
<td>2.79, 2.903</td>
<td>2.61 - 2.63</td>
<td>[9, 13, 14]</td>
</tr>
<tr>
<td>Experimental band gap</td>
<td>~3.2 eV</td>
<td>~3.0 eV</td>
<td>~1.9 eV</td>
<td>[15, 16, 17, 18]</td>
</tr>
<tr>
<td></td>
<td>~387 nm</td>
<td>~413 nm</td>
<td>~650 nm</td>
<td></td>
</tr>
<tr>
<td>Ti-O bond length (nm)</td>
<td>0.1949 (4)</td>
<td>0.1937 (4)</td>
<td>0.187 ~ 0.204</td>
<td>[10, 18]</td>
</tr>
<tr>
<td></td>
<td>0.1980 (2)</td>
<td>0.1965 (2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O-Ti-O bond angle</td>
<td>81.2°</td>
<td>77.7°</td>
<td>77.0° ~ 105°</td>
<td>[10, 19]</td>
</tr>
<tr>
<td></td>
<td>90.0°</td>
<td>92.6°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td></td>
<td>[9]</td>
</tr>
<tr>
<td>Solubility in HF</td>
<td>soluble</td>
<td>Insoluble</td>
<td></td>
<td>[20]</td>
</tr>
</tbody>
</table>
Besides these three famous phases which are found in nature, another five phases have been reported to form under high pressure [19]:

1- TiO$_2$ II or srilankite, an orthorhombic polymorph of the lead oxide structure

2- Cubic fluorite-type polymorph

3- Pyrite-type polymorph

4- Monoclinic baddeleyite-type polymorph

5- Cotunnite-type polymorph

These five phases have minor significance to research and applications, so we will disregard them in this dissertation.

The natural occurrence and the abundance of titanium oxide led to wide applications for this material based on its properties. Many of these applications are related to some properties of the titanium dioxide, we will to point out each property associated with the related applications.
2.1.3. Titanium dioxide Properties and Applications.

2.1.3.1. Pigment

As shown in table (2), titanium dioxide in all its phases has one of the highest refractive indices of any known material (average $n = 2.5$) [22]. This leads to high reflectivity from the surfaces. Thus, when deposited as a thin film, its refractive index and color make it an excellent reflective optical coating for dielectric mirrors. The powder from TiO$_2$ is used as coloring agent in paints, inks, plastics, paper, synthetic fibers, rubber, painting colors and crayons, ceramics, electronic components, candy coating, glazed fruit, coloring of skim milk and flour, cosmetics, sun tanning lotions, and toothpaste. It is the most important pigment in the world, accounting for approximately 70% of total volume [23].

2.1.3.2. Photocatalyst

The photocatalytic effect reported in TiO$_2$ has attracted considerable interest over the last three decades. The meaning of photocatalytic is light-facilitated chemical reactions. TiO$_2$ adsorbs the reactants on its surface, with the energy supplied from the electromagnetic radiation (photons). TiO$_2$ facilitates the reaction between the adsorbed reactants. We will discuss in more details photocatalytic behavior of TiO$_2$ in two phases, Anatase and Rutile, in a separate section (4.1.1).

As a result of massive investigations done in these past decades, titanium dioxide photocatalysts are known to be applicable in a range of important technological areas:
• Energy

**Electrolysis of water to generate hydrogen [24–29].**

TiO$_2$ was the first material for which successful photo-electrochemical splitting of water were demonstrated [25]. Although there are other semiconductors for which impressive photo-electrochemical (PEC) efficiencies have been achieved (like Si, GaAs, InP, InGaP, CuInSe, CdTe etc.) these could only be used for continuous photo-electrolysis over relatively short periods and that only following modification of their surfaces or coating with different catalytic materials [30]. That is in addition to the high cost of these semiconductors (which are indeed widely used in electronics and photovoltaic applications) their lack of stability in aqueous solutions disqualify them as viable candidates for PEC water-splitting. They could however be used effectively in combination with TiO$_2$, perhaps embedded within a multilayered photo-electrode.

**Dye-sensitized solar cells (DSSCs) [31–33].**

Dye-sensitized solar cells consist of dye molecules supported on the surface of titanium dioxide powder, both immersed in electrolyte. As in a conventional alkaline battery, an anode (the dye loaded titanium dioxide) and a cathode (the platinum mesh) are placed on either side of a liquid conductor (the electrolyte). Under sun light exposure, the dye molecule will absorb a wide range of photon energies; electrons in the dye will be excited to higher energy levels and then injected to the titanium dioxide. These electrons are allowed to move in the external circuit to reach the cathode, forming an electrical current in the external circuit.
• Environment

Air purification [34, 35].

Titanium dioxide is reported to promote room temperature oxidation of the major classes of indoor air pollutants; it produces the highest oxidation rates of the many photo-active metal oxides investigated [36]. Photocatalytic degradation of three kinds of methyl perfluoroalkyl ethers in air takes place on titanium dioxide particles [37].

Water treatment [38–42].

Many organic compounds are decomposed in aqueous solution in the presence of titanium dioxide powder illuminated with near-UV light. There is interest in this process as a means of purifying water from undesired organic compounds and contaminants.

Self-cleaning coatings [34, 40, 41, 43].

Another TiO₂ application that is gaining in use is so-called ‘self-cleaning glass.’ Developed in Japan, this technology is currently available from several window manufacturers in the United States and Canada. It uses a thin film of titanium dioxide on a pane of glass to significantly reduce the need to clean the glass. This is done by using TiO₂’s ability to break down organic material (using UV energy from the sun) contained in dirt. The remaining dirt is then more easily washed away, and even the TiO₂’s hydrophilic surface plays an apparent role by allowing water to spread more evenly as opposed to forming clumped droplets [44]
• Biomedicine

  Self-sterilizing coatings \[45, 46\].

Visible light induced photocatalytic inactivation has been reported for different kinds of bacteria and fungi on carbon-doped titanium dioxide and titanium dioxide modified with platinum (IV) chloride complexes surfaces.

It is very clear after this quick review of the major applications for titanium dioxide as photocatalyst that the photocatalytic activity is the most important property of titanium dioxide. For this reason, we will discuss in more details the mechanism of photocatalytic activity related to the most important applications among what we listed above, namely, Electrolysis of water and Dye sensitized solar cells in sections (3.1) and (4.1).

2.1.3.3. Catalyst

Apart from the presence of light, titanium dioxide has been found to facilitate carbon monoxide oxidation reaction when decorated with gold nanoparticles at low temperatures \[47\]. Also, it showed very good activity for hydrodesulfurization reactions, a widely-used process to remove sulfur from natural gas and refined petroleum products \[48\]. Finally, it facilitates most industrial sulfur conversion reactions.
Other applications

Besides these applications, titanium dioxide is useful in many other applications, including, but not limited to, cleavage of protein that contains the amino acid proline, electronic data storage medium, sunscreen and UV absorber and many other applications. Due to usefulness in many applications, titanium dioxide is considered a very important material for research interest and also for industrial interest.

Fig (4) it shows the world consumption of titanium dioxide in 2007.

![World Consumption of Titanium Dioxide—2007](image)

Figure (4) The world consumption of titanium dioxide in 2007 [21]
2.1.4. Titanium dioxide forms.

We started this chapter by mentioning the naturally formed titanium dioxide minerals. Actually many of the applications we mentioned earlier are rarely dependent on the mining supply for this material. This is dependence on the mining supply is not economically and industrially favorable. Naturally existed impurities in these minerals present a big problem, because some of them cannot be removed; also a need for specific dopant cannot be achieved for these already formed minerals. Another factor making the dependence on naturally formed titanium dioxide unreliable is the natural abundance of these minerals in specific locations in limited quantities. These factors among other motivated the need for another supply for titanium dioxide. An industrial supply where various techniques can be developed to provide controlled fabrication methods for obtaining titanium dioxide with high degree of purity is needed. This is of key importance. Also we desire dopants to be introduced in titanium dioxide with controlled amount. Another thing that lab fabrication of titanium dioxide is able to provide is the ability to manipulate the structure of this material in the lab. There are many fabrications technique already reported; some of them are ready to move to the industrial production stage, while others are still applicable only for research investigations and development. As a result of these fabrication techniques, titanium dioxide now can be produced in different forms. It can be produced in powder form, where it has microcrystals and nanocrystals fine structure. It can be produced in thin film form on different substrates. Also it can be produced in nanotube form and in nanofibers. The powder form of titanium dioxide is the primary form used extensively in almost all applications mentioned earlier.
Thin film form has limited utility for certain application where its special properties are required for the industrial product. Nanofibers and nanotube forms are still in the research stage, where many investigations need to be done to maximize the benefit of these new nanostructures and to explore new properties of titanium dioxide related only to its nanostructure form distinct from its bulk properties.

While the purpose of this dissertation is to explore the nanotube form of titanium dioxide, it is also important to briefly review the different forms of titanium dioxide and the fabrication techniques associated with each form.

2.1.4.1. Titanium Dioxide Powder

The production of titanium dioxide in its powder form is a well-known technique and it has been employed in industrial production for many years. Titanium dioxide is produced from either ilmenite, Rutile or titanium slag. Titanium pigment is extracted by using either sulphuric acid (sulphate process) or chlorine (chloride route). The sulphate process employs simpler technology than the chloride route and can use lower grade, cheaper ores. However, it generally has higher production costs and with acid treatment is more expensive to build than a chloride plant. But the latter may require the construction of a chloralkali (electrolysis of the chloride saltwater to produce pure chlorine) unit.

The chloride route produces a purer titanium dioxide with a smaller range of particle size distribution, but anatase phase can only be produced by the sulphate route. The sulphate route is perceived to be less environmentally friendly but acid recycling or neutralization, combined with other byproduct developments, can make it as clean as the chloride route.
I) Sulphate process [49]

1- Ilmenite is dissolved in sulphuric acid to form a mixture of sulphates (titanyl sulphate).

2- The titanyl sulphate is hydrolyzed in solution to give insoluble, hydrated titanium dioxide.

3- Heating the solid in a calciner to evaporate the water and decompose the sulphuric acid in the solid. It also turns the solid into seed crystals which can be milled to the size needed.

II) Chloride process [49]

1- Ilmenite is fed into a chlorinator together with coke and chlorine to make titanium chloride.

2- Oxidation of titanium chloride by burning it in oxygen together with another combustible gas (often carbon monoxide).

3- Adding seed crystals, the titanium dioxide is formed as a fine solid in a gas stream and is filtered out of the waste gases.

Table (3) comparison between the two methods for fabrication powder of titanium dioxide nanoparticles [76]

<table>
<thead>
<tr>
<th>Chloride Process (CP)</th>
<th>Sulfate Process (SP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less flexible due to raw material quality</td>
<td>Wider range of raw material – especially Ilmenite – available</td>
</tr>
<tr>
<td>Better product quality regarding the optical and chemical properties</td>
<td>Product quality of Rutile base material is lower</td>
</tr>
<tr>
<td>Production of anatase pigment is not possible</td>
<td>Production of anatase pigment is possible</td>
</tr>
<tr>
<td>Continuous Process</td>
<td>Batch process</td>
</tr>
</tbody>
</table>
III) The sol gel process

This is another new method which has been used recently in production of powder of titanium dioxide nanoparticles. The Sol–Gel process has the advantages of high purity in comparison with sulfate or chloride processes and easy application to thin film processes [50-55]. In the Sol Gel method, particle size and the phases of resultant TiO$_2$ can be successively controlled by changing peptizing parameters, such as temperature and acid addition (type and content). The TiO$_2$ particles dissolve and recrystallize into Rutile or anatase phase as a function of peptization temperature [56-61].

**Synthesis**

a) Dissolve titanium isopropoxide (Ti (OC$_3$H$_7$)$_4$) [62] or titanium tetraisopropoxide [50] in anhydrous ethanol, and mix with a water–ethanol solution.

b) Rigorous stirring at room temperature, White precipitates of hydrous oxides are produced instantly.
c) The amorphous precipitates are then subjected to either calcination or hydrothermal treatment to obtain either Anatase or Rutile phase.

The final product is a white powder of pure titanium dioxide nanoparticles as shown in figure (5), when this powder is examined using SEM, nanoparticle size can be investigated (particle shape and particle size) as shown in figure (6).

![Figure (5) Powder of titanium dioxide nanoparticles](image1)

**Figure (5) Powder of titanium dioxide nanoparticles [63]**

![Figure (6) Scanning electron microscope (SEM) image of titanium dioxide nanoparticles](image2)

**Figure (6) Scanning electron microscope (SEM) image of titanium dioxide nanoparticles, nanoparticle range (10nm -300 nm) (pictures courtesy of University of Washington researchers) [64]**
2.1.4.2. Titanium Dioxide Thin Film

Many applications require a thin film of titanium dioxide to cover certain surfaces, this due to its chemical and biological inertness. For this reason there was a need to have techniques to provide a thin film of titanium dioxide on certain surfaces either by deposition or precipitation.

I) Sol-gel Method [65, 79]

Sol-gel method mentioned earlier was found to provide a thin film of titanium dioxide. This can be done by either using a dip-coating technique or a spin-coating technique for a substrate. The advantage of this method is the good precision in obtaining a film of the desired phase. Also there is no thermal stress formed on the substrate as compared with sputtering method mentioned below.

II) Sputtering Method [66]

Sputtering technique is well known method to obtain thin film of metals and other materials. This has to be done in inert gas media, usually Argon. Titanium dioxide films with large and controllable microstructure have been prepared by a low temperature sputtering deposition method (DC magnetron sputtering). The sputtering target is ultra-high purity Ti plate while the sputtering gas is a mixture of high pure O₂ and Ar. The role of Argon ions (plasma) is to bombard the surface of the Ti target with high energy to eject Ti atoms, while the presence of oxygen in plasma phase is to react with these atoms to from titanium dioxide which later will be deposited on the substrate.
III) Pulsed Laser Deposited Method [67-69]

Several novel vapor deposition techniques have recently been developed that utilize energetic vapor species to achieve dense films. Pulsed laser evaporation is one of these techniques, where energetic ions are generated in the laser-induced plasma. The heat emission from the source in this technique is less than that in conventional evaporation techniques due to the pulsed and localized nature of laser heating. This is advantageous for evaporation onto heat sensitive substrates. TiO$_2$ was deposited in a pulsed O$_2$ plasma environment, where laser pluses heat the Ti target, Ti atoms will evaporate and react with the O$_2$ plasma to form TiO$_2$, and these will deposit on a substrate. Another advantage of this technique is it can precisely control the deposition of titanium dioxide in Anatase and Rutile phases with certain crystal orientation [68, 69]

Other methods

The other methods which been reported in thin film deposition include, but are not limited to: molecular beam epitaxial (MBE) [70], laser molecular beam epitaxy [71, 72], Electrophoretic Deposition (EPD) [73] and Metal Organic Chemical Vapor Deposition (MOCVD) [74, 75].
2.1.4.3. Titanium Dioxide Nanofibers

The powder and thin film forms of many materials are well known, and they have been around for more than a century for many materials. In the past decades, new forms of solid material have been reported. Due to their regular nanostructure shape, these forms exhibit properties different from the bulk structure and are called the “nanostructure” form of a given material.

Many nanostructures have been reported: nanoparticles, nanofibers, nanotubes, nanopores, nanobelts and other structures. For this dissertation, we will discuss the nanofiber form and present a detailed review of the nanotube form.

The nanofiber form is a fiber or wire of a diameter in nanometers and has a very high aspect ratio (its length divided by its diameter). The very small diameter and the very large length classify this material as a one-dimensional structure, which is different from the thin film form (two-dimensional structure) or the regular bulk form (three-dimensional structure). A film of titanium dioxide nanofiber can be grown on a substrate using different techniques.

I- Sol-gel method with the aid of anodic alumina template [77, 78]

The fabrication process involves using the standard Sol-gel method [50-62] and the anodic alumina template as follows

a) Dissolve the titanium isopropoxide in ethanol/HCl/water solution.

b) Immerse alumina template in solution for few seconds, then leave to dry in air.

c) Heat the alumina template in tube furnace for few hours at 400 °C.
Titanium dioxide will form nanofiber structures inside the nanopores of the alumina, and then the alumina can be removed by dissolution in phosphoric acid. Another method to enhance the deposition inside the pores is by having the alumina template on a conducting substrate. Under electric-field effect titanium dioxide will be guided to form inside the nanopores of the alumina template. This technique is known as electrophoresis technique [78]. The SEM image of the resulting titanium dioxide nanofiber is shown in figure (7).

![Titanium dioxide nanofiber SEM image](image)

**Figure (7) Scanning electron microscope image titanium dioxide nanofiber form by using Sol-gel method with the aid of alumina nanotemplate and electrophoresis technique. [78]**

**II- Electro-spinning Method**

Electro-spinning is a known technique to fabricate polymer fibers in micro and nanoscale. Recently this technique is reported to have a successful fabrication of titanium dioxide nanofiber [80]. The method can be explained as follows,
a) The titanium tetraisopropoxide is dissolved in a mixture of ethanol and acetic acid.

b) Feed this solution into plastic syringe equipped with stainless needle.

c) Apply high DC voltage between the metallic needle and a conducting substrate below the tip of the needle.

d) By pumping the solution into the needle, the solution will become charged, and the electrostatic repulsion on the surface of the solution will counter the action of the surface tension. As a result, the solution which emerges from the needle will not form droplets, it will form a very tiny streams. These streams will become much thinner and dry up very fast near the substrate. The result is a nanofiber deposited on the substrate as shown in figure (8).

Figure (8) Scanning electron microscope images of a) Titanium dioxide nanofiber mat. b) Titanium dioxide nanofiber on a substrate
2.2. Titanium Dioxide Nanotubes

In the past section we reviewed the different titanium dioxide forms. Recently discovered titanium dioxide nanotube is considered one of the best forms of titanium dioxide. This is because of its tubular structure which will improve the functionally of titanium dioxide in many applications, namely water splitting and dye synthesized solar cell applications. The large surface area provided from the nanotube walls (inside and outside surfaces) in addition to the perfect porosity structure of the hallow nanotube will facilitate light harvesting and allow for much larger reaction interface. In the following sections, we will survey the known fabrication techniques for formation of titanium dioxide nanotubes.

2.2.1. Template-directed method

The first report of titanium dioxide nanotube was in 1996 [81], where Hoyer reported the formation of titanium nanotube array using PMMA template. The process involved many steps as shown in figure (9).

a) Preparation of Aluminum oxide porous template.

b) Coating the Aluminum oxide with polymer.

c) Removing the Aluminum oxide template and polymer negative type structure is left which serves as the mold instead of the porous.

d) Electrochemical deposition of titanium dioxide onto the PMMA mold.
e) Removing the PMMA mold leaving behind titanium dioxide nanotube array as shown in figure (10).

Figure (9) An illustration of the process for electrochemical deposition of titanium dioxide nanotube on the PMMA mold [81]

Figure (10) Scanning electron microscope image of first titanium dioxide nanotube ever fabricated [81]
The template method is an extensively used technique in fabricating titanium dioxide nanotubes and other nanotubes. Generally we can classify the templates into two categories from geometrical point of view: positive template and negative template as shown in figure (11).

![Figure (11) Illustration of a) positive template b) negative template](image)

This method has been used by many groups and combined with many deposition techniques to fabricate titanium dioxide nanotubes with specific geometry and specific crystal structure. Shin et al have reviewed all possible routes and used the template method in fabricating oxide nanotubes [82]. Below is tabular review of the titanium dioxide nanotube fabrication by template methods:

<table>
<thead>
<tr>
<th>Template type</th>
<th>Deposition method</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive template</td>
<td>Solution-based deposition</td>
<td>[83,84]</td>
</tr>
<tr>
<td></td>
<td>Electrochemical deposition</td>
<td>[85]</td>
</tr>
<tr>
<td></td>
<td>Biomineralization</td>
<td>[86,87]</td>
</tr>
<tr>
<td>Negative template</td>
<td>Solution-based deposition</td>
<td>[88-95]</td>
</tr>
<tr>
<td></td>
<td>Atomic layer deposition (ALD)</td>
<td>[96,97]</td>
</tr>
</tbody>
</table>
2.2.2. Hydrothermal Method (Sol-Gel)

In 1998 Niihara et al reported the first evidence that titanium oxide nanotubes can be obtained easily via chemical treatment, without the need for molds for replication or templates [98]. He employed the well-known sol-gel method in specific process which yielded novel nanotubes. The process involves a lot of precise chemical steps, which will not be mentioned in this section, and it is a very long process, with certain steps requiring five days of incubating the solution. The final product is a powder of titanium dioxide nanotubes with needle shape as shown in figure (12).

![Image](image.png)

Figure (12) a) Scanning electron microscope image of a titanium dioxide nanotube formed by Sol-gel method. b) Transmission electron microscope image of titanium dioxide nanotube [98]

The hydrothermal method was extensively investigated and refined to control the fabrication of titanium dioxide nanotubes and to enhance the crystallinity in the nanotube as reported in many literatures [99-106].
2.2.3. Electro-spinning Method

Electro-spinning is a new method for fabricating nano and microfibers and tubes. The method is a very simple idea which employs high electrical charge to overcome the surface tension of certain solutions. As a result, very fine streams of the solution can be produced. These streams, when reaching the substrate, will dry up and leave only very fine fibers as described in figure (13).

Figure (13) Scheme of the electro-spinning technique for nanofiber fabrication [107]
The method can be modified to produce fine tubes. By injecting oil in the solution near the syringe and aiming to have an oil channel inside each stream, solution stream and oil channel will become very fine when subjected to high electrical charge. Thus, when drying, the oil channel will evaporate and the stream will dry up to form fine tubes in micro or nanoscale as shown in figure (14). This method was used recently to fabricate titanium dioxide nanotubes as shown in figure (15) [108, 109, and 110].

![Scheme showing a typical procedure for direct preparation of ceramic nanotubes by electro-spinning. The spinneret was fabricated from two coaxial capillaries, through which heavy mineral oil and an ethanol solution.](image)

**Figure (14)** Scheme showing a typical procedure for direct preparation of ceramic nanotubes by electro-spinning. The spinneret was fabricated from two coaxial capillaries, through which heavy mineral oil and an ethanol solution. [109]

![Scanning electron microscope image of titanium dioxide nanotubes fabricated by Electro-spinning method](image)

**Figure (15)** Scanning electron microscope image of titanium dioxide nanotubes fabricated by Electro-spinning method [110]
2.2.4. Electrochemical Anodization method

2.2.4.1. Electrochemical anodization process

Electrochemical anodization is a process of oxidizing a bare metallic surface. This oxidization process is done by the effect of applied electric field between this metallic surface and another chemically inert metal when both are immersed in a given electrolyte. The anodization process acts to uniformly oxidize the surface of the required metal. The oxide layer is controlled by many factors; in most cases, the main factors that control the oxide layer properties are the applied voltage, the electrolyte, and the duration of the anodization process. The anodization can be done through two different setups, two-electrode anodization cell or three-electrode anodization cell as shown in figure (16).

![Figure (16) Scheme for a) two electrodes and b) three electrodes anodization cell.](image)

In the two-electrode cell, the positive terminal of a DC power supply is connected to the given metal which acts as the **anode**, and the negative terminal is connected to platinum mesh which acts as the **cathode**. Both anode and cathode are immersed in a specific electrolyte. Under
appropriate voltage, when the DC power supply is switched on, an electric field is generated in the electrolyte which pulls the positive ions (hydrogen ions) towards the cathode and the negative ions (oxygen ions) towards the anode. At the metal surface, the oxygen ion loses its electrons to the metal atoms and bond with these atoms to form a metal oxide. After the first wave of oxygen ions reach the metallic surface, a metal oxide layer forms and covers the metallic surface. The successive waves of oxygen ions have to diffuse through the recently formed oxide layer to reach the metallic surface underneath and react with those atoms to form another oxide layer under the older one. In time, the oxide layer grows and becomes thick, so the diffusion rate is slower and weaker. If this process continues, only the oxide layer will reach a critical thickness where it is impossible for oxygen ions to diffuse to reach the metallic surface. Another process which keeps the anodization reaction going is the dissolution of the oxide layer in the electrolyte. Most electrolytes dissolve metal oxide; in this case, the first layer of the oxide to dissolve is the oldest layer or the first layer formed.

As a result of these two combating reactions, oxidation at the metallic surface and dissolutions at the oxide surface, the thickness of the oxide layer is controlled. On the other hand the positive hydrogen ions are pulled toward the cathode where it receives electrons and hydrogen gas is formed in the form of bubbles. At equilibrium, ionic current is continuously flowing in the electrolyte while electrical current is flowing in the external circuit. The thickness of the oxide layer can be increased by choosing conditions that will make the oxidation rate higher than the dissolution rate, which will slowly increase the oxide layer thickness. This can be observed by noticing the current drop in the external circuit as the oxide thickness increases.
2.2.4.2. Fabrication of nanostructures by electrochemical anodization

In this section we will have a historical review about the role of electrochemical anodization in early fabrication of metal oxides. The first reports of the systematic study of electrochemical oxidation of metals date back to the beginning of the early nineteenth century. In the early twentieth century, this early scientific interest was supplemented by commercial interest in the use of anodic oxide coatings for adding protective and decorative coatings on aluminum and aluminum alloys. The first commercial anodizing process was patented in 1923 by Bengough and Stuart for protecting aluminum and its alloys from corrosion by means of an anodic treatment. In 1936, Caboni reported the possibility of coloring anodic aluminum film using certain techniques. These techniques were widely used as a means to coat tableware, kettles, car bodies and other commodities [111, 112]. However, it was only after the availability of microscale characterization techniques, like scanning electron microscopy (SEM), that it was also discovered that well-ordered nanoscale structure are obtainable by electrochemical anodization as shown in figure (17) [113].

The majority of publications on electrochemical anodization phenomena deal either with the anodization of aluminum or of silicon. In the case of aluminum noteworthy milestones are:

1) The work of Keller and his coworkers [114] in 1953 describing a porous alumina model as a hexagonally close-packed duplex structure consisting of porous and barrier layers.
Also, they demonstrated the relationship of an applied potential with the geometric features of the hexagonal porous structures such as the inter-pore distance and pore diameter.

2) The first review paper dealing with anodic oxide films on aluminum by J. W. Diggle and T. C. Downie in 1968[115].

3) The studies of the Manchester group led by Thompson and Wood in the decades from 1970 to 1990 [116]. The 1970 article by O’Sullivan and Wood “The Morphology and Mechanism of Formation of Porous Anodic Films on Aluminum” [117] is one of the most cited articles on anodization of aluminum to obtain porous alumina structures.

Figure (17) a) Scanning electron microscope image of anodic aluminum oxide surface (top view) [118]. b) 3 dimensional diagram of the anodic aluminum surface

In regard to a theoretical understanding of electrochemical anodization, Thompson and Wood attributed the inherent instability of ‘field focusing’ as the mechanism for pore
creation in the barrier oxide as shown in figure (17). In their papers they suggest that the theoretic modeling of the pore formation mechanism in alumina is analogous to that for other porous materials which can be obtained via anodic treatment. Two comprehensive current reviews of nanoporous alumina are that of L. Menon [119, 120] and that of S. Shingubara [112].

Figure (18) A schematic diagram from O’Sullivan and Wood’s paper (1970) “The Morphology and Mechanism of Formation of Porous Anodic Films on Aluminum”[117] illustrating their theory that it is ‘focusing’ of electric field lines through the barrier layer that causes pore formation. The original caption reads: “Schematic representation of irregular barrier layer thickening and the distributions of current during pore initiation in pore-forming electrolytes.”
2.2.4.3. Fabrication of titanium dioxide nanotubes by electrochemical anodization

In 1999, Zwilling et al reported for the first time the possibility of fabricating self-organized porous titanium dioxide by electrochemical anodization of Ti-based alloy in an acidic, fluoride-based electrolyte [121,122]. The actual start of this method was in 2001, when Gong et al fabricated self-organized, highly uniform titanium dioxide nanotube arrays by anodizing titanium in an aqueous dilute HF electrolyte [123,124a]. Their discovery opened a huge field of research interests in mastering the electrochemical anodization method; this was driven by the belief of many research groups that the huge success of electrochemical anodization method in porous aluminum oxide can be achieved in the case of titanium dioxide nanotubes. In less than 10 years, researchers were able to refine the method and enhance the technique. The method evolved through four generations, each of which represents an important leap in the fabrication ability, namely the nanotube length. In the following sections we will go over these four generations.

Electrochemical anodization method has many advantages over all other fabrication techniques, these advantages includes, but not limited to,

a) **Simplicity**, it is a one step process that starts from a titanium foil and end up with array of titanium dioxide nanotube arrays.
b) **Scalability**, it is applicable for micro scale anodization for research, also extendable to meters in scale for industrial applications without losing control over the nanotube parameters.

c) **Economical favorable**, the cost of titanium dioxide nanotubes fabrication through this method is considered the cheapest amongst all other fabrication methods. The cost is just for the price of the titanium foil and the acids, and they can be reused many times until completely consumed.

d) **Control**, No other method offers better control over the nanotube parameters than the electrochemical anodization. It has a very narrow distribution of nanotube parameters (nanotube length, nanotube diameter and nanotube wall thickness) for each fabrication recipe, and through slightly variation of the fabrication recipe, a very wide range of nanotube parameters can be achieved. It has the ability to precisely tune the nanotube parameters from a wide range of selections.

e) **Structure**, One of the fascinating results of this method its ability to order the structure of the nanotubes in precise arrays. This makes it a self-engineered method ready for usage in many anticipating applications.

For these reasons primarily this method is the only method investigated in my dissertation.

### 2.2.4.3.1. Fluorine based electrolyte

In the following section we will follow the classification that Grimes set in his wonderful book about titania nanotube [124b] which we consider as my main reference in the section.
He classified the fabrication progress over the last decade into four generations. We will cover the first three generation of fabrication. All are based in variation in the electrolytes but they share Fluorine ions as the main constituent in these different recipes. The fourth generation has Chlorine ions instead of the regular Fluorine ions in its recipe.

**The First generation (HF electrolyte)**

The oldest method for fabricating titanium dioxide nanotube arrays is what Gong *et al* reported in 2001 [123]. The method involves HF acid as the main constituent of the electrolyte and different other components, and a range of applied voltages and corresponding duration for maximum nanotube length as shown in table (1). Let us consider the very basic recipe of 100 ml of 0.5 M HF acid as electrolyte and applied DC voltage of 10 volt for 40 minutes of anodization to a pure titanium foil of area (1x3) cm². After the anodization, arrays of titanium dioxide nanotube are formed and cover completely the titanium surface as shown in figure (19).

![Figure (19) a) Top view scanning electron microscope image of titanium dioxide nanotube arrays, b) Side view scanning electron microscope image of titanium dioxide nanotube arrays and remaining titanium foil underneath with tube length around 300 nm.](image)
The nanotubes are opened from the top and closed at the bottom and vertically oriented. These nanotubes form robust arrays; it is strongly attached to the titanium surface underneath, which may work as a conducting surface for certain applications. An illustration for this structure is shown in figure (20).

![Diagram](image)

Figure (20) Illustration of the electrochemical anodization of titanium foil and the formation of titanium dioxide nanotube arrays on the surface of the anodized titanium foil a) before anodization, b) after anodization

**Parameters involved:**

Beside the electrolyte composition, there are four main parameters in this method which controls the process, a) the applied voltage, b) the anodization period, c) the temperature of the electrolyte, d) the cathode material. We will have brief review on the role of each one of those four parameters.

A) **The Applied Voltage**

Based on reported information [125,126] about the effect of the applied voltage and by carrying out independent study, we were able to investigate the effect of the applied
voltage on the nanotube diameter, as shown in figure (21). There was a linear relationship between the applied voltage and the nanotube diameter, for a range of voltages from 10-20 volt, as shown in figure (22).

Figure (21) Scanning electron microscope images of titanium dioxide nanotube arrays fabricated at a) 11 V, b) 15 V and c) 20 V
Figure (22) A graphic representation of the linear relation between the applied voltage (V) in the electrochemical anodization process and the inner diameter (D) of the produced titanium dioxide nanotubes

B) The Anodization Time

The reported information from lectures [127] confirms that there are two critical times in the anodization process. The time in which the nanotube will start forming ($T_s$) and stop growing ($T_F$). In the very beginning of anodization process the anodization tends to form a porous, non-tubular, and spongy like structure. Then when reaching the critical time $T_s$, the anodization starts yielding a highly ordered tubular structure in the oxide layer as shown in figure (23). At that moment the nanotube length is its minimum; after this critical period $T_s$, the nanotubes grow until reaching the maximum possible length at the critical saturation period $T_F$. After this time, any growth in the nanotube will be canceled by the dissolution in the electrolyte. Many research groups don’t have much
concern about the starting critical time, but they care about the final critical time which determines the end of the anodization process. In this dissertation we will consider $T_F$ as the anodization time ($T$).

Figure (23) Scanning electron microscope top-views (a–f) of titanium dioxide nanotube arrays formed at 20 V in 0.5 wt.% HF acid electrolyte at different anodization time (a) 10 s, (b) 30 s, (c) 60 s, (d) 200 s, (e) 800 s, and (f) 1,800 s [127]
C) Electrolyte Temperature

Another factor affecting the fabrication of titanium dioxide nanotube arrays is the temperature of the electrolyte. Most samples are done in room temperature but Mor et al [128] reported that only within certain ranges of electrolyte temperatures can titanium dioxide nanotubes be produced. Their finding extended to investigating the dependence of the nanotube wall thickness on the temperature within this permissible range. The increase in the electrolyte temperature tended to produce titanium dioxide nanotubes with thinner walls [128] and shorter lengths, as seen in table (5)

<table>
<thead>
<tr>
<th>Anodization temp</th>
<th>wall thickness(nm)</th>
<th>tube length(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5°C</td>
<td>34</td>
<td>224</td>
</tr>
<tr>
<td>25°C</td>
<td>24</td>
<td>176</td>
</tr>
<tr>
<td>35°C</td>
<td>13.5</td>
<td>156</td>
</tr>
<tr>
<td>50°C</td>
<td>9</td>
<td>120</td>
</tr>
</tbody>
</table>

Table (5) Average Wall Thickness and Tube Length of 10 V Titania Nanotube Arrays Anodized at Different Bath Temperatures [128]

D) Cathode Material

The last factor affecting the fabrication of titanium dioxide nanotubes is the Cathode material. Allam et al [129] and others [130,131] reported a change in the nanotube morphology based on a change in the material of the cathode. They carried out the same
anodization conditions expect for different cathode material, where they found a significant impact on the titanium dioxide nanotube morphology. Table (6) has the results he reported.

**Table (6) The cathode materials tested, grouped according to their position in the periodic table, with the average diameters and lengths of the nanotube arrays fabricated using these cathode materials, 10 h anodization duration, in both aqueous and EG electrolytes [129]**

<table>
<thead>
<tr>
<th>Group</th>
<th>Cathode material</th>
<th>Fabricated nanotubes in aqueous electrolytes</th>
<th>Fabricated nanotubes in EG electrolytes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Average diameter ±5–7 (nm)</td>
<td>Average length ±10 (nm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Average diameter ±5 (nm)</td>
<td>Average length ±10 (nm)</td>
</tr>
<tr>
<td>Pt-group elements</td>
<td>Ni</td>
<td>143</td>
<td>1200</td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>134</td>
<td>1435</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
<td>105</td>
<td>1520</td>
</tr>
<tr>
<td>Non-Pt transition elements</td>
<td>Fe</td>
<td>99</td>
<td>2470</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>135</td>
<td>1900</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>81</td>
<td>1265</td>
</tr>
<tr>
<td></td>
<td>Ta</td>
<td>140</td>
<td>1175</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>91</td>
<td>690</td>
</tr>
<tr>
<td>Non-transition elements</td>
<td>C</td>
<td>143</td>
<td>1300</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>96</td>
<td>570</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>147</td>
<td>1220</td>
</tr>
</tbody>
</table>

Now we have an overview of the role of each of the four parameters that can affect the fabrication of titanium dioxide nanotube independently from the electrolyte type, in the following section we will show the impact of varying the electrolyte which still have HF as the main constituent while adjusting the voltage and the anodization period for each case to optimize the fabrication of titanium dioxide nanotubes.
I) HF electrolytes

The main recipe of HF electrolyte is found to yield a limited range of titanium dioxide nanotube lengths (≤ 500 nm) and diameters (25-75 nm) even by varying four parameters we mentioned earlier [123,124,125,128,127,132,133,134]. Mixture of HF with another acid enhances the anodization process or the nanotube properties; this was confirmed by many investigations as follows.

- Electrolyte formed by mixing HNO$_3$ + HF or H$_3$BO$_3$+HNO$_3$+HF results in nanotubes possessing significantly greater photo-electrochemical properties [135,132].
- Electrolyte formed by mixing H$_3$PO$_4$+HF results in nanotubes of length up to 1.1 µm [136,137,138].
- Electrolyte formed by mixing H$_2$SO$_4$+HF results in nanotubes of diameter up to 140 nm [139,140,141,142].

II) NH$_4$F Electrolytes

The high rate of titanium dioxide nanotube dissolution in HF based electrolytes make the maximum length of the nanotube limited to < 1 µm [142]. There was a great need to increase the length of the nanotube, and this led to an idea of replacing the HF based electrolyte by Fluorine based electrolyte. This was successfully reported by using an electrolyte made of NH$_4$F dissolved in the following acids: H$_2$SO$_4$ [143], (NH$_4$)$_2$H$_2$PO$_4$ [144], (NH$_4$)$_2$SO$_4$ [145], and CH$_3$COOH [147,148]. This replacement was able to increase the maximum nanotube length. For example, nanotubes with lengths up to 4 µm were reported with (NH$_4$)$_2$PO$_4$+NH$_4$F electrolyte [144].
2.2.4.3.2. Second Generation

The limitation of nanotube length is due to the fact that the chemical dissolution rate of the nanotube walls outstrips the field enhanced oxidation rate responsible for forming new nanotube walls. There were many trials to solve this problem in the first generation. The effect of the electrolyte pH was a key to solve this problem. It has been reported that the electrolyte pH affects both the behavior of the electrochemical etching and the chemical dissolution. It was found that higher pH electrolytes yielded longer nanotubes [125]. These results led to the idea of having localized acidification at the nanotube bottom to enhance the electrochemical anodization rate while a higher pH value is established at the nanotube top. This can be done by using a buffered neutral solution as the electrolyte and choosing the proper voltage and anodization time. This method of using a buffered neutral solution is the main feature of the second generation. The buffer in most cases is NaOH with Fluorine containing solutions NaF [146,148,149,150,151], NH₄F [125,152,144,153,154,150], or HF [155]. In many of these reported trials, using a buffered neutral solution did show an increase in the nanotube length, as well as an increase in the nanotube diameter beyond 100 nm.

2.2.4.3.3. Third Generation

Another way to address the fast chemical dissolution rate, which limits nanotube growth, is to reduce the water content in the water based electrolyte (aqueous electrolyte). This can be done by using another polar non-aqueous electrolyte with little water content. Under these conditions, polar organic electrolytes would have much less oxygen compared with water based electrolyte. This reduces the oxidation reaction responsible
of the formation of nanotubes, but the reduced water content also decreases the chemical
dissolution of the oxide in fluorine-containing electrolytes [156], which preserves the
nanotube walls from dissolution and thus enables the formation of longer nanotubes. This
technique is the main feature of the third generation of titanium dioxide nanotube
fabrication. It is done by many different polar organic solutions.

- **Formamide and N-Methyl Formamide**

  It was reported that a polar organic electrolyte consists of 99% Formamide (FA)
  and/or 99% of N-methylformamide (NMF) solutions containing 1-5 wt. % of
deionized water and 0.3-0.6 wt. % NH$_4$F (98%) yield a very long titanium oxide
  nanotubes up to 70 µm when anodized for 48 hours under 35 volt [157]. The
  nanotubes form a smooth array as shown in figure (24). For longer anodization times,
  the chemical dissolution rate prevails and results in shorter nanotubes (88 hours
  yielded 30 µm and 164 hours yielded 10 µm). Other reports using the same
  electrolyte to fabricate these long nanotubes include Photoelectrocatalytic
  Degradation of Phenol [158] and Study of the cation effect on electrochemical
  fabrication of titanium dioxide nanotubes [159].

  Another interesting result is the relation between the voltage and nanotube length, as
  mentioned earlier for HF electrolytes. Higher anodization voltages produce
  nanotubes with bigger diameter. The same result was found in non-aqueous
  electrolytes, but with significant increase in the nanotube length due to the increase
of anodization voltage, which is more apparent than the increase in the nanotube
diameter [159]. One can claim that, for some polar organic electrolyte, larger voltage
yields longer nanotubes.

Figure (24) Scanning electron microscope of titanium dioxide nanotube
fabrication by electrochemical anodization of titanium foil in Formamidenelectrolyte at 35 volt for 48hours (a) a cross section at lower magnification, (b) a
cross section at higher magnification, and (c) atop surface image [157]
-Dimethyl Sulfoxide (DMSO)

Another possible polar electrolyte for obtaining long titanium dioxide nanotubes is the Dimethyl Sulfoxide electrolyte containing F ions. Yoriya et al reported a successful fabrication of very long titanium dioxide nanotube arrays with lengths up to 100 µm as shown in figure (25). This was achieved by using an anodization potential of 60 V with an electrolyte of 2% HF in 98% DMSO for 70 hours of continues anodization [157,160]. Another recipe using potassium fluoride (KF), or ammonium fluoride (NH₄F) also reported successful fabrication of long titanium dioxide nanotubes [160]

Figure (25) Scanning electron microscope images of titanium dioxide nanotube arrays fabricated by using Dimethyl Sulfoxide electrolyte. a) 3.0% HF-DMSO electrolyte at 60 V for 70 h. b) and c) 2.0% HF-DMSO 40 V 70 h [160]
-Ethylene Glycol

The longest titanium dioxide nanotube arrays ever reported is 1005 µm length [161]. It is fabricated by Ethylene Glycol electrolyte containing fluorine ions. Ethylene Glycol showed an outstanding ability to grow longer nanotubes when compares with all the other electrolytes. This represents a great leap in the nanotube length from range of 100 µm achieved by other polar organic electrolyte [157,159,160] to the 1000 µm range achieved by Ethylene Glycol [161].

Paulose *et al* reported the successful fabrication of 134 µm long nanotubes by anodizing titanium foil in an electrolyte consisting of 0.25 wt. % NH₄F and ethylene glycol solution, samples anodized at 60 V for 17 hours [157]. Later, Prakasam *et al* reported a 220 µm long titanium dioxide nanotube by using Ethylene glycol electrolyte; in their work they explored a range of fluorine ion concentrations and anodization conditions as shown in table (3). The optimal condition to achieved the 220 µm length is electrolyte made up of 0.3 wt. % NH₄F dissolved in mixture of 2% DI water and 98% ethylene glycol, anodization voltage 60 volts, and anodization time of 17 hours. The longest nanotube is achieved by using electrolyte consisting of 0.5 wt. % NH₄F dissolved in mixture of 3% DI water and 97% ethylene glycol under 60 volt for 216 hours.

The titanium dioxide nanotubes formed through the Ethylene Glycol is highly ordered with very smooth surfaces. It is considered the best among the aforementioned electrolytes as shown in figure (26).
Table (7) Summary of nanotube length (in μm) obtained by varying the concentration of H₂O from 1.0 to 3.0 vol. % and NH₄F from 0.1 to 0.50 wt. % in Ethylene Glycol (Anhydrous) with Respect to Fresh and Once-Used Solution [162]

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>0.1 wt. % NH₄F</th>
<th>0.3 wt. % NH₄F</th>
<th>0.5 wt. % NH₄F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% vol. H₂O</td>
<td>fresh</td>
<td>54</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>used</td>
<td>70</td>
<td>156</td>
</tr>
<tr>
<td>2% vol. H₂O</td>
<td>fresh</td>
<td>85</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td>used</td>
<td>105</td>
<td>220</td>
</tr>
<tr>
<td>3% vol. H₂O</td>
<td>fresh</td>
<td></td>
<td>136</td>
</tr>
<tr>
<td></td>
<td>used</td>
<td></td>
<td>100</td>
</tr>
</tbody>
</table>

Figure (26) Scanning electron microscope images showing topology of a Ti sample anodized in an electrolyte comprised of 0.3 wt. % NH₄F and 2 vol. % H₂O in ethylene glycol at (a–c) 60 and (d) 65 V [162]
Figure (27) Scanning electron microscope images of a Ti sample anodized in an electrolyte comprised of 0.25 wt. % NH₄F + 1% H₂O in ethylene glycol at 60 V for 6 h showing (a) the cross section and surface of the as-anodized sample, (b) the cross-sectional and surface view after ultrasonic cleaning, and (c) the top surface view after ultrasonic cleaning revealing self-organized structure. The insert shows a high magnification image of the nanotube array top surface, (1-3) images of different magnification showing the bottom and partial cross section of a self-standing nanotube array film, synthesized by 60 V in an ethylene glycol electrolyte containing 0.3 wt. % NH₄F and 2 vol. % H₂O in ethylene glycol [162]
Glycerol

The role of Glycerol as electrolyte is similar to the role of Ethylene glycol, and fabricated nanotubes are very similar to those fabricated by Ethylene glycol as shown in figure (28). More details about the results of using Glycerol as electrolyte can be found in the following reports [163,164,165,166].

Figure (28) Scanning electron microscope images of smooth TiO2 nanotubes 7-mm long produced in glycerol electrolyte: c) top view; d) bottom view. The average nanotube diameter is approximately 40 nm and the average pore spacing is approximately 60 nm. e) Top view of an anodized sample after removal of some arrays of nanotubes. The lower part of the tubes and part of the Ti substrate surface are visible. Clearly the convex shape of the nanotube bottoms is reflected in the surface of the Ti substrate [163]
2.2.4.3.4. Chlorine based electrolyte (Fourth generation)

In the past three generations, the main ingredient in the fabrication of titanium dioxide nanotubes is the fluorine ion. This lead to a hypotheses that fluorine ions are an essential or perhaps unique requirement for the formation of nanoporous or nanotubular titanium dioxide structures because of fluorine’s unique ability to ‘dissolve’ titanium dioxide and form the complex TiF$\text{}_6^{2-}$ in solution as reported [167,168]. This hypothesis is based on the fact that all electrochemical anodically fabricated titanium dioxide nanotubes reported before had fluorine present in the electrolyte in some form or another. Typical formulations used are aqueous solutions of hydrofluoric acid or acids like sulfuric or phosphoric acid combining fluorine salts, non-aqueous polar solution containing fluorine ions. These hypotheses proved to be incorrect when Richter et al reported a successful fabrication of titanium dioxide nanotubes using chlorine based electrolytes [169].

Chlorine was not only a replacement for the more harmful fluorine, but it has offered longer nanotubes with shorter anodization time. Nanotubes up to 50 µm were fabricated in less than 5 minutes, whereas to obtain a similar length in the fluorine base electrolyte it takes up to 70 hours [170]. The main features of the fourth generation are ultrafast fabrication process and very long nanotubes. This process forms nanotubes with smaller diameter when compared with the fluorine fabricated nanotubes; the diameter is about 20 nm. There are three recipes for this chlorine based electrolyte which is 0.4 M NH$_4$Cl + 0.5 M oxalic acid, 0.4 M NH$_4$Cl + 0.5 M formic acid, and 0.4 M NH$_4$Cl + 0.05 M sulfuric acid anodized for few minutes under 17-18 voltage, the fabricated titanium dioxide nanotubes are not highly ordered as in the case of the fluorine-based electrolyte
nanotubes, especially when compared with the ethylene glycol nanotube, it form in bundles of very thin ordered nanotubes as shown in figures (29) and (30).

Figure (29) Scanning electron microscopy image of titanium dioxide nanotubes (side view) a) fabricated by anodizing titanium foil at 18 V in an electrolyte consisting of 0.5 M oxalic acid, 0.1M KCl, 0.15M NH4Cl and 0.15M KOH [169] b) fabricated by using Ethylene glycol electrolytes
Figure (30) Scanning electron microscope images showing different morphologies and views of the titania nanotubes bundles formed by anodization of titanium sheets in chlorine (0.4 M NH4Cl) containing electrolytes. The experimental conditions are not necessarily related to the morphology depicted. a) Bundles up to 10 μm long and 3 μm wide of nanotubes loosely ordered in one direction (0.5 M formic acid, 14 V). b) Tightly packed nanotubes forming ordered grains with quasi-rectangular facets (0.5 M gluconic acid, 13 V). c) Tubes agglomerations allowing a top view of the bundles (0.02 M hydrochloric acid, 17 V) d) large formations of nanotubes with a preferred growing direction (0.02M hydrochloric acid, 18 V). [171]
The main disadvantage of this fourth generation is that the formed nanotube arrays using chlorine base electrolytes do not cover all the surface of the titanium sample as it did for the fluorine-based electrolytes. Rather, it forms in certain “patches” or “bursts” of nanotubes as shown in figures (31) and (32).

Figure (31) Scanning electron microscope images of the sample surface a) after the first anodization in a HF solution; b) after the second anodization in a chloride containing solution
Figure (32) Scanning electron microscope images provide details on the formation of titanium oxide nanotubes at the surface of the titanium foil. a) A rare occurrence of a site where the nanotubes are still lying inside the bulk of the sample, tightly packed along the direction perpendicular to the surface of the sample; b) A more typical formation site, with tube bundles sticking out of the surface.
2.2.4.4. Formation Mechanism and chemistry

A) - Basics of nanotube formation – oxidation reactions

The primary oxidation reaction that occurs at the metal/oxide interface of the anode most likely is:

\[
\text{Ti (metal) } + 2\text{OH}^- \rightarrow 4e^- \text{ (to cathode)} + \text{TiO}_2 \text{ (oxide)} + 2\text{H}^+ \quad \text{(O1)}
\]

In the electrolyte protons and hydroxyls that are consumed at the cathode and anode respectively are replaced by the auto-ionization of water:

\[
\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \quad \text{(O2)}
\]

Finally, at the cathode, electrons from the anode generated in reaction (O1) are consumed typically by evolving hydrogen from the protons produced in reactions (O1) and (O2):

\[
2\text{H}^+ + 2e^- \rightarrow \text{H} \quad \text{(O3)}
\]

Together (O1+2×O2+2×O3) these reactions give the net cell reaction:

\[
\text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO} + 2\text{H}_2 \quad \text{(O4)}
\]

Figure (33) Diagram of cell during anodization showing the location of the three oxidation reactions O1-O3
This is naturally only the primary oxidation reaction and side reactions; for instance oxygen and hydrogen (or even fluorine/chlorine) evolution, also occur at the anode. That these secondary reactions occur at the anode is obvious to the experimentalist because gas bubbles appear not only on the cathode but also at the anode. However, there are significantly more gas bubbles at the cathode than at the anode.

This is to be expected since hydrogen evolution is the primary reaction at the cathode with oxygen and gas evolution reactions also being only secondary or side-reactions at the anode where the oxidation of titanium (reaction O1) is the primary electron source.

B) - Basics of nanotube formation – dissolution reactions

In addition to the oxidation reaction, dissolution reactions also occur and play a very important role in nanotube formation and morphology. It is most often suggested that dissolution occurs by the following overall reaction [125,172,163,173,168,174,175,176,177,178,157, and 179].

\[
\text{TiO}_2 \text{ (solid)} + 6\text{F}^- + 4\text{H}^+ \rightarrow \text{Ti(F}_6\text{)}^2\text{(aq)} + \text{H}_2\text{O (D1)}
\]

That is, it is believed that the oxide is primarily dissolved by the displacement of oxygen by fluorine and the concurrent/subsequent formation of water. This mechanism for the dissolution of titanium dioxide and solvation of Ti\(^{4+}\) ions involving the formation of the Ti(F\(_6\))\(^{-2}\) complex is widely accepted because of the stability and relatively low free energy of formation of the Ti(F\(_6\))\(^{-2}\) [180,181].

However, there is really no conclusive evidence that solvation does not also occur through other complexes like for instance Ti(OH)\(_4\) (whose existence has been confirmed
in non-anodic work, e.g. [182]). Hence we suggest that chemical dissolution may also occur through water forming reactions as:

\[ \text{TiO}_2 + 4\text{OH}^- + 4\text{H}^+ \rightarrow \text{Ti(OH)}_4 + \text{H}_2\text{O}, \]  
\[ \text{(D2)} \]

or:

\[ \text{TiO}_2 + 2\text{OH}^- + 2\text{F}^- + 4\text{H}^+ \rightarrow \text{TiF}_2(\text{OH})_2 + \text{H}_2\text{O}, \]  
\[ \text{(D3)} \]

etc.

However, experiments we have done on the anodic formation of porous alumina suggest that field-enhanced dissolution may very well proceed not by reactions D1-D3 but rather by the direct ejection of Ti\textsuperscript{4+} cations through:

\[ \text{Ti}^{4+} (\text{m}) + \text{TiO}_2(\text{ox}) + 6\text{F}^- \rightarrow \text{Ti}(\text{F}_6)^2(\text{aq}) + \text{TiO}_2(\text{ox}), \]  
\[ \text{(D4)} \]

Where m refers to “metal” and ox to “oxide” (refer to figure (19) for clarification) and where the Ti atoms have been ‘labeled’ as bold and italic letters to indicate the outward migration of electropositive metal atoms towards (and over) the solution interface. Hence, as the metal is being consumed by oxidation & nanotube formation some Ti atoms are being incorporated in the nanotube walls and some are ejected by field-enhanced dissolution according to mechanism D4. This field-enhanced dissolution that occurs at the nanotube (or pore) bottom is vital in that it keeps the barrier layer or ‘nanotube floor’ thickness low. A thin barrier layer corresponds to high electric fields at the nanotube bottom. This in turn leads to relatively high rates of ion transport, namely that of electronegative oxygen carrying species (OH-, O\textsubscript{2}-) that migrate inward through the oxide layer towards the metal/oxide interface and electropositive metal atoms (together with H\textsuperscript{+} cations produced by reaction O1) that migrate outwards and end up
either in solution (through Reaction D4) or in the nanotube walls. Hence, we see that the role that Reaction D4 play is that of keeping the barrier layer thin, which is a crucial condition for keeping oxidation (reaction O1) and hence nanotube formation active.

**C) - The role of fluorine and/or chlorine**

Perhaps the primary reason why virtually all authors to date cite reaction D1 as the one and only dissolution mechanism during anodic titanium dioxide nanotube formation is that this reaction overtly suggests a necessary role for fluoride ions. To date anodic titanium dioxide nanotubes have never been obtained without the use of fluorine or chlorine in the anodization electrolyte. As written, Reaction D4 appears to portray a less significant role the fluoride ions: it does not dissolve oxide and/or displace oxygen but merely allows for the energetically favorable solvation of ejected titanium cations. If the solvation of Ti$^{4+}$ cations was the only role played by fluoride ions then there should be, at least in principle, other surfactants that could conceivable do the same job (solvate Ti$^{4+}$). However, to date, no other surfactants have been found or reported. This state of affairs apparently leads most authors [125,172,163,173,168, 174,175,176,177, 178, 157, and 179] to suggest mechanism D1 as the primary dissolution mechanism enabling nanotube formation. We suggest however that Reaction D1 is not the only mechanism explaining the necessity of fluorine (or chlorine). In addition to the solvation of Ti$^{4+}$ as expressed in Reaction D4 we propose the following essential role of fluoride ions that enables nanotube formation: Whenever an electropositive Ti$^{4+}$ cation/atom reaches the oxide-electrolyte interface at the nanotube floor (oxide electrolyte interface) there are two reactions competing for the cation.
Figure (34) Schematic cross section of a nanotube showing the electric field lines present in a working cell. Most of the potential in an electrochemical cell due to the applied bias occur across the semi-conductor (oxide). The semi-conductor is thinnest at the nanotube floor. Hence, it is within the barrier layer below the nanotube bottom that the greatest potential gradient and therefore electric field is established.

Either the metal cation is ejected resulting in solvation through Reaction D4 or it is “re-incorporated” into the oxide by an oxidation reaction like Reaction O1. The relative frequency of these two reactions depends on the local concentration of oxidizing species at the electrolyte. Since both F⁻ and oxidizing species like OH⁻ and O₂⁻ are negative they will both be attracted to the positively-biased Ti/TiO₂ anode and in particular to the nanotube floors. However, these anions will repel each other and the presence of F⁻ anions would therefore dilute the local concentration of oxidizing species. This will
naturally shift equilibrium away from oxidation (Reaction O1) and barrier layer thickening towards dissolution and barrier layer thinning (Reaction D4).

Figure (35) Scanning electron microscope images showing the morphology of titanium dioxide nanotubes from the side and below. The dome-like structure shown in the schematic cross-section of figure (33) is clearly visible. The image on the left is of nanotubes fabricated using a non-aqueous solvent (ethylene glycol) and the solvent for the less ordered nanotubes on the right was water.

In summary, the presence of [F-] in the electrolyte promotes Reaction D4 in favor of Reaction O1. This balance between Reactions O1 and D4 ensures that a relatively thin barrier layer is maintained during anodization that keeps nanotube formation going. The fact that no nanotubes or pores have ever been observed in electrolytes without fluorine or chlorine suggests that the oxygen affinity of titanium is simply too high, and hence passivation too strong to allow for nanostructure formation without suppressing oxidation. The exceedingly electronegative halogen anions of fluorine and chlorine are to date the only agents that could compete with (in the sense described above) and suppress oxidation during the anodization of titanium.
Figure (36) Barrier layer of nanotubes fabricated in glycerol with 15% water. Note the ‘dome-like’ shape of the nanotube bottoms and especially the ‘thinness’ of the barrier layer below the nanotube floor illustrated in Figure (33).

Figure (37) EDX spectrum (plot of intensity (counts) vs. energy (keV)) of a titanium dioxide nanotube sample taken after fabrication but prior to annealing. The presence of fluorine was detected. Typically no fluorine can be detected post-annealing. The peaks are labeled by element and transition (K, L or M). The sample shown was anodized in 0.05M KF in ethylene glycol with 2vol% H₂O at 60V for 18h.
D)-Chemical vs. field-enhanced dissolution

Several authors make a distinction between chemical and field-enhanced (or field-assisted) dissolution of the oxide layer [183,174, 162, 176, and 157]. The group of Schmuki does not explicitly distinguish chemical dissolution from ‘field-enhanced’ dissolution as is done in the work, primarily by Grimes et al [163, 184, and 179]. They do however mention that “chemical dissolution” is enhanced at nanotube bottoms, ostensibly by a proposed ‘local acidification’ and the fact that the electric field strength there is greater. As such, Schmuki et al do implicitly recognize field-enhanced dissociation “that occurs at nanotube bottoms” although they call all dissolution by the single name ‘chemical’ dissolution and only propose the single mechanism, namely D1, for it.

**Chemical dissolution** is the dissolution process of an oxide layer or oxide nanotubes that occurs in an electrolyte even when there is no applied bias. In aqueous electrolytes the rate of chemical dissolution is expected to increase with increased acidity. The concentration of other ions such as [F⁻] and temperature could also play a role. Chemical dissolution is expected to be the major mechanism responsible for wall dissolution of nanotubes. As such, shortening of nanotubes by chemical solution at their tops is suggested as the reason for the limited length of nanotubes obtainable in aqueous electrolytes [183, 184]. Chemical dissolution also explains the phenomenon that nanotube length increases as a function of anodization time up till some optimal time after which it actually decreases upon further anodization in some electrolytes [176].
Field-enhanced (or field-assisted) dissolution occurs, however, only in the presence of an applied potential difference across the working electrode. Based on the work reported by Siejka et al. [185] on porous alumina, it is suggested that the primary mechanism for field assisted dissolution to be that of Reaction D4. We suggest that this mechanism is the dominant dissolution mechanism at nanotube bottoms under applied biases that are strong enough to form titanium dioxide nanotubes. Naturally, chemical dissolution associated with Reactions of type D1-D3 could also occur simultaneously with that of Reaction D4 at the pore bottoms and the electric field there may also have an effect on their rates. My evidence and that of Siejka et al. [185], however, suggests that the contribution of chemical dissolution to overall dissolution at the pore bottom is relatively negligible compared to that of mechanism D4 to which we designate the term ‘field-enhanced dissolution’. In summary, as do Grimes et al. [183, 162, 176, 157], we distinguish between chemical and field-enhanced dissolution. We however go one step further by associating mechanisms of the type D1-D3 with chemical dissolution and metal cation ejection according mechanism D4. It is the latter process that is implied by the term field enhanced dissolution when it is enhanced by a potential drop across the oxide layer.
2.2.4.5. Thermal annealing of titanium dioxide nanotubes

Fabricating nanostructures by the means of electrochemical anodization method has some disadvantages when compared with other methods like Sol-Gel and Chemical Vapor Deposition (CVD) special from the crystallinity aspect, where the formed nanostructure is amorphous while for the CVD method it is crystalline under certain crystal structures. The inability for the electrochemical anodization to yield crystalline nanostructure can be treated afterward by a process of thermal annealing, since titanium dioxide nanotubes is formed through electrochemical anodization one should expect the amorphous structure when examine these nanotube with X-Ray Diffraction (XRD) or Transmission Electron Microscope (TEM). Indeed TEM images showed amorphous structure for the titanium dioxide nanotubes as shown in figure (38).

![Figure (38) Smooth TiO₂ nanotubes produced in the glycerol electrolyte: a) TEM image of several TiO₂ nanotubes; b) TEM diffraction pattern of a nanotube wall; c) HRTEM image of a single nanotube [163]](image-url)
In this figure both images (a) and (c) shows visually the amorphous structure of titanium dioxide nanotubes, image (b) shows Selected Area Electron Diffraction (SAED) pattern, which confirms the absence of any crystal structure in the formed titanium dioxide nanotube.

Most of the titanium dioxide nanotube applications are based on the crystal structure of this material; especially the crystallinity in the Anatase phase which has a higher photocatalytic effect when compared with the Rutile and Brookite phases. Thermal annealing can transform the titanium dioxide from amorphous to crystalline structures. Generally speaking, the thermal annealing process for amorphous titanium dioxide is not a straight forward process with guaranteed results. It is a very tricky process, where many parameters are involved in the phase transformation, either from the amorphous phase to the Anatase phase (metastable phase) or from the Anatase phase to the stable Rutile phase – which only formed at higher temperatures when compared with Anatase phases. When we restrict ourselves to the micro and nanostructure, especially nanotubular structure, of the titanium dioxide we will find the following parameters play major role in the phase transformation process as reported by Dorian et al [19]:

- Particle size
- Particle Shape (aspect ratio)
- Surface area
- Atmosphere
- Volume of sample
- Nature of sample container
• Heating rate
• Soaking time
• Impurities (from raw materials and container)
• Measurement technique

I) **Amorphous to Anatase phase transformation**

Titanium dioxide nanotube arrays fabricated by the means of electrochemical anodization can be considered as a thin-film covering a titanium substrate. For this reason one can relate the phase transformation of these nanotube arrays to that in a thin-film of titanium dioxide with a similar length. Lee *et al* reported the onset of phase transformation from Amorphous to Anatase somewhere between 250 °C and 300 °C [186] as indicated by the XRD results in figure (39).

![X-ray diffraction of TiO2 thin as-deposited film and of films deposited at 250 °C and 300 °C. At 300 °C a distinct anatase [Ana.] (101) peak can be observed.](image)

Figure (39) X-ray diffraction of TiO2 thin as-deposited film and of films deposited at 250 °C and 300 °C. At 300 °C a distinct anatase [Ana.] (101) peak can be observed.
Grimes et al investigated this range for short titanium dioxide nanotube (<500nm). He reported the onset of phase transformation for this sample at 280 °C [187] as shown by the XRD results in figure (40).

Figure (40) GAXRD patterns of the nanotube samples annealed at temperatures ranging from 230 to 880 °C in dry oxygen ambient for 3 h. A, R, and T represent anatase, Rutile, and titanium, respectively.[187]
Titanium dioxide nanotubes can be formed in a wide range of tube diameters, wall thicknesses and tube lengths. By considering this fact and taking into account what was mentioned earlier about the effect of particle shape and size on the phase transformation, it is considerable a strong claim that each sample might have a slightly different onset temperature for the Anatase phase formation, but many research groups didn’t pay much attention to this fact; generally, they consider annealing temperature of 400°C or 450°C as a safe value that guarantees a complete phase transformation from Amorphous to Anatase.

The Anatase phase obtained by thermal annealing when investigated by the Transmission Electron Microscope (TEM) showed polycrystallinity, which is expected as a result of phase transformation by thermal annealing. Polycrystalline nanotube is less favored due to the undesired effects of the grain boundaries on the charge transport and other physical properties. This problem is considered a major disadvantage of the electrochemical anodization method, where other methods like Sol-Gel are able to fabricate a single-crystal titanium dioxide nanotube [188] as indicated in figure (41). Another problem is the phase transformation is not completed at certain temperatures. At 300°C, there is evidence of the existence of the Anatase phase but there is also evidence of the existence of the amorphous phase as shown in figure (41-b). By elevating the temperature to eliminate the amorphous phase, the unstable Anatase phase will start transforming into the stable Rutile phase as we will discuss in the flowing section. Therefore it is very tricky to get a polycrystalline nanotube made of only the Anatase phase.
Figure (41) High Resolution Transmission Electron Microscope (HRTEM) images of titanium dioxide nanotube, a) Sol-gel nanotubes, the images of a short single-crystalline anatase TiO2 nanotube (unconstrained synthesis for 23 h) with different focuses along axial direction; continuous and concentric curving of {101} planes is clearly seen although some segments of the rings are flattened [188], b) Electrochemical anodization nanotubes, two different magnification the upper shows the grain boundaries of a single Anatase crystal surrounded by amorphous phase, The lower shows a many grains as a proof of the polycrystallinity when annealed at 400°C.
II) Anatase to Rutile phase transformation

The Anatase phase is considered a metastable phase which easily transforms irreversibly to the stable Rutile phase at elevated temperature. The onset of this phase transformation is more obscure and complicated when compared with the previous transformation. The kinetics of this process typically is considered in terms of temperature and time. In terms of the former, pure bulk Anatase is considered widely to begin to transform irreversibly to Rutile in air at 600°C [189-191]; however, the reported transition temperatures vary in the range 400–1200°C [190,192-197] owing to the use of different methods of determining the transition temperatures, raw materials, and processing methods. The anatase to Rutile transformation is not instantaneous; it is time dependent because it is reconstructive [194,198,199]. Consequently, the kinetics of the phase transformation must be interpreted in terms of all of the factors that influence the requisite temperature–time conditions.

For Nanotubular structure, Grimes et al reported the onset of this phase transformation for a short titanium dioxide nanotubes (<500nm) as low as 430°C as shown in figure (27). Also he reported the complete transformation of all the Anatase phase to a pure Rutile phase at 620°C [187] and for the annealing temperatures between 430 -620°C the titanium dioxide nanotube is composed of a heterogeneous polycrystalline phase. We can summarize phase vs. annealing temperature as follows:

I) Pure Amorphous phase < 280°C
II) 280°C < heterogeneous polycrystalline phase (Anatase + Amorphous) < 430 °C
III) 430°C < heterogeneous polycrystalline phase (Rutile + Anatase) < 620 °C
IV) 620°C < Rutile phase
Chapter-3

Electrical Transport Properties

Outline

3.1. Role of Charge Transport on DSSC function

3.2. Single nanotube approach

3.3. Experimental methodology

3.5. Conclusion
3.1. Role of Charge Transport on DSSC function

3.1.1. DSSC Principle

The energy crisis is the motivation for several new inventions that can resolve this problem and avail of environment friendly resources on our planet. The extensive consumption of the fossil fuel in the past centuries ended with another great ecological crisis called “The global warming crisis”. The only alternative in the past decades was nuclear energy, which is environmentally destructive considering the nuclear waste and nuclear accidents. This has justified the search for new alternatives like solar energy; the fabrication and modification of the solar cells is the interest of many research groups all over the globe. This leads to new invention by Michael Grätzel and Brian O'Regan at the École Polytechnique Fédérale de Lausanne in 1991 [200], they invented so-called Grätzel cell also known as Dye Sensitized Solar Cell (DSSC), which represent a new idea of harvesting the solar energy through a simple mechanism. In order to understand the operation of this cell we will first describe its construction.

Construction

In the case of the original Grätzel and O'Regan design, the cell has 3 primary parts as shown in figure (42). On top is a transparent anode made of fluoride-doped tin dioxide (SnO$_2$:F) deposited on the back of a (typically glass) plate. On the back of this conductive plate is a thin layer of titanium dioxide (TiO$_2$), which forms into a highly porous structure
with an extremely high surface area. Titanium dioxide only absorbs a small fraction of the solar photons (the UV range).

![Scheme](image)

**Figure (42) Scheme represents the principle of the dye-sensitized photovoltaic solar cell as first reported in Nature by Grätzel [200]**

The plate is then immersed in a mixture of a photosensitive ruthenium-polypyridine dye (also called molecular sensitizers) and a solvent. After soaking the film in the dye solution, a thin layer of the dye is left covalently bonded to the surface of the TiO$_2$. A separate plate is then made with a thin layer of the iodide electrolyte spread over a conductive sheet, typically platinum metal. The two plates are then joined and sealed together to prevent the electrolyte from leaking. The construction is simple enough that there are hobby kits available to hand-construct them. Although they use a number of "advanced" materials, these are inexpensive compared to the silicon needed for normal cells because they require no expensive manufacturing steps. TiO$_2$, for instance, is already widely used as a paint base.
Operation

Sunlight enters the cell through the transparent electrode top contact a sequence of the operation will take place as follows

A- The incident photons strike the dye molecules on the surface of the titanium dioxide.
   Due to the broad solar spectrum, incident photons have a wide range of energies, also the dye molecule has a broad band of energy levels, therefore the dye molecules is expected to absorb all the incident photons. Upon the absorption, electrons will be excited to higher energy levels in the dye molecule.

B- Electrons in the excited states in the dye molecule have very short life time before being de-excited back. They need to be transported to another more stable level in titanium dioxide. In Anatase phase, titania has an energy gap of 3.2 eV and very low probability of electron-hole recombination, this makes the conduction band very suitable for receiving these excited electron from the dye molecule. The electrons move from the dye to the conduction band of the titanium dioxide in a process called “injection”. The energy level of the exited dye molecule should be about 0.2 - 0.3 eV above the conduction band of the TiO₂ to ensure efficient charge injection. Injection of electrons from the dye into the TiO₂ typically happens on a femto to picosecond timescale whereas charge recombination in the micro to millisecond time scale

C- The accumulated electrons in the TiO₂ conduction band are transported to the transparent electrode by diffusion as a result of an electron concentration gradient, then carried out to the external circuit.
Figure (43) Illustrative scheme describes the 6 steps involved in the cycle which converts solar energy to electrical energy

D- Meanwhile, the dye molecule has lost an electron and the molecule will decompose if another electron is not provided. The dye strips one from iodide in electrolyte below the TiO₂, oxidizing it into tri-iodide. This reaction occurs quite quickly compared to the time that it takes for the injected electron to recombine with the oxidized dye molecule, preventing this recombination reaction that would effectively short-circuit the solar cell.
E- The triiodide then recovers its missing electron by mechanically diffusing to the bottom of the cell, where the counter electrode re-introduces the electrons after flowing through the external circuit.

**Efficiency**

There are three parts of the overall efficiency of the DSSC, light harvesting efficiency, Electron injection efficiency and charge collection efficiency as illustrated in the following scheme.

![Efficiency diagram](image)

Figure (44) illustrative scheme describes the 3 factors involved in the overall efficiency of the DSSC.
3.1.2. Titanium Dioxide Nanotubes DSSC

The main function of the titanium dioxide as dye support is to provide an excellent charge separation, this when we consider its powder form. A replacement of the powder form by the nanotube form will help increasing the DSSC overall efficiency by enhancing light harvesting and electron collection and transport.

A) -Light harvesting

The excellent highly ordered tubular structure of titanium dioxide nanotubes provide a good geometry for supporting the dye molecules which ensures a high probability of the direct interaction between the incident photons from the solar spectrum and the dye molecule supported on the both inside and outside surfaces of the titanium dioxide nanotubes. The titanium dioxide powder might prevent the direct interaction between the incident photons and the dye molecule by which multiple scattering in the porous layer of packed powder this due to the lack of good geometry.

The packed powder geometry has a good degree of porosity but still missing the correct geometry that facilitate the reach of incident photons to the dye molecules, while the nanotube structure provides both good porosity that allows the electrolyte to reach the dye molecules and also good geometry that facilitates the direct interaction between the incident photons and the dye molecules as illustrated in figure (45)
Figure (45) Illustration for a comparison between the light penetration and interaction with the dye molecules in both powder and nanotube form of the titanium dioxide. Dye molecules appear as tiny particles on the surface of nanotubes and powder.

B) -Charge transport

The tubular structure thought to provide less scattering for the electrons just injected from the dye molecule into the titanium dioxide in its journey to reach the electrode, while for titanium dioxide powder electron scattering occurs at the physics boundaries of each grain which dramatically affect the charge collection ability of the titanium dioxide in the powder form. From this perspective important investigation shall be carried out to study the electron transport in the titanium dioxide nanotube along the nanotube from one end.
to the other end, in a trial to resemble the conditions which electrons encountered in ordered be to collected by the electrode at one end of the nanotube in DSSC case. This opens up a bigger question regarding the electrical transport properties of titanium dioxide nanotubes and the factors that affect it. In this chapter, conclusive investigations that answer this question will be presented.

Figure (46) Scheme illustrate the path of the injected electron in both cases of titanium dioxide power and in titanium dioxide nanotube before reaching the electrode
3.2. Single Nanotube Approach

Titanium dioxide nanotubes fabricated by electrochemical anodization are formed in the form of an array of nanotubes vertically oriented; these nanotubes are connected to each other by physical bonds as shown in figure (47). In order to understand the behavior of each nanotube in the charge transport and the effect of nanotube diameter, length and the effect of thermal annealing on the electrical properties, we need to disperse these bundles for single level study, which is a very challenging procedure. However, it will be able to provide more accurate measurements and precise results compared to the study of electrical properties of bundles of nanotubes.

Figure (47) Scanning electron microscope image of titanium dioxide nanotube bundle shows the physical bonds between the nanotubes which hold them together in a robust array
3.3. Experimental methodology

In this section we will mention the details of the experiments we carried out in this investigation and all the techniques employed.

3.2.1. Titanium dioxide nanotube fabrication

The study of the electrical transport properties of a single titanium dioxide nanotube using direct IV measurements implies certain criteria on the nanotube must be fulfilled. One of these criteria is the length of the nanotube, which should be long enough to facilitate many experimental steps involved in the investigation. Fabricating very long nanotubes will be the first step of my investigation.

We used Ethylene Glycol electrolyte which yielded the longest titanium dioxide nanotube. The fabrication procedure is mentioned in detail to ensure consistency if the final results need to be reproduced.

A) Electrolyte preparation

For a 100 ml of the required electrolyte, first we will dissolve 0.33425 grams (3% wt. %) of $\text{NH}_4\text{F}$ in 2 ml of DI water using magnetic stirrer for 10 min. Then we mix the 2ml solution with 98 ml of Ethylene Glycol to ensure 2% $\text{H}_2\text{O}$: 98% EG ratio, after mixing the two volumes stir the mixture for 10 min; the electrolyte is ready to use.
B) Titanium Sample preparation

High purity 320 µm thickness titanium foil is cut into smaller sample area (1x3 cm²). The titanium sample is cleaned by ultrasonic shaking in acetone medium for 5 min followed by ultrasonic shaking in Isopropanol medium for 5 min and finally by rinsing with DI water for 1 min and dried using compressed air. The sample should be handled with clean tweezers and avoid direct contact with bare hands to eliminate any kind of contamination.

C) Anodization cell Operation

The clean titanium foil is attached to the positive terminal of Agilent 6811B power supply to work as anode, while the negative terminal is attached to Platinum mesh (cathode) in a “Two-electrode” anodization cell as shown in figure (49). Set the potential difference to 60 Volts. Immerse the two electrodes in the electrolyte and switch on the circuit. You will notice a formation of tiny bubbles at the cathode due to the formation of Hydrogen on the surface of the Platinum mesh; also bubbles are formed on the surface of the titanium sample.

The electric current in the anodization circuit should increase for a moment, due to the onset of anodization process, then decrease due to the formation of oxide layer and consumption of Hydrogen ions as they leave the electrolyte in gas form. This behavior is shown in figure (50). The anodization process is continued for 8 hours.
Figure (48) Power supply (Agilent 6811B) interfaced with a computer to apply voltage or current (DC or AC) and record the same.

Figure (49) Photograph showing anodization in a beaker with a two electrode set-up. The nearest electrode is the titanium foil forming the working electrode (anode) and at the far end is platinum mesh being the counter electrode (cathode).
Figure (50) Chart shows the anodization current vs. time during the formation of nanoporous alumina.

When done, the sample should be taken out of the electrolyte immediately after the end of the anodization period. The sample is washed by Isopropanol followed by DI water finally dried by compressed air.

D) Sample characterization

With the naked eye, one can see the formation of a greenish layer on the sample surface compared to the sample before anodization. This is an early indication of the successful formation of titanium dioxide nanotube arrays on the titanium surface. This color is directly related to the thickness of the oxide layer, i.e., the length of the formed nanotubes. The longer the nanotubes, the darker the color, as shown in figure (51)
Figure (51) (a) Sample before anodization (Ti foil), (b) sample after anodization in HF electrolyte for 30 min. and (c) sample after anodization in EG for 4 hours

The more conclusive characterization of the sample is done by using the scanning electron microscope (SEM); side view images show the formation of a layer of titanium dioxide nanotubes on the surface of the titanium as shown in figure (52).

Figure (52) Scanning electron microscope image shows titanium dioxide nanotube arrays covering the surface of the titanium foil.
Top view show the thin porous layer of titanium dioxide covering the nanotubes mouth with other particles leftover from the nanotube wall chemical dissolution in the electrolyte as shown in figure (53).

Figure (53) Scanning Electron Microscope image of a) top view of the freshly fabricated titanium dioxide nanotube arrays using ethylene glycol showing surface covered by particles which need to be cleaned. b) Same sample after sonication for 10 min in isopropanol bath.
In order to clean the surface of the nanotube and expose the nanotubes mouth another cleaning process should follow the anodization. The detritus on the surface can be easily removed by sonication in either Isopropanol or DI water for 10 minutes then rinsed by DI water and dried by compressed air. The sample is taken to the SEM for feature characterization. The SEM investigation unveils the beauty of the titanium nanotube arrays as shown in figures (53 b) and (54).

Figure (54) Scanning electron microscope images of titanium dioxide nanotube arrays fabricated by using Ethylene glycol electrolyte after sonication for 30 min. a) side view shows the removal of the top layer. B) nanotubes from the bottom side. C) Top view shows the clean opened nanotubes’ mouth. D) bottom view of the nanotubes closed side (nanotubes bottom)
Energy Dispersive X-Ray Spectroscopy (EDS), sometime known as (EDX), is the simplest way to investigate the elemental composition of the sample. The EDS instrument is usually found as an additional feature for the SEM. By carrying out this investigation using the SEM, we were able to confirm composition of my sample have titanium and oxygen as shown in figure (55). Employing the quantitative elemental analysis feature in the EDS, we found titanium to oxygen ratio is 1: 2, which is proof of the titanium dioxide structure (TiO$_2$).

Figure (55) EDS spectrum (plot of intensity (counts) vs. energy (keV)) of a titanium dioxide nanotube. The presence of fluorine was detected. Typically no fluorine can be detected post-annealing. The peaks are labeled by element and transition (K, L or M). The sample shown was anodized in 0.05M KF in ethylene glycol with 2vol% H2O at 60V for 18h.
3.3.2. Single Nanotube Separation

As we mentioned earlier, titanium dioxide nanotubes form in bundles with physical bonds holding them together. The exception to this general rule, as mentioned in chapter 2, is the use of DMSO electrolytes, which have the ability to fabricate partially loose nanotubes, separated at the top and connected at the bottom as shown in figure (56). To set a general study for all kinds of long nanotube electrolytes we had to consider the DMSO as special case and look for a general way to study Ethylene Glycol and Glycerol fabricated nanotubes.

Figure (56) Scanning electron microscope images of titanium dioxide nanotube arrays. a) DMSO nanotubes under low magnification image, it shows the separated upper portion of the nanotubes. b) DMSO nanotubes
under high magnification image, it shows absence of physical bonds between individual nanotubes. c) EG nanotubes under low magnification image, it shows the compact nanotube arrays. d) EG nanotubes under high magnification image, it shows the physical bonds between individual nanotubes.

My concern about these two electrolytes comes from the interest of many research groups in these specific electrolytes, this due to their superiority in fabrication of ultra-long nanotube arrays with excellent geometry for DSSC and water splitting applications.

The first trial was by sonicating the sample for different times in high purity isopropanol medium, then removing the sample from the formed suspension. Then we release droplet from suspension on a clean silicon wafer and let it dry. The surface of the silicon wafer is investigated by SEM. The SEM images show the debris of broken nanotube bundle, broken nanotube walls, and conglomerated small particles. There is a very small probability of finding a portion of an intact single nanotube –albeit too short to be useful, as shown in figure (57)

![SEM image of debris of nanotubes](image-url)
This process yields circular traces on the silicon wafer due to the action of evaporation of isopropanol and the precipitation of these particles. The competition between the isopropanol evaporation rate and the isopropanol surface tension controls the contact angle between the isopropanol and the silicon wafer. As isopropanol evaporates, it reduces the enclosed volume below the surface. Consequently, the contact angle between the surfaces is lowered, so at a certain critical value the surface tension will cause a driving force toward the inside of the droplet and parallel to the surface of the silicon wafer. As a result of this force, the droplet will suddenly decrease its diameter until the contact angle returns back to its initial value, and this sudden shrink in the droplet diameter forces the suspended particles on the droplet rim to precipitate and accumulate on the external perimeter of the droplet. This is then observed as circular traces left behind the droplet at it dry as shown in figure (58).

Figure (58) Low magnification SEM image shows the circular arcs of nanotube debris
Most of the particles are found in these circular arcs, but elsewhere the density of particles is much less, which makes finding a single nanotube portion greater than 10 µm very challenging. The chances of finding a suitable single nanotube can be improved by using a suspension to contain longer single nanotubes in higher proportion. The chances can also be improved by tweaking the releasing method to ensure even dispersion of particles on the silicon wafer surface.

A) A method for obtaining high yield of long single nanotubes

After many trials to disperse the titanium dioxide nanotube arrays into individual nanotubes with lengths greater than 10 µm, the only successful method found was using ultrasonic mechanical shaking of the sample in solution. However, this method has its drawbacks. On the one hand, it breaks the physical bonds between individual nanotubes in the nanotube bundle to disperse them, but on the other hand, it also breaks the nanotube into smaller pieces, especially the thin walls at the nanotube mouth. In order to maximize the effect of one process and minimize the effect of the other, we need to get deeper understanding of each process independently.

B) Releasing one nanotube out of the whole bundle by sonication

The physical bonds holding the nanotubes together exist along the nanotube with certain repetition (on average each 200 nm of the nanotube length has
one bond). These bonds surround the nanotube form all direction to connect it to the surrounding six nanotubes. Nanotubes on the side of the whole nanotube arrays have fewer bonds compared with the nanotubes inside the bundle. Furthermore, the nanotubes on the edges of these sides have the least number of bonds among all nanotubes. When the ultrasonic waves hit the tube at the side or at the edge and shake it, the few bonds holding those nanotubes to the bundle will easily break. Thus these nanotubes will loosen up and finally detached from the bundle, longer sonication time will release more single nanotubes from bundle’s side, but will also destroy all single nanotubes previously released, which dramatically lowers the final yield of the single nanotubes found in the suspension. In addition, when these waves hit the upper part of the nanotube arrays, they break apart the thin nanotube walls, producing undesired tiny particles and debris in the suspension. From this information we can easily conclude the following

i) An increase in the side area of the nanotube array will increase the probability of obtaining intact single long nanotubes by ultrasonic shaking for very short time, avoiding the secondary destructive effect at longer sonication time. Increasing the side area of the nanotube arrays can easily be achieved by cutting the sample into smaller pieces in a very specific way as illustrated in figure (59).
Figure (59) Schematic explaining the cutting method used to increase the side surface area, this to obtain larger number of nanotubes with less physical bonds connecting them to the main bundle. a) Sample before cutting. b) Sample after being cut into smaller pieces of effectively much larger side surface area.

ii) Before cutting the sample into small pieces, the sample has to undergo a very rigorous cleaning process by sonication. This is to clean the surface of the nanotube arrays from unwanted debris, and also to remove the thin nanotubes walls, which are found at the nanotube mouth. This process involves sonication of the sample in isopropanol several times, each of which should take 20-30 min in a fresh isopropanol bath. Finally, the sample should be rinsed by isopropanol before cutting into small pieces.
iii) After sonication of the small pieces of the sample in isopropanol for 10 seconds, the obtained suspension is separated from the sample pieces with a pipette in a new container for future release on a silicon wafer.

C) Releasing single nanotubes on silicon wafer

In order to carry out an investigation at the single nanotube level using the Electron Beam Lithography (EBL) technique, we have to make sure that

i) The single nanotube must be horizontally aligned on the silicon wafer; no particles should exist under the nanotube. Otherwise, the height of the sample at these specific locations would be greater than the diameter of the nanotubes, and this would invalidate the cylindrical approximation for the nanotube.

ii) The single nanotube location and its immediate area (~50 µm radius) are free of large debris and particles. Otherwise, these might smear the PMMA layer in the coating process, or cut the gold electrodes afterward in the deposition or lift off processes as we will mention in the following section.

iii) The single nanotube is at least 100 µm from the silicon wafer edges, and the separation between any two candidate nanotubes should be greater than 200 µm to avoid future overlap of the electrode patterns.
Spin coating is the method that will fulfill the aforementioned criteria. It can be done by releasing a droplet of the suspension on a silicon wafer, which acts as the substrate, and spinning the substrate at high speed. The high spinning speed will spread the droplet evenly on the substrate surface. The spread droplet will momentarily form a thin film of liquid that rapidly dries without having the circular trace issues as mentioned earlier. Also due to inertia, the big particles and debris will be centrifuged to the outer edges of the substrate, while the desired single nanotubes and other tiny particles will be found equally dispersed on the substrate surface. The surface density of single nanotubes can be increase by spinning more than one droplet sequentially.
3.3.3. **Electron Beam Lithography Technique**

The nanotube submicron dimensions require special techniques in order to measure the electrical transport properties. The main challenge is the difficulty of placing nanoelectrodes on the nanotube ends. Electron Beam Lithography (EBL), which is a technique for writing nanopatterns on a substrate, can also be used in writing nanoelectrodes on a nanotube lying on a substrate. Photolithography is another technique to do the same task with more ease, but it has two problems with respect to my samples, a) the resolution limit of the written patterns cannot go below 200 nm, and b) the pre-specified locations of the electrodes in the mask are hard to work for random locations of nanotubes on the substrate. A third method for carry out this job is the Focused Ion Beam Lithography (FIB), which is similar to EBL, but since this instrument was not accessible during my study, we will consider EBL as the proposed method for carrying out this investigation.

The underlying complexity of EBL made this task very hard to accomplish. After many unsuccessful trials and failures, we were able to master this technique and employ it in a very precise procedure for successful placing gold electrodes on a single nanotubes lying randomly on the silicon substrate. A brief description for this procedure is shown in figure (60). The following procedure represents a code for successful samples after too many failures; for this reason, we will discuss these steps in more detail.
Figure (60) Graphical illustration of the main steps involved in EBL from a) to g)
3.3.3.1. **Substrate Preparation**

A) **Cleaning process**

New silicon wafers (3in wafer of 500 µm thicknesses) is cleaned by **Piranha cleaning** followed by HF cleaning (see appendix B for more detail about these cleaning processes).

B) **Oxide layer growth**

Silicon dioxide layer of 0.5 µm is grown on the silicon wafer surface by wet oxidation, this layer works as a good insulator that covers the semiconductor substrate for future electrical measurements.

C) **EBL for reference points**

Before releasing the nanotubes on the silicon substrate, the substrate should have reference points that work as Cartesian coordinate system. It is very important, where the locations of randomly placed single nanotubes can be specified with respect to these points. Each substrate should have at least two reference points for future coordination transformation and corrections, both translational and rotational corrections. If we consider a square shape of the substrate of side length 1 cm, one can have these reference points on the square corners. The reference points should be very tiny. Smaller reference points means more accurate coordinates. Also it should have large marks so it can be easily found in the substrate under low magnification or by the naked
eye. One shape we were able to design that meets these criteria is as shown in figure (61)

![Figure (61) The design of the reference point, the big mark to easily locate it on the substrate, the X and Y axes for more precise alignment.](image)

X and Y serve as the X-axis and Y-axis, when these axes aligned with the SEM display axes, random nanotube orientation can be specified relative to X and Y. The big mark is a square of side length 100µm similar to the length of X and Y, while the thickness of X and Y axis is about 1~2 microns. O represents the origin of the coordinate system which is the vertex of intersection between X and Y axes, usually for
precise EBL writing this point can be highly precise with an error less than 100 nm.

The process of EBL writing will be mentioned in detail in the following section. Briefly it involves a) spin coat PMMA, b) write the designed pattern for the reference point by EBL, c) sample developing, d) Electron beam deposition of gold layer, e) lift off process and f) dicing the 3 inch wafer into smaller (1 cm x 1 cm) square.

Each square substrate at the end should look like figure (62)

Figure (62) Graphical illustration of silicon substrate ready to be used for releasing nanotubes randomly.
3.3.3.2. Releasing single nanotubes on the prepared substrate

After dicing the sample into smaller substrates, each substrate should be cleaned by Piranha cleaning process to remove any organic waste that might exist on the surface. Then the substrate is placed in spinner where the suspension of nanotubes is spun on the substrate multiple times for a good density of single nanotubes. When done, the sample is taken to the SEM to identify suitable single nanotubes. In the SEM, first we have to find the reference points and align its X and Y axes with the SEM display X and Y axes. When aligned, we need to record the coordinates of the origins of those reference points with respect to SEM stage coordinate system i.e. \((X_a, Y_a)\) and \((X_b, Y_b)\). The search for good single nanotubes in suitable locations is a very tedious task. If we don’t have good density of nanotubes on the substrate surface, finding one good nanotube is difficult to impossible. In locating the nanotube, we should only use the X and Y stage movements; we shouldn’t ever change the stage rotation or tilt. For a good nanotube, we need to record two things, a) the coordinate of the nanotube middle as given by the SEM stage coordinate system. b) The orientation of the nanotube with respect to the SEM display X and Y (or in other word the X and Y of reference point a)
- Sample Annealing

The sample is now ready for the next stage of EBL writing, but first samples need to be transformed from the amorphous single nanotube to polycrystalline single nanotube; this is the right stage for carrying out the thermal annealing process, where the single nanotubes on the substrate is introduced unto the furnace as shown in figure (63). The annealing conditions are the following:

1- Heating rate of 1 degree per minute (1°C/min).

2- Final temperature is either 300°C or 400°C for one hour.

3- Cooling rate of 1 degree per minute (1°C/min) back to room temperature.

4- Annealing medium, oxygen gas.

Figure (63) Thermolyne 79400 annealing tube furnace with Lindberg furnace controller
3.3.3.3. PMMA Spin Coating

The sample should be covered by the resistive layer, in my case it should be a positive resist layer, we will use a polymer called Poly (Methyl Methacrylate) or (PMMA). This material is very sensitive to electrons; when exposed to electron beam, it creates chain scission or (de-cross-linking) within the PMMA, allowing for the selective removal of exposed areas by a chemical developer.

A) The Sample Geometrical factor

- One of the known facts about the EBL technique is that in order to ensure an easy “lift off” process, the thickness of the PMMA layer should be at least three times the thickness of the required metal layer deposited afterwards. Another fact is that the thickness of the metal layer used to make electrodes should be greater than or equal to the height of the nanotubes as illustrated in figure (64). Most of the nanotubes we will use have a diameter 150 nm, to ensure good coverage by the gold layer over the nanotube as illustrated by figure (65), let us consider a gold layer of 200 nm, this implies PMMA layer with minimum thickness of 600 nm. For more easy lift off we will consider an 800 nm layer.

B) Undercut for Smooth Liftoff

The lift-off process should be delicate without any mechanical shaking that might remove the nanotubes off the surface; this can be done by creating undercut.
Figure (64) Thickness ratio between PMMA, Gold and titanium nanotube

Figure (65) Graphical illustration of the gold electrode when passing over the nanotube

This method is achieved by having two layers of PMMA, the bottom layer should be either PMMA with lighter molecular weight or PMMA co-polymer called MMA, and the top layer should be PMMA with
heavier molecular weight. When exposed to electron beam, the MMA will have bigger range for electrons relative to PMMA, thus after exposure and development the lower layer will have a wider trench compared to the upper layer as shown in figure (66). This will enable the stripper solution to have better access to the interface between the PMMA and the silicon substrate.

Figure (66) Schematic comparison between the cross sectional view of both PMMA layer and bi-layer of MMA covered by PMMA when developed after E-beam writing.

C)-Spin coating parameters

   i. Bottom layer

   For PMMA co-polymer (MMA Microchem), spun at 1500 rpm for 60 seconds, and then baked at 150°C for 90 second, a thickness of 150 nm of the MMA is formed.
ii. Top layer

For PMMA (950 A7 Microchem), spun at 4000 rpm for 60 second, and baked at 180°C for 90 second, a thickness of 800 nm of PMMA is formed. The total PMMA thickness is now about 1µm

3.3.3.4. E-beam writing

Electron beam writing is done under the SEM, where the electron beam used for imaging will play another role in “burning” the resist layer (PMMA) in certain pattern, for this reason E-beam writing must be done with imaging mode switched off. This means we cannot see where the beam is with respect to the sample, so we have to depend on accurate coordinates of the nanotube location with respect to the reference point made earlier on the silicon substrate. When all coordinates with respect to the reference point are known, accurate alignment of the reference point and the SEM stage orientation is achieved, and the X and Y of the reference point are precisely aligned with the X and Y of the SEM display, then the imaging mode is turned off, and the E-beam should be blanked before executing any movements. Using the nanotube coordinates, the stage is guided to move to the single nanotube locations so that the E-beam will hit right at the same location of the nanotube, and this will write the pattern on nanotube. Due to limited SEM stage accuracy regarding nanometer precision, there is a large probability of offset that shifts the
pattern from the position of the nanotubes. For this reason a modification is made in the pattern to ensure 100\% probability of finding the single nanotube. The design of that pattern is shown in figure (67) where there are 12 electrodes in the pattern, each one has a very narrow straight part so as to find the nanotube in a larger area, and it is connected to 50x50 µm square pads for micro probing.

Figure (67) Design of the electrodes system used to hunt random nanotubes.
When writing is completed, the sample is taken for developing

-Developing process

a) Sample is immersed in a mixture of 1:3 of MBKI: IPA for 80 seconds.
b) Sample is immersed in IPA for 20 seconds.
c) Sample is rinsed by DI water for 5 minutes.
d) Sample is dried by flow of Nitrogen.

The sample is investigated under optical microscope to confirm the completion of the developing process. The written pattern should be seen as clear trenches formed in the PMMA layer crossing the nanotube as shown in figure (68).

Figure (68) Graphical illustration of the sample after development, empty trenches exposes the nanotube at certain locations
3.3.3.5. E-beam deposition

These empty trenches will be filled with gold, but before depositing gold, the substrate should be cleaned to ensure removal of any remaining PMMA or other organic waste. The cleaning process that can guarantee the removal of all organic materials on the surface is oxygen plasma cleaning. It should be used carefully so as not to destroy the PMMA layer or widen the trenches when longer time is used. There are several methods for depositing gold in these empty trenches: electroplating, thermal evaporation, electron beam evaporation, and sputtering. The most effective method for EBL is the electron beam evaporation. It has a directional deposition ability which facilitates the lift off process, and very precise in attaining the required thickness. In my case, we will deposit 200 nm gold layer, but since the used substrate is made of silicon with a 0.5 µm top layer of silicon oxide, the adhesion between the silicon oxide surface and gold layer when deposited is very poor, for this reason another metal is used as an intermediate layer to strengthen the adhesion between the gold and the silicon oxide surface. Titanium or chrome can be used, and in most of samples, 10-15 nm of Chrome was deposited followed by 150-200 nm of gold.
3.3.3.6. Lift off

After depositing gold on the substrate and in the trenches, the unwanted gold and the PMMA layer should be lifted off. This is done by immersing the sample in acetone (stripper of the PMMA) face down for few hours until the PMMA layer is completely dissolved and the gold layer above falls. The lift off process should be very gentle; any mechanical shaking may remove the nanotube from the surface of the substrate as shown for early trials in figure (69). The sample is then taken to the SEM for final check of the success of the whole process of placing gold electrodes across the nanotube. This check is needed to distinguish the unsuccessful samples from the successful ones before we start measuring the electrical transport properties using the Probe Station. The probe station has an optical microscope, which cannot be used to check good samples.

Figure (69) Scanning electron microscope image of broken gold electrodes. This is due to harsh lift off process, where the nanotube got lifted with the PMMA layer.
3.3.3.7. Method for effective E-beam deposition

SEM images reveal an important observation that gold electrodes easily crack when crossing the nanotube. After many investigations to understand the source of this problem, we were able to confirm the role of thermal stress as the only reason for this behavior. The difference between the thermal expansion coefficients of the gold and silicon results in different thermal stresses, mainly in the area of contact between the gold and silicon, tensile thermal stress occurs in the gold layer while compression thermal stress occurs in the silicon substrate. The weakest points in the gold electrodes are the crossing points: where the gold electrode crosses over the titanium dioxide nanotube. During the cooling stage, the thermal stress intensifies, and at certain point it will crack the gold electrodes at its weak points. As a result of this unavoidable cooling process, cracks will form in the gold electrodes as shown in figure (70). These cracks disconnect the electrodes from the nanotube, and undermine the whole technique for studying a single nanotube.

After extensive experimental studies, we were able to find two solutions for this problem. **First**, strengthen the weak points by depositing a thicker gold layer (larger than 300 nm), which will reduce the probability of crack formation but not eliminate it. The only drawback to this method is the high expense associated with consuming more gold in the e-beam evaporator.
Figure (70) Scanning electron microscope image of gold electrodes crossing over single titanium dioxide nanotube where a crack in the electrodes is formed. A) Low magnification image of the crack at different electrodes. b) High magnification image of the crack in one electrode

Second, strengthen the weak points by using “tilted angle deposition” technique, instead of placing the sample normal to the vapor flux, as shown in figure (71-a) we will tilt the sample such that the deposition will
have a good coverage on the nanotube sides, where weak points form, as well as the substrate. In this case we will do the titled angle deposition two times to ensure a complete coverage of both sides of the nanotube as shown in figure (71-b). Each layer is about 100 nm thick.

Figure (71) a) Schematic explains the physical vapor deposition problems regarding the formation of cracks in the deposited metal layer. b) titled angle deposition technique we used to overcome the formation of crack in the metal layer when crossing over the nanotube.
3.3.3.8. Micro probing for measurement

The successful sample is taken to the “four probe station” where micro probes are used to contact the pattern pads for electrical measurements as shown in figure (72).

Figure (72) Photo taken under the optical microspore of the four probe station, it shows the four probe tips touching the gold pads, while the nanotube is invisible under optical microscope resolution

There are two possible techniques to do the measurements, either to use the two probe method or to use the four probes method. We will use the two probe method, and we will introduce in the results section a proof for the efficiency of this method. In my study we used the picoampere current source to supply the current through the nanotube, and then we used nanovoltmeter to measure the voltage across the nanotube. The results will be mentioned in details in the following section.
3.4. Results

3.4.1. Releasing single long nanotube

By applying the aforementioned experimental steps for obtaining and releasing long single nanotubes, we were able to achieve a considerable yield of long nanotubes (length greater than 10 µm). In some cases up to 30 µm of intact smooth nanotube were obtained as shown in figures (73).

Figure (73) Scanning electron microscope image of four single nanotubes on the silicon wafer. The length of the nanotube is between 20 and 35 micron.
3.4.2. Accuracy and improvement of pattern writing

After extensive work, we were able to overcome the limited precision of SEM stage movement. To go beyond the machine accuracy in both translational and rotational movements, we had to carry out a series of coordinate-corrections along with refinements of the pattern design. Finally we were able to accurately find any single nanotube on the substrate as shown in figure (74).

Figure (74) Scanning electron microscope images showing enhanced writing accuracy through different stages. The lower image is wide-view with low magnification showing the nanotube in the center of the pattern crossed by four electrodes.
3.4.3. Crack elimination

There are two possible solutions to overcome the problem of the gold electrode crack, as shown in figures (75) and (76)

a) Thick gold layer deposition (200 nm and 300 nm gold to 150 nm TiO$_2$).

Figure (75) Scanning electron microscope images of a) 200 nm thick gold electrodes cross over single titanium dioxide nanotube with 150 nm diameter no cracks are observed. b) 300 nm thick gold electrode crossing smoothly over nanotube with 150 nm diameter.
b) Tilted angle deposition (gold two layers, each of 80 nm thickness to 150 nm TiO$_2$)

First, 80 nm gold layer is deposited by tilting the substrate by 45° angle with respect to the horizontal. Then, another 80 nm gold layer is deposited by tilting the substrate by -45° angle with respect to the horizontal.

Figure (76) Scanning electron microscope images of gold electrodes crossing over single titanium dioxide nanotube. The gold electrode consists of two gold layers each of which is deposited using tilted angle deposition method. The different view is to confirm the absence of any crack formation.
3.4.4. IV curve for amorphous nanotube

The IV measurement for amorphous nanotube shows a linear relationship between the applied voltage and the electrical current passing thought the nanotube. This behavior is found to be the same for all the studied samples, as shown in figure (77).

Figure (77) IV curve for 2 micron long amorphous titanium dioxide single nanotube
3.4.5. IV curve for annealed nanotube

When the single nanotube is subjected to thermal annealing as described earlier the annealing section (section 3.3.3-B) first for final annealing temperature of 300°C, the IV characteristic showed a nonlinear behavior for all the studied samples as shown in figure (78).

Figure (78) IV curve for 2 micron long titanium dioxide single nanotube annealed at 300 °C. The resistance deviates from the constant value and changes from R1 to R2 over the applied voltage range (0-40 volt)
And for final temperature of 400°C it showed the same behavior with an increase in the nonlinearity for all the studied samples, as illustrated in figure (79).

Figure (79) IV curve for 2 micron long titanium dioxide single nanotube annealed at 400 °C. The resistance changes widely from R1 to R2 over the applied voltage range (0-40 volt)
3.5-Discussion and Conclusion

A) Development of successful technique

One of the major achievements in this investigation is the development of a successful technique for obtaining single nanotubes from titanium dioxide nanotube arrays. This technique is applicable for all kinds of titanium dioxide nanotube arrays, not only for Ethylene glycol or Glycerol electrolytes. Another important achievement is the development of high precise experimental procedure for writing nanopatterns using electron beam lithography on randomly located nanoparticles in a substrate. We were able to enhance this technique to the extent that 100% accuracy is repeatedly achieved. This technique is widely applicable to all kinds of nanotubes and nanowires and not limited to titanium dioxide nanotubes.

B) Ohmic behavior of amorphous titanium dioxide nanotube

The IV curve for amorphous single titanium dioxide nanotube shows a linear relation between the current passing through the nanotube and the potential difference across certain segment of the nanotube. This ohmic behavior can be attributed to the amorphous phase of the titanium dioxide, which is a wide band gap semiconductor in the Anatase, Rutile and Brookite phases. The resistance of segment of a single titanium dioxide nanotube is 20.7 Giga-Ohm; this segment has length of 2 microns with outer diameter 170 nm and nanotube wall thickness 45 nm. Apparently, this very high resistance value can be classified among “insulators”, especially when we consider that the length of the sample is only 2 microns. Resistance is not a very conclusive quantity to judge the
behavior of a certain material; instead, resistivity will be a more meaningful quantity to
describe the intrinsic electrical properties of titanium dioxide nanotube. To find the
resistivity value we need consider the three dimensions of the nanotube segment:
nanotube length, nanotube circumference and nanotube wall thickness

\[ L = 2000 \text{ nm}, \quad C = \pi D = 534 \text{ nm} \quad \text{and} \quad T = 45 \text{ nm} \]

Where \( L \) is length, \( C \) is circumference, and \( T \) is wall thickness.

The ratio between these three dimensions is 44:12:1, thus we cannot use the sheet
resistivity approximations where two dimensions must be much greater than the third
dimension, or the line approximation where two dimensions is much smaller than the
third dimension. We had to model this situation using the correct geometry of the
nanotube. Finally, we were able to develop a simple model, with a few approximations,
that enabled me to carry out good estimation of the nanotube resistivity. For details about
this model please see appendix C.

By knowing the nanotube length “\( L \)”, nanotube average radius “\( r \)”, nanotube wall
thickness “\( t \)” and finally the measured nanotube resistance “\( R \)”, we can estimate the
nanotube resistivity “\( \rho \)” using the following formula:

\[
\rho = \frac{R(2L\pi rt + (\pi r)^2 t)}{L^2 + \pi rt L}
\]

The estimated resistivity of the studied nanotube segment is \( 2.34 \times 10^2 \) (\( \Omega \cdot \text{m} \)), when
compared with other materials like the values shown in table (8) the resistivity of single
Titanium dioxide nanotube is classified as a semiconductor resistivity, even when it is in the amorphous phase.

<table>
<thead>
<tr>
<th>Good conductors: Cu, Au</th>
<th>$\approx 10^{-8}$ (Ω.m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good insulators: Paraffin</td>
<td>$\approx 10^{17}$ (Ω.m)</td>
</tr>
<tr>
<td>Semiconductor: Silicon</td>
<td>$\approx 10^{2}$ (Ω.m)</td>
</tr>
</tbody>
</table>

Table (8) Resistivity range from good insulators to good conductors

When recalling the early motivation for the whole investigation, we found ourselves obligated to compare the resistivity of titanium dioxide nanotube to that of titanium dioxide powder, this to provide a quantitative proof of the superiority of titanium dioxide nanotube over titanium dioxide powder in charge transportation. The comparison is done between the amorphous titanium nanotube and titanium powder in Anatase and Rutile phases as provided in table (9)

<table>
<thead>
<tr>
<th>Material</th>
<th>Amorphous Nanotube (calcined)</th>
<th>Anatase Nanopowder (calcined)$^{[201]}$</th>
<th>Rutile Nanopowder (calcined)$^{[201]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity</td>
<td>$2.34 \times 10^{2}$ (Ω.m)</td>
<td>$\approx 10^{5}$ (Ω.m)</td>
<td>$\approx 10^{1}$ (Ω.m)</td>
</tr>
</tbody>
</table>

Table (9) Comparison between titanium dioxide nanotube resistivity and titanium dioxide powder

From this comparison we found that “amorphous nanotube” has three orders of magnitudes better electrical conductance than “Anatase nanopowder” which is usually used as the dye support in DSSC, while it has five orders of magnitudes better electrical conductance that “Rutile nanopowder”.
C) - Resistance variation along titanium dioxide nanotube

Another important observation regarding the topology of the nanotube array is that SEM images confirms that nanotube from inside has a conical shape, which means the wall thickness will change from nanotube mouth to nanotube bottom as shown in figure (80).

Figure (80) Scanning electron microscope images shows titanium dioxide nanotubes at different location from bottom to top, and below is sketch of the proposed conical shape of the nanotube inside.

This observation raised an important question. Will the resistance of the nanotube segment vary from one location to other based on the change of the nanotube wall thickness? In order to answer this question we investigated two consecutive nanotube segments for two samples as shown in figure (81).
Figure (81) Scanning electron microscope image three gold electrodes crossing over single titanium dioxide nanotube, where two nanotube segments can be studied

These two segments have the same length and same outer diameter, the only difference is the wall thickness in these two cases. By carrying out series of IV measurements for

a) the first segment between electrodes (1) and (2)

b) the second segments between electrodes (2) and (3)

c) the whole nanotube between (1) and (3)

We were able to repeat these measurements for another sample; the summery of all these measurements is listed in table (10)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_1$ (1-2) X$10^9 \Omega$</th>
<th>$R_2$ (2-3) X$10^9 \Omega$</th>
<th>$R$(1-3) X$10^9 \Omega$</th>
<th>$R_1+R_2$ X$10^9 \Omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>21.1</td>
<td>42.9</td>
<td>63.9</td>
<td>64.1</td>
</tr>
<tr>
<td>S2</td>
<td>13.4</td>
<td>32.1</td>
<td>45.7</td>
<td>45.6</td>
</tr>
</tbody>
</table>

Table (10) List of resistance measurements for two samples (S1) and (S2). Each sample underwent series of resistance measurements for different segments
From this table we can conclude the following conclusions,

i. When comparing the first segment resistance (R1) with the second segment resistance (R2) we found more than 200% increase in value. This observation holds for both samples (S1) and (S2). This fact when combined with the expected change in the nanotube wall thickness from one place to another forms strong evidence for my claim that titanium dioxide nanotubes have varying resistance along the nanotube from top to bottom, and this behavior is only attributed to the change in nanotube wall thickness.

ii. When comparing the measured resistance of the whole nanotube portion (R1-3) with the algebraic sum of the measured resistance R1 and R2, we found almost two similar numbers; this finding itself represents strong proof that the contact resistance between gold electrodes and titanium dioxide nanotube is considerably small and can be neglected. Therefore the two probe measurements can provide accurate values for IV measurement and there is no need to apply the four probes technique that requires at least four gold contacts across the nanotube.
D)-Thermal annealing effect on the electrical transport properties.

The applications for titanium dioxide mainly are related to the either the Anatase phase or the Rutile phase. As mentioned earlier, these phases can be obtained by thermally annealing the amorphous titanium dioxide nanotubes. By carrying out the same procedure on thermally annealed single nanotubes, we were able to demonstrate gradual deviation of the IV curve from its linear behavior as observed in the amorphous phase. This nonlinearity is attributed to the formation of the anatase phase as anticipated. By comparing of the 300°C IV curve with the 400°C we were able to observe the following

a) There is an increase in the nonlinearity of the IV cure as the annealing temperature increases. This can be understood in terms of the increase in anatase phase formation at 400°C where compared with 300°C as proved by the XRD results in the in chapter 2. This increase in the anatase phase is associated by a decrease in the amorphous phase, which is more electrically resistive. When we compare the amorphous 300°C and 400°C, we notice the phase transformation effect on the electrical resistance as shown in figure (82).

b) By calculating the resistance, and consequently the resistivity, of the thermally annealed nanotube at different voltage values, we were able to demonstrate a dramatic reduction in the resistance values when compared with the amorphous nanotube resistance. This reduction is approximately a factor of 2 for the 300°C sample and a factor of 15 for the 400°C sample, as listed in table (11). This makes the annealed nanotube much better than the powder in DSSC.
Figure (82) IV curves for both amorphous titanium dioxide nanotube and titanium dioxide nanotube annealed at 300°C

<table>
<thead>
<tr>
<th>$T_{\text{final}}$ (°C)</th>
<th>R1 ($\Omega$)</th>
<th>R2 ($\Omega$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>$6 \times 10^9$</td>
<td>$2.6 \times 10^9$</td>
</tr>
<tr>
<td>400</td>
<td>$58 \times 10^6$</td>
<td>$4 \times 10^6$</td>
</tr>
</tbody>
</table>

Table (11) list of thermally annealed nanotubes’ resistance range (R1-R2) over applied voltage range (0-40 v)

c) By studying the IV curve of the annealed samples for consecutive nanotube segments, we were able to demonstrate a very clear change in the resistance from one segment to another as illustrated in figure (83). This is another proof
that the change in resistance along the single nanotube is due to the change in the wall thickness as introduced before.

Figure (83) IV curves for two samples annealed at 300°C (S8 and S9) a) IV curve for two consecutive segments (6-7) and (7-8) of sample S9, where change in resistance is observed. b) IV curve for two consecutive segments (6-7) and (7-8) and the total nanotube (6-8) of sample S8 also change in resistance values is observed. Barrier formation and diode behavior
A Schottky barrier is proved to form between titanium dioxide and gold as reported in literature [202,203]. The linear behavior of the amorphous nanotube IV curve does not contradict these anticipations since the Schottky barrier is related to the Anatase or Rutile phases when in contact with gold. The linearity of the amorphous IV curve is an evidence of a possible ohmic contact resistance between gold and the amorphous titanium dioxide.

In order to investigation the formation of the Schottky barrier, and thus the possibility of a Schottky diode, we will explore the IV curve in forward and reversed flow of electrical current over a complete cycle. The results showed symmetry of the IV behaviors in both current flow directions, which rules out any formation of a diode like barrier between the gold electrodes and the single nanotube as shown in figure (84).

Another important conclusion is that there is no sign of breakdown voltage, even at voltages of 20 volts. The importance of this observation lies in a deeper understanding of my case. The IV measurement is done through two gold electrodes sandwiching a segment of nanotube, according to this description we should have a contact barriers at two locations as illustrated in figure (85).
Figure (84) Full cycle IV curve for a) single titanium dioxide nanotube annealed at 400°C. b) Commercial diode
The work function of gold is about 5.2 eV while the work function of titanium dioxide is about 4.5 eV. This makes electrons flows in from the titanium dioxide side to the gold side, so the barrier will have a forward connection when current flows from titanium dioxide to gold and reverse connection the other way as illustrated in figure (85).

For any connection, we have used voltages greater than the breakdown voltage in order to allow for current to pass through this interface. This mean we should have avalanches in both sides preceded by very small leakage current as illustrated by figure (86).
Figure (86) Schematic illustration of the anticipated IV curve for annealed titanium dioxide nanotube if Schottky barriers were to form between the gold electrodes and the nanotube.
But this model does not match my results, which might be an evidence of a more complicated situation in the contact between the gold electrodes and the titanium dioxide nanotube. This behavior is worth detailed investigation which can be done in the future.
Chapter 4

Optical properties of free standing Titanium dioxide nanotube arrays

1- Introduction
2- Experimental method
3- Results and discussion
4- Conclusion
4.1. Introduction

4.1.1. Photoelectrochemical (PEC) activity of titanium dioxide.

The Photocatalytic activity is considered the most important property of titanium dioxide. Hydrogen production by water splitting through the Photoelectrochemical process is the most anticipated application for this material. In this section, we will give a brief review of this process, and highlight the role of the optical property of titanium dioxide nanotubes in the Photoelectrochemical process.

Discovery

In 1967 Akira Fujishima, then a graduate student at the University of Tokyo, observed that gas bubbles evolved on the surface of an aqueous titanium dioxide electrode when exposed to strong light. He found that the bubbles consisted of oxygen gas and that hydrogen was generated at the platinum electrode. Thus, it was discovered that water can be decomposed into hydrogen and oxygen using light and a small bias [204]. This discovery only really caused ripples in 1972 after Fujishima and his former adviser Kenichi Honda published their findings in Nature [25]. To find out whether their method could generate a sufficient amount of hydrogen as an energy source, Fujishima & Honda covered the rooftop of a building with titanium dioxide films made by heating titanium plates in air. The experiment was conducted on a clear summer day but only 7 liters of hydrogen were generated per square meter of titanium dioxide film. The energy conversion efficiency was only 0.3%, which indicated that the photocatalyst in its native form was probably not suitable for economically viable energy conversion [204].
Although progress did not come as quickly as was initially anticipated, solar to hydrogen efficiencies on the order of 7% have recently been reported[205]—significantly higher than the early Fujishima-Honda experiment and close to the 10-20% efficiency that would make this technology a viable large scale energy source.

### 4.1.2. Mechanism of water splitting

Good reviews for primary mechanism and side reactions that may occur during Photoelectrochemical water cleavage are presented by Diebold [206] and Nowotny et al. [207]. In this introduction the basic chemical steps of the process (illustrated in figure 87) will be presented. In part because of the formation of the electrical double layer, the titanium dioxide surface has a natural affinity. For hydroxyl ions in solution that typically coat the surface [208] (step 1 in figure 87). The TiO$_2$ photocatalyst can absorb photons with energy in excess of its band gap ($h\nu \geq E_g$). This process results in the creation of a free electron-hole pair (step 2 in figure 87). Because of the band bending in the depletion layer that naturally accompany a semiconductor in solution holes tend to migrate to the oxide surface (step 2 in figure 87) whilst the excited electrons typically migrate inward towards the titanium below the oxide layer. If they escape recombination, the electrons are both collected and conveyed along an external circuit to a cathode (where H$_2$ will be generated) or they find their way to a co-catalyst (step 5 in figure 87). Holes that reach the TiO$_2$ surface oxidize hydroxyls in a redox reaction which leads eventually to the generation of oxygen at the anode (step 4 in figure 87). Simultaneously electrons that reach the cathode or co-catalyst can reduce protons and generate hydrogen. The fact that
the titanium dioxide bandgap is situated in such a way that it can facilitate these reactions can be seen in figure (88).

Figure (87) The steps in direct photochemical water splitting. 1) Auto-ionization of water at the electrolyte-oxide surface. 2) Absorption of photons creates hole – free electron pairs. 3) Holes that escape recombination migrate to the electrolyte-oxide surface. 4) Electron transfer from adsorbed hydroxyl ion to a surface hole that leads to the formation of a 5) chemisorbed O- species and hydrogen ions (protons). 6) Oxidation of the chemisorbed Ospecies and a second hole result in the formation of adsorbed atomic oxygen radicals, O*. 7) Desorption of oxygen radicals and their subsequent association leading to the formation of gaseous oxygen. 8) Free electrons migrate to a cathode/co-catalyst/proton reduction site. 9) Hydrogen generation [205,206].
4.1.3. Band gap role

The single largest obstacle to the realization of commercially viable solar Photoelectrochemical systems that use titanium dioxide to perform water-splitting is the large bandgap of titanium dioxide. TiO$_2$ exists in three crystalline phases: rutile ($E_{BG} = 3.05$ eV), anatase ($E_{BG} = 3.23$ eV) and brookite ($E_{BG} = 3.26$ eV).

![Figure (88) The band positions of several semiconductors in contact with aqueous electrolyte at pH 1. The lower edge of the conduction band is in red and the upper edge of the valence band in green. The energy scale is indicated in electron volts using either the normal hydrogen electrode (NHE) or the vacuum level as a reference. On the right side the standard potentials of several redox couples are presented against the standard hydrogen electrode potential. Note that although titanium dioxide straddles the two redox potentials for water its conduction valence](image-url)
band is considerably lower than it need be. In that sense cadmium sulfide (f.i.)
appears a more ideal material if not for its lack of stability. A common idea is to
make multilayer electrode so that a wider spectrum of wavelengths can be harvested
by materials with different band-gaps. (figure adapted from [209]).

The large electronic bandgap of titanium dioxide means that it only absorbs wavelengths
in the ultraviolet region, which constitute less than 5% of the solar spectrum energy. It
has been estimated that an overall solar to hydrogen efficiencies of at least 10% are
needed to produce economically competitive hydrogen [210]. Clearly, practical
photoconversion efficiencies using titanium dioxide can be achieved only if a method is
found to extend the photoresponse of titanium dioxide into the visible portion of the
solar spectrum while maintaining its excellent long term stability and photoconversion
properties. Broadly speaking, there have been two major strategies directed towards this
goal: a) the doping or bandgap engineering of titanium or b) the use of co-catalysts or
dye’s with TiO₂.

4.1.3. Sources of inefficiency

It is very useful to identify the different contributions to inefficiency in a PEC system.
The following are the major energy losses:

i. For an ideal pure crystalline material all photons with energies below the
bandgap (Eg) will not be absorbed. Hence, only the fraction of photons with hv
$\geq E$ is available for conversion.
While all photons with energy $h\nu \geq E$ can potentially be absorbed, the energy in excess of $E_g$ is dissipated as heat, and consequently the fraction of photon energy in excess of the bandgap is also lost.

Naturally, not all photons with the required energy do necessarily get absorbed; hence there are optical losses associated with different types of reflection and absorption.

There are irreversible processes associated with 1) recombination of the electron-hole pairs, 2) ohmic resistivity of the electrodes and electrical connections, and 3) over-potentials at the electrode/electrolyte interface.

4.1.5. Light harvesting by titanium dioxide nanotube arrays

Enhancing the light harvesting can be done by reducing the reflection of the incident light, and using the appropriate surface geometry. Titanium dioxide nanotube arrays have an excellent geometry that provides very high aspect ratio, where the active surface area of a sample reaches up to 10,000 times the sample surface area (for more detail about the aspect ratio of titanium dioxide nanotubes, please review appendix A). This property combined with the high index of refraction of titanium dioxide material ($n_{ave} \approx 2.5$) and the vertical tubular structure makes it excellent structure for very efficient Hydrogen production by water electrolysis. The hypothesis of efficiency enhancement emanate from the following facts.
a) Very large interface between the water and titanium dioxide is provided by this nanotubular structure.

b) The vertically aligned tubular structure when combined with the high index of refraction of the tube walls provides a light trap for the incident spectrum. The portion of the light photons that do not get absorbed by the nanotube walls in their first incidence, will reflect off the surface of the nanotube walls due to its high index of refraction, these photons will perform a series of inner reflections, in each one it will lose the absorbed part at the water-titanium dioxide interface as illustrated by figure (89), this maximizes the probability of complete absorption of all the incident light photons.

Figure (89) Scheme of the expected behavior of light inside titanium dioxide nanotube, where multiple reflections for the incident light are expected
4.1.6. Optical properties importance

These expectations motivated many research groups to investigate the behavior of titanium dioxide nanotube arrays in the water splitting process, they investigated the role of doping these nanotube with different dopants to shrink the band gap to absorb more photons from the solar spectra, and also they investigated the role of co-catalysts or dye when supported on TiO$_2$.

Despite the high competition of getting very long titanium dioxide nanotube arrays between research groups, none were able to explain the behavior of the electromagnetic wave propagation in these very long nanotubes. There was a belief that the longer the nanotube, the more light it will be able to harvest; this thought emanated from a paper published by Grimes et al [211], where he reported that for samples of length from 200 nm to 1.5 micron of titanium nanotube arrays, the light was able to propagate without any considerable reflection expect from the titanium layer underneath. This idea implicitly generalized for any length, but no previous work was reported about investigating the optical properties of long titanium dioxide nanotubes. The importance of this investigation emanates from the need of optimizing the titanium dioxide nanotube arrays length to reach the maximum possible harvesting of the solar spectrum. Without increasing the resistance for the bias circuit involved in the Photoelectrochemical process

The ability to peel off the long titanium dioxide nanotube arrays from the titanium substrate and form free standing arrays made this investigation more feasible. The free standing titanium dioxide nanotube arrays can be fabricated in a wide range of nanotube
lengths, but it has a minimum value where it became impractical to obtain ultrathin free standing arrays due to its fragility. In this investigation, we were not able to obtain good samples of free standing arrays with less than 26 micron. The flakes should have two properties that enable us to carry out the optical measurement accurately:

a) It should be larger than the light spot coming out from the light source in the spectrometer involved in the investigation.

b) It should be very flat, intact, free of any cracks, free of any titanium remains below the barrier layer, and have a clean surface of open mouth nanotubes.
4.2. Experimental methodology

4.2.1. Sample preparation

The titanium dioxide nanotube arrays will have a very poor adhesion to the titanium substrate if fabricated using Ethylene glycol electrolyte or Glycerol with less than 1% water content. When the sample is rinsed and dried after long fabrication period (>6 hours) the titanium dioxide nanotube arrays will spontaneously peel off the titanium surface as illustrated in figure (90).

![Figure (90) Photo of titanium foil after anodization in 99% EG and 1% H₂O, the titanium dioxide nanotube arrays peeled off the surface](image)

The free standing titanium dioxide nanotube arrays can form flakes considerably good for our purpose. The naked-eye observation demonstrated a difference between the two sides.
of these flakes; it has a shiny side which is characteristic of the nanotube bottoms and the
other side is dull which is characteristic of the nanotube mouths.

Figure (91) Flakes of titanium dioxide nanotube arrays, the right shows the dull
side of the flake while the two flakes on the left show the shiny side of the flake.

The sample is taken to the scanning electron microscope for more conclusive
investigation about the sample surface. It is confirmed that the shiny side is made of
nanotube bottoms, while the dull side is made of the nanotube mouths as illustrated in
figures (92) and (93)

Figure (92) Scanning electron
microscope image of side view of free
standing titanium dioxide nanotube
arrays
Figure (93) Scanning electron microscope images of a) the shiny side of the flake which showed the bottoms of the nanotube arrays b) the dull side of the flake which showed the mouths of the nanotube arrays

We can consider the flakes as a film made of nanotube arrays, this film has homogenous thickness everywhere, and it has two sides, we will name them as closed side (the shiny side) and open side (the dull side).

Figure (94) Graphical model of the free standing nanotube arrays, a) closed side of the flake (nanotubes bottoms) b) open side of the flake (nanotubes mouths)
4.2.2. Experimental setup

4.2.2.1. Normal incidence

In this setup, the transmittance and specular reflection from the samples are measured using normal incidence procedure, the beam of light is allowed to fall with normal incidence upon the open side and normal incidence on the closed side of each sample.

The light source emits a wide range of wavelengths (300 nm – 1100 nm) so as to resemble the solar spectrum.

![Normal Incidence Diagram](image)

Figure (95) Scheme of the normal incidence optical measurements, $I_o$ is the incidence beam intensity, $I_T$ is the transmitted beam intensity and $I_r$ is the backward reflected beam intensity
The light beam is delivered to the sample surface using coaxial fiber optic cable. The beam is delivered by the central fiber optic channel, while the surrounding 5 channels carry the reflected rays to the spectrometer as illustrated in figure (96).

![Diagram of coaxial fiber optic cable]

**Figure (96) Scheme of the coaxial fiber optic cable**

The transmitted beam is carried to the spectrometer using another fiber optic cable which is perfectly aligned with the center channel of the primary coaxial fiber optic cable.

**Spectrometer**

We used light source “Hamamatsu photonics K.K. High power UV-VIS fiber light source” Model L10290, and “Ocean Optics HR4000CG-UV-NIR” High-resolution spectrometer. The reflection from both sides of the sample is found to be diffused reflection. This made the obtained results from the normal incidence represents only a qualitative value. In order to calculate the absorbed portion of the spectrum we need to measure the total reflection off the sample surface using more accurate method.
4.2.2.2. Integrating sphere

Integrating sphere spectrometry deals with diffuse reflection from a sample. It measures the total diffuse reflection quantitatively to a very high degree of accuracy.

The reflected rays will undergo a series of reflections until the intensity inside the sphere become homogenous everywhere. By integrating over the inner surface area of the sphere we can accurately estimate the value of the total reflection off the sample surface.

Figure (97) Graphical illustration of integrating sphere spectrometer

The integrating sphere spectrometer used in the system is “Varian Cary 3” spectrophotometer in diffuse reflectance geometry with a “Labsphere DRA-CA-30I” integrating sphere.
4.3. Results and discussion

4.3.1. Normal incidence

We were able to prepare four samples for this investigation, each of which had the same nanotube inner diameter of 160 nm, but with different nanotube lengths of 26 µm, 39 µm, 69 µm and 106 µm. For each sample, we measured the transmittance and reflection from the closed side and from the open side. These measurements were normalized to the actual intensity of the incident beam and averaged over 10 repeated runs of the spectra.

\[
\text{Transmittance (\%)} = \frac{\text{Transmitted intensity}}{\text{Incident intensity}}
\]

\[
\text{Reflectance (\%)} = \frac{\text{Reflected intensity}}{\text{incident intensity}}
\]

4.3.1.1. Reflectance

Figure (98) Reflectance measurement of 26 micron thick titanium dioxide nanotube arrays
Similar results obtained for the other three samples

Figure (99) Reflectance measurements of 39, 69 and 106 micron samples
From the previous graphs of the reflectance relative intensity versus wavelength, we observe the difference between the closed, shiny side and the open, dull side. The reflectance of the closed side almost double the reflectance of the open side for all samples used in the investigation.

The data of all samples were represented by one chart for a comparative study as shown in figure (100)

![Figure (100) Comparative chart of samples reflectance a) from closed sides b) from open sides](image)
The reflectance increases with sample thickness as seen by comparing the 26-micron and 39-micron closed side results (figure 100 a), where the reflectance increased from 10% to 25%. However, when the thickness increased from 39 microns to 106 microns, we did not observe any considerable increase in reflectance.

The open side results also showed an increase in reflectance from 6% to 10 % as the thickness increased from 26 microns to 39 microns. In addition, there was a small change in reflectance (10 % to 12%) as thickness increased from 39 microns to 106 microns.

Regarding the wavelength dependence, as illustrated in figure (100), reflectance from both sides of all samples involved in this investigation is minimum in the visible light range (400 nm – 700 nm). Reflectance in the infrared region (700 nm – 1100 nm) is higher than the visible region regardless of which side is illuminated.

Reflectance in the near ultraviolet region (200nm -400nm) showed different behavior for the closed side samples when compared with the open side samples. For closed side reflectance, there was a peak or local maximum for all samples around 260 nm, but for open side reflectance, there was a local minimum around the same wavelength 260 nm. This behavior didn’t change as the thickness increased on both cases but it became sharper at larger thickness (106-micon sample) when compared with small thickness (26-micon sample).
4.3.1.2. Transmittance

The transmitted beam intensity was collected concurrently with reflected intensity for each sample. Despite, the change in reflectance from closed side to open side for each sample, the transmittance of both sides of each sample is almost identical, see figure (101).

Figure (101) Transmittance measurement of 26 micron thick titanium dioxide nanotube arrays. Open side curve in black color and closed side curve on blue color.
Similar results obtained for the other three samples

Figure (102) Transmittance measurements of 39, 69 and 106 micron samples
Since the transmittance measurements are independent of which side of the sample is used, we will choose the open side results to carry out a comparative study of the transmittances of all samples involved in this investigation.

From this study, as illustrated by figure (103), we found that the increase in sample thickness is associated with decrease in transmittance for both the visible range and infrared range (400 nm - 1100 nm), but not for the ultraviolet range (200nm - 400nm). This saturation can be explained in terms of the band gap of titanium dioxide, and this will be explained in more detail in the following section.

![Figure (103) Comparative chart of samples reflectance from open sides](image-url)
4.3.2. Integrating sphere

In order to get accurate quantitative measurements for reflectance, transmittance, and absorbance, we measured one sample at Yale University for analysis by integrating sphere spectrometry. The sample has an inner diameter of 160 nm and nanotube length of 60 microns. The measurement is repeated to check consistency, and the final result is taken by averaging the two measurements. Both sides of the sample are studied.

4.3.2.1. Transmittance

The transmittance from both sides looks identical as illustrate by figure (104). This behavior is consistent with results obtained from the normal incidence investigation.

Figure (104) Transmittance through 60 micron thick titanium dioxide nanotube arrays measured by using integrating sphere spectrometry
The transmittance showed wavelength dependence. In the ultraviolet region, the transmittance is almost zero, but for visible and IR regions (450nm - 850nm), the transmittance increases with increasing wavelength to about 50% of the incident beam intensity at 800 nm. The bandgap for the titanium dioxide in its three crystalline phases is approximately 3 eV which is equivalent to 413 nm wavelength. All the samples under investigation are in the amorphous phase which has a more complicated bandgap. If we make the assumption that the bandgap of the amorphous titanium dioxide is approximately 3 eV we can explain the extinction of transmittance at smaller wavelengths (350nm-450 nm) as a result of absorbing these wavelengths which carry energies equal or greater than the bandgap energy of the titanium dioxide.

In order to emphasize our claim we need to study the total reflectance from the same sample and investigate the behavior of short wavelengths. If a small reflection is found in that region we can assure our claim. Another benefit from studying the total reflectance is to help explain the increase in transmittance as the wavelength increases,

The transmittance through the closed side is slightly higher than transmittance through open side at long wavelengths (550nm-850 nm) and slightly lower at short wavelengths (350nm-450nm). The two curves crossover at 500nm. This observation will be discussed in the following section.
4.3.3.2. Reflectance

The main purpose of using the integrating sphere spectrometry is to study the quantitative diffuse reflectance for the titanium dioxide nanotube arrays. In this way, it is possible to accurately estimate the absorbance as a function of nanotube length. The results obtained for our sample is illustrated in figure (105).

![Total Reflectance Graph](image)

**Figure (105) Total reflectance by 60 micron thick titanium dioxide nanotube arrays measured by using integrating sphere spectrometry**

Consistent with the normal incident results, the reflectance of the closed side is higher than the reflectance of the open side, but it only doubled in a certain range of wavelengths (550nm - 850nm). For wavelengths between 350nm and 500nm the reflectance showed a completely different behavior with two main features as follows:
a) The closed side reflectance is smaller than the open side reflectance over that range.

b) The closed side reflectance has a local minimum around 400 nm, while the open side has local maximum around 380 nm.

The two curves cross over at 530 nm.

By subtracting the total reflection and transmission from the initial beam intensity for each wavelength we were able estimate the absorbance of each sample as shown in figure (106).

![Absorbance](image)

**Figure (106) The absorbance of 60 micron titanium dioxide nanotube arrays**

The absorbance showed maximum value around 400nm (3.1 eV) which confirms the assumption of the absorption of these wavelengths by the amorphous titanium dioxide bandgap.
4.3.3. Open investigations

One of the main interesting observations that we are still interested in pursuing is the reflectance inversed behavior for closed and open sides. Our approach to solve this issue is directed by geometrical difference between each surface. For closed side, the surface is free of any holes and is composed of nanocaps due to the bottom of the nanotubes resembling a hemispherical cap. Thus, the material of the closed side is only titanium dioxide. However, for the open side, the surface is more complicated. It is composed of nanotube mouths which do not resemble any kind of known surface roughness.

The full picture of this surface comes from the fact that the nanotube wall thickness varies along the nanotube, from very thin at the tube mouth to very thick at the tube bottom, see figure (107)

![Figure (107) Scanning electron microscope images of titanium dioxide nanotube arrays at different locations](image)

When we consider propagation of the electromagnetic waves inside this material, we have to recognize that the structure of this material varies from one depth to another,
where a combination of titanium dioxide and vacuum (or air) controls the effective dielectric properties of each depth as illustrated by figure (108)

![Diagram](image)

**Figure (108) The variation in the cross-section of the titanium dioxide nanotube arrays along the nanotube length**

A good approximation for this problem is to consider the titanium dioxide nanotube arrays as a film consisting of a series of thin films, each of which has an effective dielectric constant and effective extinction coefficient slightly lower than the thin film before as illustrated by figure (109). Then we study the reflection from all these thin films and any possible interference using computer simulation. The effective dielectric constant and extinction coefficient for certain thin film can be calculated by using the effective
medium theory based on the fraction of vacuum (or air) in the film with respect to the titanium dioxide using the following formula:

\[ \varepsilon_{\text{eff}} = \varepsilon_{\text{TiO}_2} \frac{\varepsilon_{\text{Vac}}(1 + 2\delta) - \varepsilon_{\text{TiO}_2}(2\delta - 2)}{\varepsilon_{\text{TiO}_2}(2 + \delta) + \varepsilon_{\text{Vac}}(1 - \delta)} \]

Where \( \varepsilon_{\text{TiO}_2} \) and \( \varepsilon_{\text{Vac}} \) are the dielectric constants of titanium dioxide and vacuum, respectively, and \( \delta \) is the fractional volume of vacuum in the thin film.

Figure (109) Stack of thin films each of which has slight lower dielectric constant than the film below, the darkest layer represents the thin film with the highest dielectric constant (mostly TiO\(_2\)) while the brightest layer has represents the thin film lowest dielectric constant.

In the previous investigation, all samples were in the amorphous phase. In order to study crystalline titanium dioxide nanotube arrays, we have to thermally anneal the formed flakes. The main challenge we encountered in this regard was that the flakes curl up and
break into very tiny pieces when annealed, as shown in figure (110). This represented the main challenge for our failure to study annealed free standing titanium dioxide nanotube arrays.

Figure (110) Free standing titanium dioxide nanotube arrays before and after annealing
4.3. Conclusion

In conclusion, we were able to obtain free standing titanium dioxide nanotube arrays large enough to conduct our investigation with thicknesses ranging from 26 microns to 106 microns.

Regarding the transmittance measurements, we found that as the sample thickness increases, the transmittance decreases and approaches saturation at 70 microns. So any increase in the nanotube length over 70 microns will be ineffective for harvesting more photons. The two sides of a given sample enabled us to study which side should be exposed for incoming light, by investigating the optical properties of each side. We found that the transmittance can be considered independent of the choice of illuminated side, which confirms the similarity of the transmittance through the open side versus the closed side. From the integrating sphere results, we were able to demonstrate the strong dependence of the transmittance on the wavelength, for short wavelength in the near UV range, transmittance was almost completely suppressed. By increasing the wavelength over 430 nm to the end of the involved spectrum (850 nm), we found the transmittance increased until it reached about 50% at 800 nm. The short wavelength transmittance behavior is understood in terms of the energy band gap of the amorphous titanium dioxide, but the long wavelength behavior is yet to be explained, our approach to understanding this behavior is that we propose to understand the reflection behavior first. We cannot understand transmittance behavior by itself without looking at the reflectance behavior which is still an unsolved puzzle.
Regarding the reflectance measurements, we found that the reflectance is totally dependent on the choice of sample sides. For the closed side, shiny side, the overall reflectance was almost double the reflectance of the open side, dull side. The thickness of sample increase the reflectance only up to 40 microns, any increase thickness over 40 microns did not result in any considerable increase in the reflectance. This piece of information supports our claim that some reflections are happening at deeper layers in the sample and not solely at the surface, as suggested by the porous structure of the sample. From the integrating sphere measurements we were able to observe unexpected behaviors in reflectance when compared with the normal incidence results.

As normal incidence results provided, reflectance from the closed side is always greater than that from the open side, but from the integrating sphere we found that this is true only for wavelengths greater than 550 nm. For wavelengths below 450 nm, the reflectance of the open side is greater than that of the closed side. The open side reflectance showed a local maximum around 380 nm, while the close side reflectance showed local minimum around 400 nm. The two curves crossover at 500 nm.

The specular reflection in the normal incident investigation was the only recorded portion of the total reflection, which includes specular and diffused reflections. Due to the absence of holes or pores in the closed side surface and the low surface roughness, it reflects more specular than diffused spectrum, and vice versa for the open side. This explains the increase in reflectance from the closed side when we use normal incidence measurements. The more accurate results are the integrating sphere results. It measures both the diffused and specular reflections and measures the total reflection of the surface.
Regarding the unexpected behavior of the reflectance measurements, from a simple physics perspective, rough surfaces always reflect less than smooth surfaces. However, this statement is not always true, especially if we consider thin film interference where certain wavelengths, under the destructive interference conditions, are prohibited from reflection no matter how smooth the surface. This argument might be the key to solve the reflectance puzzle. The structure of the nanotube arrays which have nanopores with varying diameters along the nanotube length represents a complex medium for the electromagnetic waves. The reflection and propagation of these electromagnetic waves in that complex medium is controlled by the effective dielectric constant and the effective extinction coefficient. When we consider the variation in the pore diameter, we realize that the effective dielectric constant does not have a fixed value, but it varies along the nanotube length. A good approximation for this case is to consider the sample as a stack of thin films each of which is a complex thin film with its own effective dielectric constant and extinction coefficient. This approach needs to be pursued to understand the behavior of the electromagnetic wave in this complex form of titanium dioxide.

Regarding the absorption, we were able to demonstrate maximum absorption (90%) around 400nm (3.1 eV), which confirms the hypotheses that amorphous titanium dioxide nanotube arrays have energy bandgap around the same value. The absorbance has strong wavelength dependence; it decreases as the wavelength increases from 400 nm to reach minimum value (20%) around 850 nm. From this, we can conclude that titanium dioxide nanotube arrays permits the propagation of IR while absorbs UV spectrum.
Chapter-5

Catalytic properties of Titanium dioxide nanotube arrays

1- Introduction

2- Gold activity from bulk to nanoscale

3- Titania surface a support

4- Attachment techniques

5- Modified deposition precipitation

6- Control over attachment process

7- CO oxidation

8- Results and discussion
5.1. Introduction

In the past two chapters we mainly focused on two important physical properties for any material, the electrical transport and the optical transport properties. There we noticed the importance of the large surface area that titanium dioxide nanotube arrays can provide. One major property which relies on large surface area is the catalytic ability of any new material to enhance chemical reaction or biological process. From this point of view new materials need to be studied for catalytic activity. In this chapter I will explore the ability of titanium dioxide nanotube arrays to exhibit catalytic activity for certain chemical reactions.

5.2. Gold activity from bulk to nanoparticles

Gold was considered for long time to be a noble metal with poor catalytic properties until the discovery of Haruta et al in 1987 [212], who demonstrated that nanosize gold clusters supported on the oxides of 3d transition metals, namely, Fe, Co and Ni have very good catalytic properties for CO oxidation at temperatures as low as 200 K. His discovery draw the attention of many research groups to carry out more investigations to understand the role of both the gold nanoparticles and metal oxide support, to develop a controllable technique for the fabrication process which yield highly efficient catalyst.
Valden el al [213] was able to demonstrate the catalytic activity dependence on gold nanoparticles size when supported on single crystalline titanium dioxide thin film. He studied the conversion rate of CO to CO$_2$ for gold nanoparticles with sizes ranging from 1 nm to 7 nm, as illustrated in figure (111).

Figure (111) a) CCT STM image of Au/TiO$_2$ (110)-(1x1) as prepared before a CO:O$_2$ reaction. The Au coverage is 0.25 ML, and the sample was annealed at 850 K for 2 min. The size of the images is 50 nm by 50 nm. b) The activity for CO oxidation at 350 K as a function of the Au cluster size supported on TiO$_2$(110)-(1x1) assuming total dispersion of the Au. The CO:O$_2$ mixture was 1:5 at a total pressure of 40 Torr. Activity is expressed as (product molecules)/(total Au atoms)$\times$1 second$^{-1}$ [213].

Titanium dioxide support:

The catalytic behavior of gold nanoparticles for CO oxidation is not solely related to the gold nanoparticles and its size, but is a combination of properties of gold nanoparticles and the properties of its metal oxide support. Titanium oxide as a support is preferable considered for its
chemical inertness and stability. Many research groups studied gold supported titanium dioxide in many forms, mainly, thin film like the work done by Haruta group and Valden group, and powder from which is pioneered by Moreau and Bond group. Several methods such as thermal evaporation [213], chemical vapor deposition [214] and precipitation-deposition from solution [215] have been employed for the attachment of gold nanoparticles to monolithic titanium dioxide thin films and excellent catalytic properties for the oxidation of CO to CO$_2$ have been reported. A direct relationship between the effectiveness of the catalyst and the diameter of the gold nanoclusters has been demonstrated, with a maximum in the rate of oxidation reported for gold nanoparticles of diameter $\sim 3.5$ nm$^2$.

Figure (112) Electron micrographs image of gold nanoparticle supported on titanium dioxide powder. Gold nanoparticles range 4–20 nm [216]
5.3. Titanium dioxide nanotube arrays as support

As the total surface area of the support directly impacts the effectiveness of catalytic reactions, it is expected that increased surface area will result in improved catalytic effectiveness. To this end it is useful to investigate structure of titanium dioxide nanotube arrays as support instead of uniform films or powder. There are at least two factors supporting the superiority of titanium dioxide nanotube arrays over any other forms of titanium dioxide:

a) Titanium dioxide nanotube arrays can be fabricated with nanotube length up to 1000 µm using Ethylene Glycol electrolyte [217]. This means an extraordinary aspect ratio is attainable. Or in another words, a very large surface to volume ratio is provided by this highly ordered tubular structure of titanium dioxide. More detail about the large surface to volume ratio of titanium dioxide nanotube arrays is explained in appendix A.

b) Highly ordered titanium nanotube when opened from the bottom side, it will form a very good path for gases or generally fluids. This property is required, especially, for catalytic application, where gases must be brought together to react on the surface of the catalyst. The tiny hollow structure of these nanotubes forces the reactant molecules to come close to each other and also be surrounded by the catalyst. This environment is ideal for efficient reaction with the aid of a catalyst. The reaction rate can be increased by following more reactant gases though the nanotubes.

For these factors and others we anticipate that titanium dioxide nanotube arrays will be the ideal support for gold nanoparticles to perform efficient catalytic abilities.
5.4. Successful trials on other forms of Titanium dioxide

A) Thin film

The first report for gold nanoparticle catalytic activity when supported on titanium dioxide was done on thin film, the simplest method deposit gold nanoparticles on thin films is the physical vapor deposition [212,213,218,219,220]

B) Hydrothermal nanotube

Previous reports of gold nanoclusters supported on geometrically-disordered titanium dioxide nanotubes (routinely synthesized by a hydrothermal treatment of anatase nanoparticles pioneered by Kasuga et al [221]) have featured good coverage of gold particles over the nanotube surface and greatly improved catalytic properties were obtained in comparison to similar systems of gold

![Image](image-url)

Figure (113) Au-loaded nanotubes. (a) Typical TEM image. (b) HRTEM image showing the clearly resolved lattice image of fcc Au \( d(111) \) 0.24 nm[222]
C) Powder

Using precipitation deposition method, Moreau and Bond where able to master the deposition of gold nanoparticles on titanium dioxide powder [215,216]

Other methods such as, photochemical deposition [223] and pressure impregnation [224] of titanium dioxide nanotubes arrays inside alumina templates, electrochemical deposition [225] and dispersion of colloidal gold nanoparticles solution [226] on ordered titanium dioxide nanotubes obtained by anodization have been also reported, and in the last case an important increase in the oxygen reduction reaction rate has been also observed when compared to gold supported titanium dioxide flat film [226]. However, to our knowledge no report on controlled, uniform attachment of gold nanoclusters on geometrically-ordered titanium dioxide nanotubes arrays using deposition-precipitation technique has been recorded to date.

We provided detailed information in chapter 2 on the fabrication of ordered titanium dioxide nanotubes arrays by anodization techniques, which indicates excellent control over nanotube diameter (25-250 nm) and length (0.5 µm to 1000 µm, limited only by the initial thickness of the titanium foil). These developments have led to the attainment of high aspect ratio titanium dioxide nanotube samples with well controlled morphologies and large surface areas. These features, combined with the intrinsic properties of TiO₂, boosted the performance of photocatalytic and photovoltaic devices employing such materials. Addition of a second material with metallic properties to the nanotubes has also been recently reported; for example,
Macak et al [226] demonstrated successful filling of the nanotubes with copper using an electrodeposition method.

In this work there are two main investigations; first, developing a method that achieves controlled attachment of gold nanoparticles on ordered titanium dioxide nanotubes arrays; second, studying the catalytic activity of gold nanoparticles on this new support for CO oxidation reaction.
5.5. Development of gold deposition technique

5.5.1. Experiment methodology

a) Titanium dioxide nanotube arrays sample preparation

In this investigation I used two different kinds of sets of samples, the first set of samples is short titanium dioxide nanotube arrays fabricated by using HF electrolyte with fixed nanotube length around 400 nm and range diameters from 25 nm to 75 nm. The sample area varies from 1 cm$^2$ to 10 cm$^2$. The nanotubes layer is strongly attached to the titanium surface underneath.

The second set of samples is long titanium dioxide nanotube arrays fabricated by using Ethylene Glycol electrolyte with nanotube length around 10 µm and nanotube diameter around 150 nm, in these samples nanotube layer can be easily peeled off the titanium surface and form free standing nanotube array, this property will play a major role in the second investigation.

b) precipitation deposition method

Gold nanoparticle formation and attachment to the nanotube surfaces was achieved with a variation of the deposition-precipitation method pioneered by Haruta et al [212] and successfully employed by Moreau et al [215,216] for titanium dioxide thin films. This process involves soaking the samples in a basic Sodium hydroxide solution (NaOH) containing Chloroauric acidic salt (HAuCl$_4$) as source of gold atoms. In previous experiments [215] a key element to obtain small diameter nanoparticles was to maintain a
constant pH solution value of 9. This constraint necessitated periodic adjustment of the concentration of sodium hydroxide during the deposition process, since the pH evolved in time as the solution was depleted in gold salt. This adjustment created further complications in controlling the nanoparticle deposition when adjusting other parameters such as the total surface of the sample or the morphology of the nanotubes. Another problem with this technique is that, all successful trials relayed on the precise amount of titanium dioxide in the solution as key factor, but in our case it is impossible to find out the amount of titanium dioxide precisely in the sample, this due to the existence of titanium layer under the nanotube arrays and the huge challenge of peeling off the nanotube arrays, especially in short nanotube case.

These two major problems prevented me from getting any successful deposition when I used the precipitation deposition technique for my samples. After many failures I was motivated to modify this technique. I was able to develop another method of applying the precipitation deposition technique to our samples, which lead me finally to unprecedented control of gold nanoparticles deposition, this method itself published in Journal of Materials Chemistry in recognition of its importance in this field [228]

C) Modifying the precipitation deposition method

In our modification approach only three external parameters were found to be critical in controlling the dimension and coverage of the gold nanoparticles on the titanium dioxide nanotube surface:

a) The initial concentrations of gold and NaOH in the solution.
b) The solution temperature during the deposition process.

c) The deposition process duration.

The procedure consists of four steps as illustrated in figure (114)

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Figure (114) Graphical illustration of the experimental procedure for the modified precipitation deposition method

I. Titanium dioxide nanotube arrays fabrication, we started with short nanotube sample (small aspect ratio: 70 nm diameter and 400 nm length) with a total sample surface area of 4 cm² (2cm x 1 cm x 2 sides)

II. Solution preparation is done by mixing a solution of 2x10⁻³ M HAuCl₄·3H₂O (Alfa Aesar, metals basis, 99.99%) with another solution of 8.8x10⁻³ M NaOH
(flakes, Fisher Scientific), both in de-ionized water. 25 mL from each solution were used for a final 50 ml mix of $1 \times 10^{-3}$ M HAuCl$_4$·3H$_2$O and $4.4 \times 10^{-3}$ M NaOH (“standard NaOH concentration”).

III. The nanotubes samples were immediately soaked in the final solution, and the container was closed.

IV. The container is placed on hot plate with temperature of 140°C for one hour (“standard soaking time”). The temperature of the solution raised in one 60 minutes it will reach value around 70°C as illustrated by another independent investigation in figure (115)

![Figure (115) The temperature of the solution measured during the heating over hotplate with surface temperature 140°C, the initial temperature of the solution was the room temperature.](image)

Figure (115) The temperature of the solution measured during the heating over hotplate with surface temperature 140°C, the initial temperature of the solution was the room temperature.
temperature (20°C) for 3 different successful samples S1, S2 and S3 and it saturated around 60°C.

V. After the deposition, the samples were taken out and washed with DI water for 10 - 20 seconds and then dried using air stream for 1 min.

VI. The sample color turns into blue or dark blue as the first indication of successful deposition of gold nanoparticles on the nanotube surface as shown in figure (116)

![Image of sample photos](image_url)

Figure (116) Photo of sample (a) before deposition, (b) after deposition for short nanotubes and (c) after deposition for long nanotubes sample.
5.5.2. Results and discussion

A) Successful attachment method

The sample is taken to SEM for investigation, where successful deposition is observed as provided by figure (117). Very good coverage of gold nanoparticles is achieved, the gold nanoparticles is very small compared with the nanotube dimension (~ 5nm to 70nm). The gold nanoparticles appears on the SEM images as tiny grains on the surface of the titanium dioxide nanotubes, especially when compared with the nanotube surface before deposition (blank nanotubes).

Figure (117) High resolution SEM image of low aspect ratio titanium dioxide nanotubes (a) before and (b) after the first successful deposition of approximately 2 nm diameter gold nanoparticles on the tubes walls; c) Larger view demonstrating uniform coverage all over the nanotubes array d) EDX analysis of the same sample exhibiting gold peaks, thus confirming the nature of the deposited material.
To confirm the chemical composition of these tiny nanoparticles, EDS analysis is done, the EDS spectra showed peaks for titanium and oxygen as expected for the nanotube composition, and also it showed gold peaks is smaller than Ti and O₂ peaks, this is expected from the SEM images that indicate the ratio of gold to titanium dioxide is very small as illustrated in figure (117-d)

The low aspect ratio nanotube samples (short tubes) were furthermore subjected to a systematic investigation into the attachment of gold nanoparticles for different deposition parameters. Good size uniformity and good surface coverage of the nanoparticles on both the inside and outside surfaces of the nanotubes has been achieved. Nanoparticle diameters < 5 nm, optimum for maximum photocatalytic efficiency [213] and large surface coverage have been achieved.

**B)-Gold nanoparticles size dependence**

Results concerning the dependence of the size of the deposited gold nanoparticles on the soaking time are displayed in figure (118) where it is noted that the average diameter of the gold nanoparticles increases with increased soaking time. In this work nanoparticle diameters ranged from 2 nm for 1 h soaking time to almost 7 nm for 20 h soaking time. The narrow full-width at half maximum (FWHM) values of the accompanying histograms indicate good control over the particle size for the given soaking time values. figure (118) also illustrates that nanoparticle surface coverage increases with increasing time, a result attributed to growth of individual particles. For
soaking times longer than 10 hours (Fig. 118c and 118d), the coverage is almost complete.

Figure (118) High resolution SEM images of gold attached titanium dioxide nanotubes for different soaking times: 2 h (a), 3 h (b), 10 h (c), and 20 h (d), and the corresponding size distribution of the particles (e-h). Scale bar is 20 nanometers for all SEM images; histograms were constructed based on 46 particles measurements for all plots; histogram x scales were adjusted to depict average diameter increase from 2 hours to 3 hours, and from 10 hours to 20 hours respectively.
The particles grow to impingement approaching a uniform coverage of the titanium dioxide substrate with a gold layer suggesting the possibility of developing a Schottky-type bilayer.

The increase in particle diameter with increasing soaking time is also noted in figure (119). It is also observed that for long soaking times the nanoparticle diameter begins to saturate to a value of around 7 nm. Correspondingly, the average particle density is found to decrease with increased soaking time due to merging of individual particles although the areal coverage continues to increase.

Figure (119) a) Dependence of the particles average size with respect to as the soaking time, b) Dependence of particle density with respect to external as the soaking time
In contrast, soaking times of 3-4 hours create nanoparticles with average diameter < 5 nm. As mentioned earlier, such particles have great potential for photocatalytic applications.

c) **The effect of sample surface area**

Figure (120) also demonstrates that increasing the total surface area of the nanotube samples does not result in significant changes in either the nanoparticle size or nanoparticle density on the tube surface beyond a soaking time of 1h. This result suggests that the initial Au concentration in the solution is sufficient to allow the same number of particles to form and attach per unit area.

![Figure (120) Dependence of a) the particles average size and b) particle density with respect to the soaking time](image-url)
D) **The surface coverage dependence**

The dependence of the percent coverage of Au nanoparticles on the soaking time and on the total surface area of the sample is shown in Figures (121 a, b). The percent coverage increases with increased soaking time until it begins to saturate to a value of around 75%. The process is reasonably scalable as seen from figure (121b). There is very little change in percentage coverage as a function of sample surface area. The coverage varies from approximately 20% at 4 cm$^2$ to 10% at 20 cm$^2$.

**Figure (121)** Dependence of the surface coverage on a) the soaking time, b) the sample flat surface area
E) The gold loading from the solution

By considering that the nanoparticles has spherical shape, and based on our measurement of coverage density, we were able to estimate the gold loading dependence on the soaking time, which reached 16% after 20 hours of soaking time as illustrated by figure (122)

![Graph showing gold loading percentage vs. soaking time](image)

**Figure (122)** The estimated dependence of gold loading percentage with respect to soaking time.

F) Long nanotube samples

While the above characteristics were obtained on low-aspect-ratio titanium dioxide nanotubes, when we applied the same recipe for 10 µm long nanotube samples we got a very bad deposition as shown in figure (123), where a few large gold particle deposited
Figure (123) High resolution scanning electron microscope image shows a very poor deposition with large gold nanoparticle size around 20 nm.

After few adjustments we were able to achieve good deposition with long nanotubes similar to what we had with short nanotubes. This was done by slightly changing the recipe of the solution. The concentration of NaOH in the soaking solution was reduced from $4.4 \times 10^{-3}$ M to $3.8 \times 10^{-3}$ M in the final 50 ml mixture. As shown in figure (124), it can be clearly seen that gold nanoparticle deposition occurs uniformly over the entire length of the nanotube walls, both on the interior and exterior surfaces. No preferred growth direction for individual particles is seen and, no re-nucleation sites, superimposed on the original particles, are detected. These overall characteristics lead to a uniform coating of the available surface, without filling or clogging of the nanotubes.
Figure (124) High resolution scanning electron microscope images of high aspect ratio titanium dioxide nanotubes (a) before and (b) after the successful deposition of gold nanoparticles; c) Side view showing uniform deposition on the whole length of the nanotubes; d) Side view of broken nanotubes demonstrating similar uniformity of gold nanoparticles deposition both inside and outside the tubes.

The study of gold nanoparticles size and coverage dependence on soaking time is done on low-aspect ratio titanium dioxide nanotubes using SEM images, despite its limited accuracy compared with TEM images, it will provide a correct coverage density on each side of the nanotubes walls, which allow us to estimate correctly the total amount of gold deposited on the surface of nanotubes. Also it is extremely hard to release low aspect-ratio (400 nm length) titanium dioxide nanotubes from the surface of the sample, and to place it on TEM grid for investigation.
Large aspect-ratio nanotubes are easily transferred from the sample to TEM grids for more detailed imaging and characterization (figure 125). Figures 125a and 125b confirm the uniform coverage of gold nanoparticles on the nanotubes walls. The size of the gold particles for this particular sample was found to be $2.08 \text{ nm} \pm 0.93 \text{ nm}$, as averaged over 80 particles.

Figure (125) a) TEM image of gold nanoparticles supported on a fragment of a high aspect ratio titanium dioxide nanotube b) TEM image of the nanotube wall exhibiting gold particles on both sides. c) HRTEM image revealing the crystalline structure of the gold nanoparticles on the
amorphous titanium dioxide support d) EDX spectrum of the TEM sample, with the relative concentration of the elements of interest shown in the inset.

In the high-resolution (HR) TEM images (Fig. 125c) the morphology of the gold nanoparticles may be analyzed in detail; many nanoparticles with well-defined facets (pentagonal, hexagonal and octagonal) can be observed, suggesting that most of them are single crystals.

The average lattice spacing may be determined from the HRTEM images (Fig. 125c) as 2.48 Å. This result is within 5% of the literature value for the (111) plane spacing distance of 2.35 Å. Energy-dispersive X-ray spectroscopic analysis (Fig. 125d) indicates that the elemental concentrations are as follows: the atomic ratio Ti: O is very close to the predicted 1:2 value, and the weight percent of gold nanoparticles with respect to titanium dioxide nanotubes is estimated as 22.3%.
5.6. Catalytic activity of gold modified Titanium dioxide nanotube arrays.

The beauty of the gold modified titanium dioxide nanotube arrays and the simplicity of the involved technique should not distract us from the main purpose of developing this material. The catalytic activity measurement will judge the functionally of this material. This investigation is done for both the short nanotube arrays and long nanotube arrays.

The short nanotube arrays didn’t give a noticeable catalytic activity, this due to the limited amount of titanium dioxide in the sample, where a very thick layer of titanium still attached strongly to the nanotube arrays. This chunk of titanium will consume most of the available volume without providing catalytic activity. In another word, the volume equipped by the sample is mostly non-functional.

On another hand the long titanium dioxide nanotube when used in this investigation it did show a good catalytic activity. For this reason, I mainly used in this investigation only titanium dioxide nanotubes as flakes that were easily peeled off the surface of the titanium substrate; this to ensure that the sample under investigation consists only of nanotubes supporting gold nanoparticles.

Another important factor in this investigation is that all samples involved are amorphous titanium dioxide nanotube arrays supporting gold nanoparticles. The importance of this remark is
we reported the onset of catalytic activity of amorphous titanium dioxide as support, where all the reported successes with this material used the crystalline phases.

9- Reaction pathway

Carbon monoxide oxidation reaction with the aid of gold nanoparticles when supported on titanium dioxide surface at room temperatures is extensively studied by M. Haruta group, they were able to develop a propose mechanism of this reaction as described below [228]

\[
\begin{align*}
\text{Above 300 K:} & \\
\text{Au(p)-CO} + \text{TiO}_2(p)-\text{O}_2^- & \rightarrow \text{CO}_2(g) + \text{TiO}_2(p) + \text{e}^- + \text{Au}^{\delta+}(p)-\text{O}^{\delta-} \\
\text{Au(p)-CO} + \text{Au}^{\delta+}(p)-\text{O}^{\delta-} & \rightarrow \text{CO}_2(g) + 2\text{Au}(p)
\end{align*}
\]

\[
\begin{align*}
\text{Below 300 K: accompanied by} & \\
\text{Au(p)-CO} + \text{TiO}_2(p)-\text{O}_2^- + \text{e}^- & \rightarrow \text{Au}(p) + \text{TiO}_2(p)-\text{CO}_3^{2-}
\end{align*}
\]

\((s): \text{step}, (p): \text{perimeter}, (g): \text{gas phase}\)

Figure (126) The reaction pathway of the CO oxidation reaction of Au/TiO\(_2\) as published in [228]

At the perimeter interface of the gold and the titanium dioxide, O\(_2\) molecules bind to the titanium dioxide and donate oxygen to the CO, which are bound to the gold. However, below 300\(^\circ\)K, the reaction is incomplete, and carbonate (CO\(_3^{2-}\)) will form and bind to the surface and stay, causing the sample to deactivate
5.6.1. Experimental Methodology

The catalytic activity measurements is done in a closed CO reactor, the sample is placed in a closed chamber where the reacting gases (CO and O₂) are allowed to flow over the sample, where the reaction will take place, then leave the chamber for measuring their levels and compare it to input levels. Any catalytic activity from the sample will be demonstrated as increase in the CO level of the output compare to the input level. Also the increase in the chamber temperature is another indication of the reaction between oxygen and carbon monoxide. This due to the exothermic nature of the reaction, actually it is considered as a combustion reaction.

The gas level is measured by gas chromatograph instrument. The high toxicity of the carbon monoxide gas require extremely careful handling of the whole setup, where a well-sealed pipes is used and check before running the CO gas from the CO gas cylinder to the gas chromatograph, from the gas chromatograph to the reactor (chamber contains the sample), from the reactor to the gas chromatograph and finally to safe ventilation outlet.

The reactor consists of well-sealed chamber that contains the sample, it has a thermometer to measure inside temperature of the chamber and it has external heater to raise the temperature of the chamber, consequently the reaction, if needed. The chamber has two separate inputs, each delivers one of the reacting gases to the chamber, and it has one output that carries out the product to the gas chromatograph
Figure (127) Scheme of the system setup used to investigate the catalytic activity of gold modified titanium dioxide nanotube arrays for CO Oxidation reaction.

In this system setup the “Upstream” expression is used to describe the gases levels before entering the reactor, and the expression “Downstream” is used to describe the gases levels after it leaves the reactor.

The sample under investigation is about 0.1 grams of gold modified titanium dioxide nanotube arrays that were peeled of the titanium substrate, then crushed and placed in the chamber.
5.6.2. Results and discussion

A- Chamber temperature increase

Measurements were taken at room temperature, and a steady increase in temperature was noticed for about 20 minutes, reaching a peak at about 37 degrees Celsius. This was a good sign, leading to the belief that the sample had self-started, as platinum-iridium oxidizers typically have to be given a large temperature bias before they will begin to work.

B- Gas levels

Measurements of 4 upstream and 4 downstream measurements were taken. Two of each was system check runs with no CO to make sure that upstream and downstream measurements were consistent. The two CO oxidation runs are presented below in figure (128).

Different elements in the gas appear on the gas chromatograph (GC) readout at different times. In the data table underneath, the number in the left column denotes which peak and the second number denotes the magnitude of the amount of gas that is present. By comparing the relative magnitude of the CO peak up and downstream from the reaction, we can get an idea of how much of the gas is being converted to CO₂. Run 6 shows that only 24% of the CO leaves the reaction chamber, when compared to run 5, and although the downstream CO peak on run 8 appears larger than the downstream CO peak on run 6, the Upstream CO peak on run 7 is also larger than the upstream run on run 5, and in fact only 25% of the CO remains in run 8 when compared to run 7.
Figure (128) The gas chromatograph (GC) readouts of two runs, a-b first run upstream and downstream respectively, c-d second run upstream and downstream respectively.
After two weeks of sitting in the reaction chamber the sample was tested again. This time 3 downstream and two upstream CO oxidation runs were taken. Shown below is an example of the integrator readouts. The average magnitude CO upstream was 1,087,750, downstream was 880,000 ± 71,000, meaning that on average, 81 ± 6% of the CO remained after the reaction. The sample showed extremely good conversion capabilities on day one but after two weeks it failed to do so again as shown in figure (129)

Figure (129) The gas chromatograph (GC) readouts of one run after two weeks, a) upstream and b) downstream measurements

This very large decrease in the amount of CO conversion could be due to two possible reasons. The reason could simply be that a gold catalyst supported on titanium dioxide may not have a very long lifetime, and that the gold deactivates as a catalyst after a short period of time. The other possibility is that since these
experiments were started from room temperature, carbonate built up on the surface, preventing CO from being oxidized at that location, as predicted by Haruta et al [229]. It is important to note that we are measuring the amount of CO before and after the reaction, not the amount of CO₂, so either explanation could account for the lack of CO molecules downstream.

After reviewing the results from the first sample, it was decided that a second sample should be tested. The reason the longer titanium dioxide nanotube sample was chosen this time was because of difficulties depositing gold onto the flakes. Titanium dioxide flakes are extremely delicate, so much so that they cannot even be lifted with tweezers, and have a tendency to get crushed when being put in and out of the gold deposition solution. It is also much more difficult to image the gold nanoparticles on titanium dioxide nanotube flakes on the SEM because charging on the long, 20 + micron flakes is a large obstacle to overcome, and the desire was to calculate the fill factor, which needs a good estimate of the number of gold particles on the sample.

Another adjustment in the experimental procedure is introduced; this by heating the reaction chamber above 300 Kelvin to eliminate the possibility of carbonate buildup as explained by Haruta et al [229].

C) Temperature effect

A total of 24 measurements were taken, these measurements were divide to server three different experimental conditions as follows

i) Runs 1-8 were taken at room temperature, (25 degrees Celsius)
ii) Runs 9-17 the chamber was heated externally to 100 degrees Celsius

iii) Runs 18 – 24 the chamber was heated to 200 degrees Celsius.

**Room temperature (25°C)**

At room temperature, runs 2 and 4 had an average CO magnitude of 650,000, and run 3, the first downstream run of the day, had a CO magnitude 77,400, indicating that only 12% of the initial CO remained after the reaction. The temperature was seen to rise from 23.3 to 23.7 degrees Celsius over 16 minutes, but began to fall afterwards, indicating a short-lived reaction. Unfortunately, for downstream runs 5 and 7, no change in CO levels was observed when compared with upstream measurements, indicating that the catalyst had lost its activity.

**Temperature of 100°C**

We proceeded to heat the reaction chamber to 100 degrees Celsius by an external oven in an attempt to jumpstart the reaction and potentially decompose some of the carbonate that could have potentially accumulated on the surface. At this temperature, the upstream CO magnitude was 947,000 ± 43,000. The temperature was only set to rise to 100 degrees Celsius but rose to 134 degrees Celsius after 12 minutes of passing the 100 degree set-point, indicating a possible reaction. At its highest temperature a downstream measurement was made and had a CO magnitude of 550,000, indicating only 58% of the original CO remained. After this maximum, the temperature dropped back down to 100 degrees over 14 minutes. Multiple downstream measurements were taken however no change in CO content was observed when compared to upstream measurements.
Temperature of 200°C

We proceeded to heat the chamber again to 200 degrees Celsius, but no downstream measurements revealed any reaction.

D) -The Turnover frequency

The turnover frequency is a measure of the rate at which the individual CO molecules are converted to CO$_2$ per second per gold particle. Haruta et al. [229] showed in a study that the optimal gold particle size for CO oxidation is approximately 3.5 nm in diameter.

![Figure (130) Turn over frequencies and band-gap measured by STM as a function of the diameter of Au islands deposited on TiO$_2$ (depicted from [229])]
To calculate the turnover frequency, an estimation of the number of gold particles was necessary. Measurements of average tube diameter, tube length and tubes per square unit of area were obtained through the SEM, and the macroscopic surface area was measured with a ruler. $2\pi*diameter*length$ gives the total surface area for the inside and outside of the nanotube. The number of tubes per unit area, times the macroscopic surface area (front and back) gives the number of nanotubes. Finally, the number of gold dots per unit area, times the total surface area, will give a good estimation of the total number of gold nanoparticles. By knowing the rate of CO flow through the chamber, and dividing it by the number of gold atoms, we know the ratio of CO to gold per second, and can calculate the turnover frequency by the percent of CO converted.

The sample under investigation had an estimated $6.5 \times 10^{15} \pm 6 \times 10^{14}$ gold particles. For the room temperature run, which saw an 88% conversion, the fill factor is calculated to be $2.8 \pm .3$ CO molecules converted per site per second, which is low, compared to M. Haruta’s value of 4 for nanoparticles 3.25 nm in diameter. A possible explanation could be that it is difficult for the gas to make its way the very bottom of the nanotubes, so the particles deep in the tubes may not be doing much work, bringing the turnover frequency down. The turnover frequency of the smaller reaction that happened at 100 degrees was only 1.3 CO molecules converted per site per second. However, the chemical reaction that these turnover frequencies are
describing could either be a short lived CO oxidation, or the absorption of carbonate onto the surface of the titanium dioxide.

E) Carbon adsorption

In order to investigate the probability of carbonate adsorption by titanium dioxide nanotubes during the reaction, the sample used for the turnover frequency measurement has been analyzed under Energy Dispersive X-Ray Spectroscopy (EDS) after CO runs had been completed. Sample holders were washed with acetone and samples were attached with copper tape, to avoid erroneous carbon contamination. If carbonate had been absorbed onto the surface, we would expect EDAX to reveal carbon peaks, which they do, at 14% atomic %. We were also expecting a stronger oxygen peak, more than 2x the size of the titanium dioxide peak, but this was not observed. In reality, we should have done EDAX analysis before we tested the sample as well, so that we could compare the size of the observed peaks before and after. Since we did not observe an increased oxygen peak from the carbonate, we can only rely on the carbon peak, and EDAX is not very good with detecting carbon, so the results may not be trustworthy without an EDAX analysis of the sample before testing to compare to.
5.7. Conclusion

Regarding the gold deposition investigation, the successful uniform deposition of gold nanoparticles on titanium dioxide arrays by a simplified deposition-precipitation approach has been demonstrated. It is noted that the soaking time has an important influence on the correlated values of the nanoparticles size and coverage percentage of the TiO$_2$ surface. The process is scalable for large surface areas and long nanotubes (as demonstrated for up to 20 cm$^2$ and 5-6 microns respectively). The use of high-aspect-ratio nanotubes significantly increases the effective surface area, and the process may be tailored by as proper adjustment of the nanoparticle diameter or extension of the coverage percentage towards 100% by increasing the time of soaking. These results illuminate a way to improved devices for photo-activated water splitting or for photocatalytic oxidation of carbon monoxide, as well as for other applications involving hybrid semiconductor-metal combining materials, such as metal-semiconductor Schottky bilayers.

Regarding the catalytic activity investigation of the gold decorated titanium dioxide nanotube arrays, from all the previous experimental results, we were able to demonstrate catalytic activity of gold nanoparticle supported on titanium dioxide nanotube arrays, especially when we precisely tailored the gold nanoparticle size around 3.5 nm. The length of the nanotube is considered an important factor in the catalytic activity, as we demonstrated the inability of short nanotube to provide any considerable amount of CO
to CO₂ conversion, we found long nanotube sample demonstrate, in some cases, a conversion percentage up to 88%.

The onset of this catalytic activity on amorphous titanium dioxide is a major discovery, which need to be studied in more detail and to check how the crystallinity of the sample might change the catalytic activity as the sample transforms from amorphous to crystalline phase.

The problem regarding the instability of the conversion rate of a given sample need to be explore with more investigation, these investigation need to address possibility of carbonate adsorption on the titanium dioxide nanotube surface, and also effect of these adsorbed molecules, if any, on the reaction pathway.
Appendices

1- Appendix A

2- Appendix B

3- Appendix C
Appendix A

Aspect ratio and effective surface area

The aspect ratio of an object is the ratio of its longer dimension to its shorter dimension. It may be applied to two characteristic dimensions of a three-dimensional shape, such as the ratio of the longest and shortest axis, or for symmetrical objects that are described by just two measurements. In our case the aspect ratio of titania nanotube is the ratio between the length and the outer diameter of the nanotube.

\[
\text{Aspect Ratio} = \frac{\text{Nanotube length}}{\text{Nanotube outer diameter}}
\]

The titania nanotube arrays form in a vertical order on the surface of the titanium foil. It is clear from SEM Investigations that titania nanotubes follow the closest packing fashion to form an array of vertically aligned nanotubes as shown in figures (1).

Figure (1) SEM images of titania nanotube arrays
It have been demonstrated from several SEM images that the titania nanotube has varying wall thickness along the nanotube. The wall thickness changes from very thin, almost less than 10% of the nanotube radius, at the top to very thick, almost 80% of the nanotube radius at the bottom as shown in figure (2).

![SEM images of titania nanotubes at different locations](image)

**Figure (2) SEM images of titania nanotubes at different locations**

This variation need to be studied as function of final nanotube length, where we expect to have a dependence of this variation from top to bottom on the final nanotube length. One evidence for this dependence is for short nanotube of length 0.5 µm (fabricated by using 0.5 M HF solution) SEM images demonstrate almost no change in the nanotube wall thickness from top to bottom, but for a longer nanotube of length of 60 µm (fabricated by using Ethylene glycol and 0.3 wt. % of KF) SEM images demonstrate a huge variation of the wall thickness from top to bottom. Another important phenomenon we were able observe that the nanotube outer cross-section is changing from circle at the top to hexagon at the bottom. Consequently the void between nanotubes at the top (circular tube cross-section) shrinks and almost vanishes at the bottom (hexagonal tube cross-section) to optimize the closest packing at the bottom as shown in figure (3).
Figure (3) SEM images of top and bottom of titania nanotube arrays

Let’s consider the ideal case, where the titania nanotube arrays follow a honeycomb structure on in a horizontal plane to the growth direction as shown in figure (4). Also let consider the case where the outer shape of the nanotube is represented by a symmetrical cylinder.

Figure (4) 3D graphical model of titania nanotube arrays
The area hexagonal unit cell is given by the formula

\[
Area = \frac{3\sqrt{3}}{2}a^2
\]

Where "a" is the side length of the hexagon unit cell. Each unit cell has four nanotubes. Consider the outer diameter of a nanotube is \( R \) and the inner diameter is \( r \) at the top side of the nanotube arrays. Under these assumptions we can calculate the void area in the unit cell as follows

\[
\text{Void area} = \text{area of hexagon} - \text{cross sectional area of four cylinders}
\]

From cross section perception, the cross sectional area of the cylinder is define as

\[
\text{Cross sectional area} = \pi(R^2 - r^2)
\]

Therefore

\[
\text{Void area} = \frac{3\sqrt{3}}{2}a^2 - 4\pi(R^2 - r^2)
\]

It clear that \( a = 2R \)

\[
\text{Void area} = \frac{3\sqrt{3}}{2}4R^2 - 4\pi(R^2 - r^2)
\]

We estimated that in many cases the inner radius \( r \) at the top is almost 90% the outer radius \( R \)

Under these considerations

\[
\text{Void area} = \frac{3\sqrt{3}}{2}4R^2 - 4\pi(0.19)R^2
\]

\[
\text{Void area} = 8R^2
\]

Which means that ratio between the cross section area of four tubes and the area of the hexagon is almost 23%. And the remaining 77% is just void area.

Now let consider real three dimensional case, where the length of the nanotube and its side area will play a major role in increasing the effective area (area of nanotubes) to the actual area (area of the hexagon). The outer shape of the nanotube is varying from cylindrical at the top to
hexagonal at the bottom as illustrated in figure (3). Despite this variation in the shape, the value of the outer diameter at of the cylinder the top almost equals the diagonal value of the hexagon at the bottom. Meanwhile the inner diameter shrinks from its maximum value at the top to its minimum value at the bottom. In order to simplify the geometry for further calculations lets approximate the real geometry of the nanotube to perfect cylindrical shape from the outside with outer radius $R$ while it has a conical shape from the inside as shown in figure (5).

![Figure (5) Scheme of the change in the nanotube wall thickness along the nanotube](image)

The inner radius $r$ changes its value from $0.9R$ at the top to $0.2R$ at the bottom. The reason for choosing these two parentages (90% and 20%) is supported by many SEM images, where I was able to measure roughly the inner radius $r$ and compare it with the outer radius at many locations along the nanotube. The side area of a the outer cylinder of length $L$ side area = $2\pi RL$

The area of the inner cone bit complicated, I’ll carry out this derivation for finding the side area of a cone with two radii "$R$" and "$r$". First consider the simple case of a cone of radius $R$ and side length $S$ as shown in figure (6.1). The area of the side is given by

$$A = \pi RS$$
Now we will divide this cone into two parts, the upper part is a cone with radius \( r \), while the lower part is a cylinder with two different radii \( r \) and \( R \). We are interested in finding the side area of the bottom part of bigger cone. The bigger cone has a side length \( X \) while the upper cone has side length \( D \) as shown in figure (6.2).

\[ \text{Figure (6) Scheme of the side surface area of a cone} \]

Since Area of upper cone \( (A_U) = \pi rD \)

And Area of bigger cone \( (A_T) = \pi RX \)

Therefore the area of the lower part is \( (A_L) = A_T - A_U \)

For the upper cone \( D = \frac{r}{\sin\theta} \)
Therefore \( A_U = \pi \frac{r^2}{\sin \theta} \)

Similarly for the bigger cone \( X = \frac{R}{\sin \theta} \) and \( A_T = \frac{R^2}{\sin \theta} \)

Therefore the side area of the lower part is \( A_S = \frac{\pi}{\sin \theta} \left( R^2 - r^2 \right) \)

From figure (6.3) it is clear that \( \sin \theta = \frac{(R-r)}{\sqrt{L^2 + (R-r)^2}} \)

Therefore is \( A_S = \pi \left( R + r \right) \sqrt{L^2 + (R-r)^2} \) ......................................................(1)

Equation (1) represents the area of the inner surface of the nanotube. We can now with a high degree of accuracy estimate the total surface area of the nanotube, this can be done by dividing the total tube area into five parts (four surfaces) the first part is the outer cylindrical shape with area \( A_1 \), second part is the top part of the tube which can be represented as a ring of an area \( A_2 \), third part is the inner cone with an area \( A_3 \), fourth part is the inner cap at the end to the cone inside the nanotube with area \( A_4 \) and the last part is the bottom outer cap with an area \( C \) as shown in fig (7). The last part can be ignored since in a real situation of titania nanotube arrays this cap will be in contact with the titanium layer underneath. Only we have to take the area of this cap into consideration of try to estimate the area of free standing titania nanotube arrays, where the cap will be exposed to the surrounding media.
Figure (7) Scheme of the nanotube inner and outer surfaces

Now consider the total area of the nanotube to be only the sum of the first four parts $A_1$, $A_2$, $A_3$ and $A_4$, consider that $A_4$ is the area of half of spherical shell with value $2\pi r^2$. From equations (1), (2) and (3) the total area of the nanotube is given by

$$A = A_1 + A_2 + A_3 + A_4$$

$$A = 2\pi LR_1 + \pi (R_1^2 - R_2^2) + \pi (R_2 + r)\sqrt{L^2 + (R_2 - r)^2} + 2\pi r^2 \quad \text{.........................(2)}$$

In order to understand the weight of each of these four terms in the total area of the nanotube let’s consider three real situations of short nanotube and intermediate nanotube and long nanotube, and I will use the measured values of $L$, $R_1$, $R_2$ and $r$ to find the value of each term and its percentage in the total area of the nanotube.

**Short nanotube:** using 0.5 HF for 30 min at anodized at 15 Volt

$L = 500 \text{ nm}, R_1 = 30 \text{ nm}, R_2 = 27 \text{ nm} \text{ and } r = 24 \text{ nm}$

<p>| $A_1$ (nm$^2$) | $A_2$ (nm$^2$) | $A_3$ (nm$^2$) | $A_4$ (nm$^2$) | $A_{Total}$ (nm$^2$) |</p>
<table>
<thead>
<tr>
<th>Aspect ratio L/D</th>
<th>A₁ %</th>
<th>A₂ %</th>
<th>A₃ %</th>
<th>A₄ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.3333333333</td>
<td>52.7951</td>
<td>0.30093</td>
<td>44.8766</td>
<td>2.02733</td>
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</table>

**Intermediate nanotube:** using 0.3 wt.% NH₃F in 98% Ethylene glycol and 2% DI water at 60 volt for 2 hours. L = 5,500 nm, R₁ = 80 nm, R₂ = 70 nm and r = 20 nm

<table>
<thead>
<tr>
<th>A₁ (nm²)</th>
<th>A₂ (nm²)</th>
<th>A₃ (nm²)</th>
<th>A₄ (nm²)</th>
<th>A_Total (nm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2764602</td>
<td>4712.39</td>
<td>1555153</td>
<td>2513.27</td>
<td>4326979.82</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aspect ratio L/D</th>
<th>A₁ %</th>
<th>A₂ %</th>
<th>A₃ %</th>
<th>A₄ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>34.375</td>
<td>63.8922</td>
<td>0.10891</td>
<td>35.9408</td>
<td>0.05808</td>
</tr>
</tbody>
</table>

**Long nanotube:** using 0.3 wt.% NH₃F in 98% Ethylene glycol and 2% DI water at 60 volt for 24 hours. L = 60,000 nm, R₁ = 80 nm, R₂ = 70 nm and r = 20 nm

<table>
<thead>
<tr>
<th>A₁ (nm²)</th>
<th>A₂ (nm²)</th>
<th>A₃ (nm²)</th>
<th>A₄ (nm²)</th>
<th>A_Total (nm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30159289</td>
<td>4712.389</td>
<td>16964606.22</td>
<td>2513.27</td>
<td>47131121.4</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Aspect ratio L/D</th>
<th>A₁ %</th>
<th>A₂ %</th>
<th>A₃ %</th>
<th>A₄ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>375</td>
<td>63.9902</td>
<td>0.01</td>
<td>35.9945</td>
<td>0.00533</td>
</tr>
</tbody>
</table>
It is now very clear the weight of the second and the fourth terms ($A_2$ and $A_4$) is negligible and only the remaining two terms are only responsible of the total surface area of the nanotube. The outer surface has almost twice the area of the inner surface. Therefore we can reduce equation (2) into
\[ A = 2\pi LR_1 + \pi (R_2 + r)\sqrt{L^2 + (R_2 - r)^2} \]  
\[ \text{………………………………………(3)} \]

Now let go back to the actual area of the hexagon and the effective area of four nanotubes existed in that hexagonal unit cell. We know that area of the hexagon (the actual area) in terms of the nanotube outer radius $R_1$ is given by

\[ \text{Actual Area} = 6\sqrt{3} R_1^2 \]

Using equation (3) the total area of four nanotubes is given by

\[ \text{Effective area} = 4 \times \{ 2\pi LR_1 + \pi (R_2 + r)\sqrt{L^2 + (R_2 - r)^2} \} \]

To study the ratio between the effective area and the actual area as a function of length, let’s consider the long nanotube case, where the length of the nanotube can reach hundreds of microns while the outer radius $R_1$ remains around 80 nm.
As predicted by equation (3) the relation between the effective area and nanotube length is linear, but what is really interesting in this chart is four orders of magnitude we have when the length reaches 200 µm. This huge increase in the effective surface area while the actual surface of a unit cell is constant only due to increase in the nanotube length, also this increase is relative to the actual area of the unit cell (the area of the hexagon). There is another factor also will increase the effective area not relatively to the area of the unit cell but with respect to a and actual unit area, let consider this unit area as 1 cm², this factor is the nanotube outer diameter (or its outer radius \( R_1 \)), by decreasing the nanotube outer radius \( R_1 \) (consequently \( R_2 \) and \( r \) will also decrease) the unit cell area of the hexagon will decrease, but in the same time the number of unit cells in 1 cm² will increase. If we consider a fixed the nanotube length \( L \), while decreasing the nanotube outer radius \( R_1 \), the number of unit cell in in 1 cm² will increase; consequently the effective area
of this 1 cm$^2$ will increase due to decrease in the nanotube outer radius. When plot this relation we found that the effective area almost has a power dependence on the tube radius.

![Graph showing Tube Radius vs Effective Area](image)

When we combine the effects of increasing the nanotube length and decreasing the nanotube outer radius we expect the effective area to increase drastically as shown in figure (8) where effective area value can reach more than 70,000 cm$^2$ for an actual area of 1 cm$^2$ this for nanotube arrays of 200µm in length and 10 nm in radius.
Figure (8) Chart of the effective area dependence on the nanotube radius and length
Appendix B

Wafer cleaning process

1-Piranha cleaning

Piranha solution, also known as piranha etch, is a mixture of sulfuric acid (H₂SO₄) and hydrogen peroxide (H₂O₂), used to clean organic residues off substrates. Because the mixture is a strong oxidizer, it will remove most organic matter, and it will also hydroxylate most surfaces (add OH groups), making them extremely hydrophilic (water compatible).

Method

1- Materials

- Dedicated crystallization dishes (3) large enough to hold wafer and stir bar so they do not interfere with each other (pyrex or quartz) or dedicated bench dip slots

- Hot plate with electronic stir

- Magnetic, Teflon coated stir bar

- Thermometer that goes up to 150°C

- Sulfuric Acid (H₂SO₄)

- Hydrogen Peroxide (H₂O₂)

- DI Water

- Acid safe gloves
- Face shield
- Acid Apron
- Fume hood
- Teflon wafer dipper
- Graduated cylinder (pyrex or quartz)

2- Procedure

1. Fill two rinse beakers with DI water.

2. Place magnetic stir bar in bottom of third beaker.

3. Place beaker on hot plate/stirrer.

4. 5:1 H$_2$SO$_4$: H$_2$O$_2$ Piranha solution
   a. Pour sulfuric acid into beaker, enough to cover the top of the wafer in Teflon dipper completely when immersed (Do not put wafer in the solution yet). For 125 mm crystallization dish use about 100 mL H$_2$SO$_4$.
   b. Heat sulfuric acid to approximately 80°C.
   c. Measure out H$_2$O$_2$ in a graduated cylinder so that it is 1/5 the volume of the H$_2$SO$_4$. For 125 mm crystallization dish use about 20 mL H$_2$O$_2$.
   d. Very slowly add the H$_2$O$_2$ to the H$_2$SO$_4$. 
e. Turn on stirrer. Stir the mixture slowly. If the H₂O₂ floats on top of the H₂SO₄, use a stirring rod to mix the two. Be careful, this will cause the two to react more quickly.

5. Heat solution to 100 to 110°C. The solution should begin to bubble vigorously as it approaches 100°C. If this does not happen wait a little longer and/or add more H₂O₂.

6. Keep solution between 100 to 110°C for the entire clean.

7. Immerse wafer in H₂SO₄: H₂O₂ for 10 minutes.

8. Carefully remove wafer from solution. Be careful of dripping.

9. Immerse wafer in rinse beaker with running DI water for 5 minutes.

10. Immerse wafer in second rinse beaker with running DI water for 5 minutes.

11. Air dry wafer.

12. Piranha solution can be used many times before its efficacy is spent.

2- Thin Oxide removal by HF cleaning

This step is to remove the thin oxide film that forms during the Piranha clean. This film can contain a lot of contaminants that the Piranha clean removed from the wafer, so it is important to also remove the oxide film.
Method

1- Materials

• 10:1 H$_2$O: HF solution

• HF safe container for dipping wafers

• HF safe tweezers

• DI Water

• Acid Safe Gloves

• Acid safe gloves

• Face shield • Acid Apron

• Fume hood

• Air gun

• Hot plate or oven set >100°C

2- Procedure

1. Dip wafer in 10:1 H$_2$O: HF solution for 15 sec.

2. DI rinse for 5 minutes.

3. Dry wafer with air gun.

4. Post bake wafer above 100°C for >2 minutes to remove all moisture.
Appendix C

Resistivity calculation

The gold electrode is not contacting the nanotube from everywhere; we can estimate the contact to cover only half of the nanotube circumference as illustrated in figure (9a). In order to carry out the calculation of the nanotube resistivity we will consider the case where we will unfold the nanotube to form a sheet as illustrated in figure (9b). The gold electrode in this new geometry will be in contact with the titanium dioxide sheet in small area as illustrated by figure (9c). We can approximate this situation by splitting the titanium dioxide sheet into two segments with resistances $R_1$ and $R_2$ respectively, and in parallel connection with the two gold electrodes at the end of the nanotube segment as illustrated by figure (9d). In this case, the measured resistance of the nanotube is the equivalent resistance of this parallel combination of $R_1$ and $R_2$.

$$R = \frac{R_1 R_2}{R_1 + R_2}$$

Where

$$R_1 = \rho \frac{L}{ST}$$

And

$$R_2 = \rho \frac{L + S}{ST}$$
Figure (9) Illustration of the contact between the gold electrodes and the nanotube, a) cross-sectional view of the real situation, b) geometrical representation of the case when the nanotube is unfold (cross section), c) Top view of the unfolded nanotube, d) an
approximation of the unfolded nanotube as two segments both in contact with gold electrodes

Where $\rho$ is the resistivity of the titanium dioxide nanotube, “$L$” the length of the nanotube segment and “$T$” is thickness of the nanotube wall, $S = \pi r$, where “$r$” is the average radius of the nanotube which is defined in terms of the nanotube outer radius ($R_o$) and the nanotube inner radius ($R_i$)

$$r = \frac{R_o + R_i}{2}$$

By substituting $R_1$ and $R_2$ in $R$ we will get

$$R = \frac{\rho (L^2 + SL)}{(2SL + T^2)}$$

Therefore the resistivity of the titanium dioxide nanotube is given

$$\rho = \frac{R(2SL + T^2)}{(L^2 + SL)}$$
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