FORMATION OF TITANIUM DIOXIDE NANOTUBES VIA TWO-STEP ANODIZATION

Submitted in accordance with the requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Hons.)

by

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for Degree of Manufacturing Engineering (Hons). The member of the supervisory committee is as follow:

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ABSTRAK

Tiub nano TiO_2 dihasilkan pada foil titanium melalui proses anodisasi. Dalam usaha untuk meningkatkan sifat tiub nano titania yang dihasilkan tersebut, proses anodisasi dua langkah telah dijalankan. Beberapa kayu ukur telah disiasat yang merangkumi kesan masa anodisasi dan voltan anodisasi pada sifat morfologi dan struktur tiub nano titanium dioksida yamg dihasilkan melalui proses anodisasi dua langkah. Kerajang titanium telah terlebih dahulu dibersihkan dan kemudian melalui proses elektrolisis di mana ia telah menjadi anod dan batang karbon akan bertindak sebagai elektrod lawan. Elektrolit yang digunakan untuk kedua-dua proses anodisasi adalah etilena glikol yang mengandungi 0.3g NH_4F. Proses anodisasi dua langkah memberi tumpuan kepada pertumbuhan tiub nano titania dengan bantuan tapak yang ditinggalkan melalui penghapusan tiub nano yang dihasilkan melalui langkah pertama anodisasi. Kaedah rawatan ultrasonik telah digunakan dalam bahagian penyingkiran. Ciri-ciri morfologi dan struktur tiub nano yang dihasilkan telah diperhatikan dan dikaji dengan menggunakan kaedah pencirian pelbagai jenis seperti mikroskop elektron pengimbasan pelepasan bidang (FESEM), pembaluan sinar X (XRD) dan teknik spektroskopi raman. Hasil kajian ini telah diuji untuk menilai sifat aplikasinya khususnya dalam aplikasi fotokatalisis. Pertumbuhan panjang dan diameter tiub nano titanium dioksida yang dihasilkan melalui proses anodisasi dua langkah dijangka berkadar terus dengan masa dan voltan anodisasi.

ABSTRACT

TiO_2 nanotubes are synthesized on titanium foil via anodization process. In order to enhance the properties of the titania nanotubes developed, two-steps anodization is conducted. Several parameters were investigated which inclusive of the effect of anodizing time and anodizing voltage on the morphological and structural properties of titanium dioxide nanotubes manufactured through two-steps anodization. The titanium foil was cleaned thoroughly beforehand and has gone through electrolysis where it was used as the anode and carbon rod acted as the counter electrode. The electrolyte used for both anodization was ethylene glycol containing 0.3g of ammonium fluoride (NH_4F). Two-steps anodization process focuses on the growth of titania nanotubes through the aid of concaves left by the removal of nanotubes produced via the first step anodization. Ultrasonic treatment method was used in the removal part. The morphological and structural properties of the nanotubes produced were observed and studied by using assorted characterization methods such field emission scanning electron microscopy (FESEM), X-Ray Diffraction (XRD) and Raman Spectroscopy technique. The product of this study was tested in order to evaluate its application properties specifically in photocatalysis application. The growth of titanium dioxide produced via two-steps anodization in length and diameter was expected to be directly proportional to the anodizing time and voltage.

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LIST OF ABBREVIATIONS

ATNTs	-	Anodic titania nanotubes
CO_2	-	Carbon dioxide
D.C	-	Direct current
EG	-	Ethylene Glycol
H	-	Hydrogen
H_2O	-	Water
H_2S	-	Hydrogen sulphide
H_2SO_4	-	Sulphuric acid
HCl	-	Hydrochloric acid
HF	-	Hydrofluoric acid
HNO_3	-	Nitric acid
NH_3	-	Ammonia
NH_4F	-	Ammonium fluoride
NTs	-	Nanotubes
O_2	-	Oxygen
OSA	-	One-step anodization
SEM	-	Scanning electron microscopy
SO_2	-	Sulphur dioxide
TiO_2	-	Titanium dioxide
TNAs	-	Titania nanotubes arrays
TNP	-	Titania nanoporous
TNTs	-	Titania nanotubes
TSA	-	Two-steps anodization
XRD	-	X-ray diffraction

LIST OF SYMBOLS

%	-	Percent
~	-	Approximately
°C	-	Degree Celsius
°C/min	-	Degree celsius per minute
Å	-	Angstrom
cm	-	Centimetre
eV	-	Electron volt
g/cm^3	-	Grams per centimetre cube
m	-	Metre
ml	-	millimetre
mm	-	Millimetre
N_2	-	Nitrogen gas
nm	-	Nanometre
V	-	Voltage
W/mK	-	Watt per metre per Kelvin
wt. %	-	Weight percent
µm	-	Micrometre

CHAPTER 1
INTRODUCTION

This chapter will introduce the background of study as well as problem statement, objectives and scopes. The content of this chapter will further discuss the purpose of this research to be carried out.

1.1 Background of Study

Pertaining to their beneficial high surface area, self- organizing titanium nanostructures have an enormous opportunity as an outstanding photocatalyst (Wang and Chen 2013). The single- dimensional nanostructures have a small fusion of electron- hole pairs induced by light and high photocurrent conversion efficiency (Zhang et al., 2014). Many nanostructured titanium dioxode materials have been patented. These nanostructures were properly created via assorted ways. (Jin et al., 2013). 1D titanium dioxide nanostructures have efficiently enhanced their photocatalytic characteristics in comparison with other titanium forms of their high surface- to- volume ratios, high surface areas and highly ordered structures. (Choi,2011).

The titania nanostructures could be produced by template technique (Qu et al., 2014), sol-gel technique (Fateh et al., 2013), hydrothermal processes and anodic oxidation method (Zhang et al., 2014). Pertaining to its huge ability to be controlled, anodization has become one of the frequently widely used techniques, exceptionally because of its capabilities in the manufacture of 1D titanium dioxide nanostructures (Zhang et al., 2014). Alternating preparation requirements, like anodization time, applied voltage, temperature, titanium layer roughness, calcination parameters and electrolyte composition, inclusive of fluoride concentration, solvent, water content, pH, viscosity, conductivity, and organic additives can be done to modify the photocatalytic activity of titania nanostructures as well as their morphological structures (Nis et all., 2014).

1.2 Problem Statement

Nano- templates have been given such spotlight to the ongoing regular arrangement of nanowires and nanoparticles to investigate the size- dependent or low- dimensional features of these nanostructures. (Murray et al., 2000). The basic mastery of incredible optical transmission by means of subwave hole arrays (Ebbesen et al., 1998), electrokinetic transition of energy via capillary tube banks or channel arrays (Osterle et al., 1964), Nanochannel fluid transport (Whitby et al., 2007), large Tc superconductivity in nano-entrenched composites (Yang et al., 1996), the lasing event of quantum dots entrenched in nanochannels must cultivate nanotemplates with highly ordered regular nanochannel arrangement (Klimov et al., 2000). There are several methods in which highly- ordered regular nanostructures are manufactured in a managed and repeatable way. (Li et al., 1999).

The preceding manufacturing ways revealed by others for the development of highly- ordered TiO_2 nanotubes (Shankar et al., 2007) has been stated that the utilization of NH_4F electrolytes has been massively revamped, and yet the TiO_2 nanotubes seem to have a large pore size allocation and a bumpy top surface whereas they began with a rough Ti substrate omitting an electropolishing step. The bumpy Ti surface allows a distinction in the allocation of the electric field upon the metal surface amid anodization in the absence of the electropolishing step. Concaves are therefore created with a wide diameter distribution and a contoured Ti surface given the difference in the rate of growth of each oxide nanotube. The TiO_2 nanotube arrays are therefore irregular, although monotonous anodization is carried out on the Ti substrate (Zhang et al., 2007). The requirements to manufacture extremely highly ordered sets of metal oxide nanotubes are the electropolishing of the metal valve and a two- steps anodization process.

Moreover, self- ordering was achieved by rearranging the cell configuration at an suitable anodizing time with such an adequate anodization voltage. The periodic concave actually causes the electric field to be focused solely on the textured surface of the Ti. In other words, each concave behaves as a epicenter of pore nucleation for homogeneous pore productivity, shortening the time needed to achieve the steady- state current. In consequence, highly self-organized TiO_2 nanotube arrays have been developed in a short period of time. The highly ordered TiO_2 nanotube arrays seem to be very crucial not only for the fundamental study of nanostructures but also for the manufacture of useful equipment (Park et al., 2006). In addition, such metal oxide valve nanotube panels with a long range have a tremendous ability for a wide variety of applications.

1.3 Objectives

There are two main objectives for this research which are:

i. To produce TiO_2 nanotubes via two-step anodization.

ii. To characterize the morphology and structural properties of TiO_2 nanotubes produced by two-steps anodization.

1.4 Scopes

This research covered the study on the formation of self-organized TiO_2 nanotubes by two-steps anodization by removing the nanotubes produced in the one-step anodization and also the photocatalytic properties produced by the end product. The effects of anodic parameters such as applied voltage and anodizing time were studied. The phase formation, morphology, structural and characterization on TiO_2 nanotubes produced by two-steps anodization were determined by scanning electron microscope (SEM), x-ray diffraction (XRD), Raman spectroscopy and UV lamp chamber.

1.5 Rational of Research

The rational of research are as follows:

i. Titanium dioxide nanotube has been extensively studied to provide benefit for the humankind. This study is conducted to form titanium dioxide nanotube via two-step anodization.

ii. Develop the ability to fathom the crucial role of parameters in generating optimum titanium dioxide nanotubes through research and experiments.

1.6 Research Methodology

This project consists of five crucial parts which inclusive of sample preparation, anodization process, specimen testing, data analysis and result as well as conclusion illustrated in the Figure 1.1 below. During sample preparation, things will be done from cutting foils into desired measurement, cleaning, and setting up apparatus for anodization process including the electric circuit and the electrolyte preparation. Anodization process will be conducted two times in order to accomplish two-step anodization. The nanotubes from the first-generation process will be removed thoroughly which requires meticulousness to make sure no oxide layers left on the foil for the second step anodization. The formed titania nanotubes will then be tested and analyzed to study the structural properties. The result gained will be studied and conclusion will be made at the end of the project.

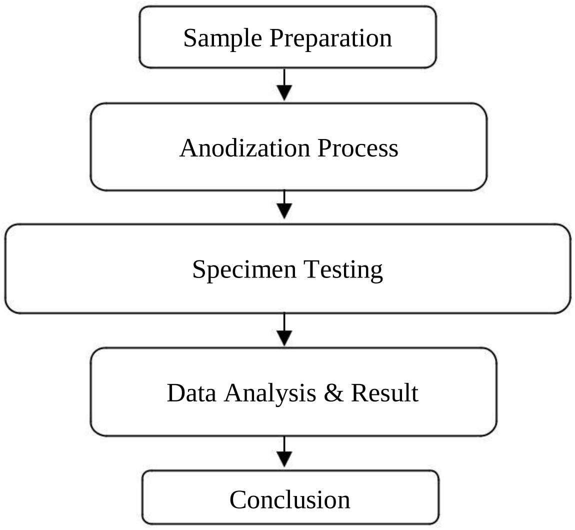

Figure 1.1: Flowchart of framework.

1.7 Thesis Organization

This thesis consists of five chapters. Chapter 1 is the introduction which will cover the background study, problem statement, objectives, scope, and rational of research are portrayed in order to give better understanding of the particular aspects of this study addressed in this thesis which followed by Chapter 2, the literature review to provide supportive findings on the same matter. Chapter 3 is the methodology applied to conduct this project followed by Chapter 4 which provides results and analysis of this study. Chapter 5 will provide the conclusion and recommendations executed from this project which will be needed for the betterment of the future studies.

CHAPTER 2

LITERATURE REVIEW

This chapter will first deliberate on the literature review which pertaining to titania or titanium dioxide (TiO_2) and its properties. Next, titanium dioxide in nanotubes form will be discussed alongside with its general properties. In this study, the application of titanium dioxide nanotube will be focusing on photocatalyst which will be reviewed in the photocatalysis discussion. The method of synthesizing titanium dioxide nanotubes consists of two-steps anodization will also be reviewed.

2.1 Introduction to TiO_2

Whether you're painting a wall, applying sunscreen, or eating a sweet, the chances are titanium dioxide is involved. What is titanium dioxide? Why is it widely used? Titanium dioxide is found around the world in several kinds of rock and mineral sands. It most commonly occurs is the mineral ilmenite and sometimes is the mineral rutile (Figure 2.1). Once mined, two different process can be used to extract a usable titanium dioxide. The same minerals are used to create the metal titanium. In its pure extracted form, titanium dioxide is a fine powder that is the whitest and brightest of all known pigments. It reflects visible light, scatters and absorbs ultraviolet light, is non-toxic and it does not react with other chemicals.

As one of the world's most commonly used colorants, titanium dioxide has been safely used for more than 90 years. In fact, this powder forms the basis of almost all man-made pigments. It is used to brighten and strengthen the colors of products from paints, paper and plastic to food, pharmaceuticals and cosmetics. One of the greatest assets of titanium dioxide is the different quality it displays depending on what form it will be used. Pigment grade titanium dioxide is designed to scatter visible light, which can make all colors even and strong. This unique quality also contributes to the sustainability of different objects. Titanium dioxide extends the lifetime of plastics; it also protects wood and metal when used in paints.

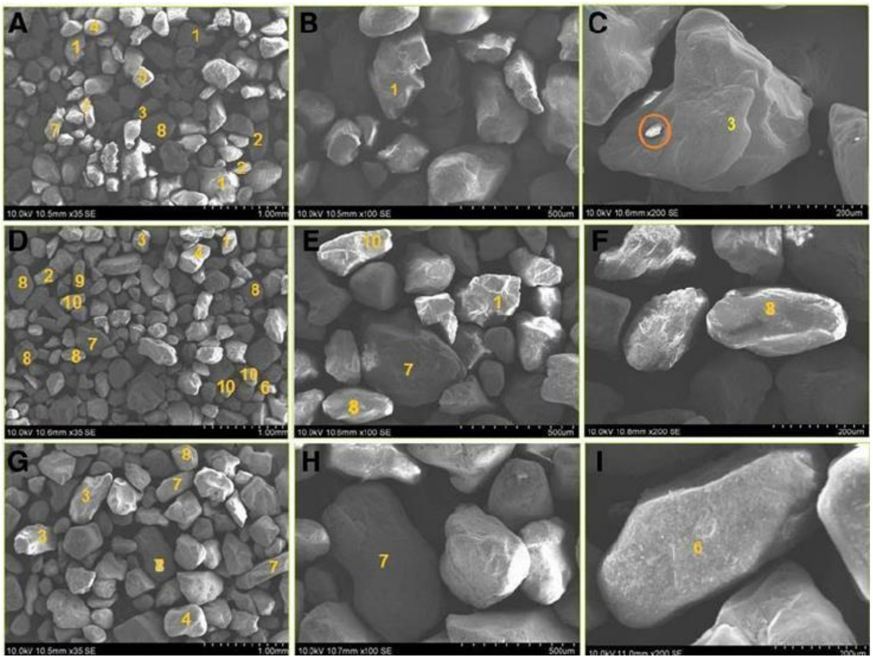

Figure 2.1: SEM microphotographs of minerals collected from pits, of Sagarnagar coast, Visakhapatnam, mostly heavy minerals which are underwent past high energy events. 1. quartz 2. sillimanite 3. ilmenite 4. garnet 5. titaniferous magnetite 6. rutile 7. Zircon 8. monazite 9. Hornblende 10. magnetite. a, d, g overview of grains with angular to subrounded mixed grains; b Quartz with triangular, ‘V’ shaped pits at the edges; c depression filled with precipitation in Ilmenite; e Quartz with triangular pits with sharp edges; f elongated, smooth surfaced monazite, pits at the edges; h subrounded elongated Zircon; i Rutile with smooth edges (Devi et al. 2013).

Titanium dioxide can also be produced as a much finer powder that is transparent and more effective at protecting against UV light. This makes it a key ingredient in sunscreens, improving their protection and making them kind to the skin. When used in food products, titanium dioxide is known as E171 and is approved for use by the European Food Safety Authority. It appears in many products, from chewing gum to cheese, where it is used as a whitener, or to stop food and drink from sticking together. As well as these uses, the different properties of titanium dioxide mean it is a valuable element in a wide range of different applications for industry and consumers. Its bright white color makes our road safer. It is also used in trucks to reduce the level of air pollution from diesel engines.

Titanium dioxide is a key ingredient in making the world a brighter, cleaner and safer place.

Titanium dioxide is polymorphous and known as titanium (IV) oxide or titania. Rutile is the only type of crystal structure which has been commercially used apart from the other two which are anatase and brookite (Figure 2.2). The solubility of titanium dioxide depends on solutes. Unlike in dilute alkali and acid, titania is soluble in hot concentrated H_2SO_4, HCl and HNO_3. It has the biggest surface area, the most pigment volume with a small amount of relative density in commonly used white pigments. Other than that, titania also has incredible electrical properties due to its high electric constant. As a semiconductor, its conductivity is directly proportional to temperature and very reactive towards hyperoxia. The purity of titania plays an important role to its melting point.

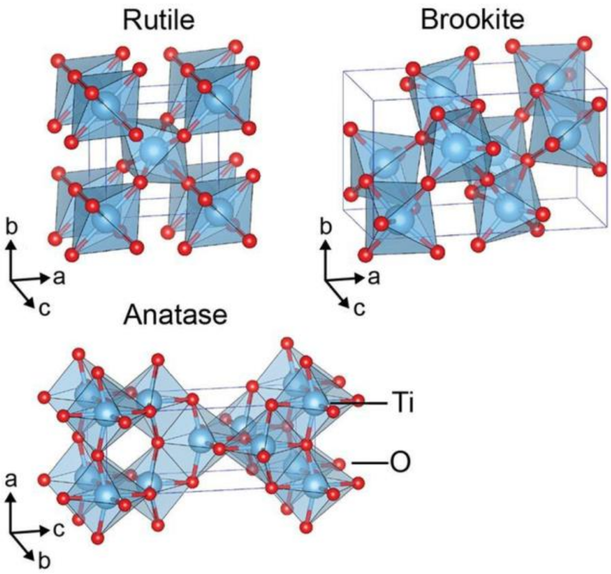

Figure 2.2: Crystal structures of TiO_2 rutile (tetragonal, P42/mmm), brookite (orthorhombic, PBCA) and anatase (tetragonal, I41/AMD) polymorphs (Haggerty et al. 2017).

When it comes to hygroscopicity, titania has it on a minimum level. As the hydrophilic is related to surface area, thus moisture absorption is directly proportional to the size of surface area and is also relevant to surface treatment and nature. Despite having a good thermal stability, titania is also known for its stable chemical properties. Apart from being non-toxic, titania also has partial acid sexual oxide which means it has no reaction toward O_2, H_2S, SO_2, CO_2 and NH_3. Except from alkali and hot HNO_3, titania has zero solubility in H_2O, fatty acids, weak organic acids and other organic acid. For the material manufactured under normal temperature, almost no reactivity will occur.

2.2 TiO_2 Nanotubes

Nanostructured titania materials which fixate on protein binding demonstrate high biocompatibility, low toxicity and have a good retention of biological activity. The consequences and wide specific area for these properties of titania nanostructured materials were mostly due to their quantum confinement (Yanhong et al. 2004). Some properties of titania nanotubes have already been explored which inclusive of extremely high sensitivity to hydrogen when benefitted as gas-sensors, has high photo response when annealed, could exceedingly transform their surface wettability, able to project remarkable light conversion efficiencies when dye-sensitized and able to act as a catalyst in order to allow photocatalyst to become active in visible light. Furthermore, titania is a very functional non-toxic, not harmful to the environment, corrosion proof material as it is frequently used in paint, white-pigments and sun blockers (Roy, Berger, and Schmuki 2011) A lot of the essential properties of titania has been captivating such high fascination pertaining to its ability to supply the fundamentals for many exceptionally good useful attributes. Several features related to the outstanding performance of titania nanotubes are shown in Figure 2.3. The schematic image of nanotubes is shown in Figure 2.4 where hollow tubes are aligned and organized.

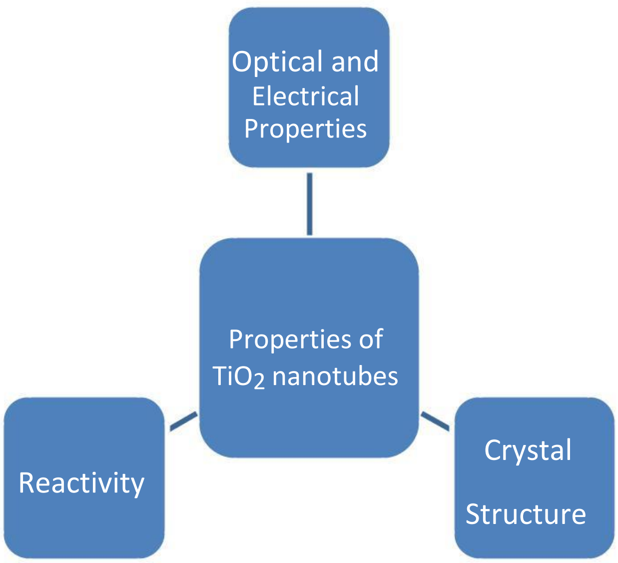

Figure 2.3: The properties of TiO_2 nanotubes related to the outstanding performance. (Grimes and Mor 2009)

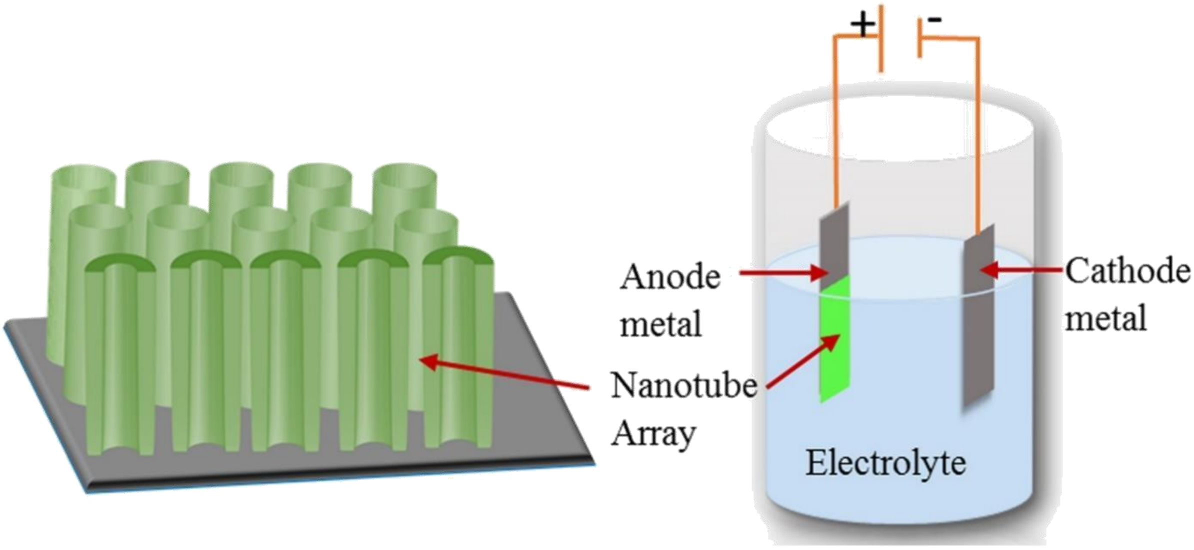

Figure 2.4: A two-electrode anodization setup for fabricating the titanium dioxide nanotube architecture where hollow tubes are aligned and organized (Rao, Torabi, and Varghese 2016).

Generally, the categories of nanosized oxides can be grouped into zero-dimensional (0D), one-dimensional (1D) and two-dimensional (2D) (Tiwari, Tiwari, and Kim 2012). The sample of each category will be shown in Figure 2.5 whereas Figure 2.6 will show the classification of nanomaterial particularly. Some of the outstanding electronic properties of one-dimensional (1D) nanostructure are inclusive of quantum confinement effect or high electron mobility, high mechanical strength and high specific surface area (Wang, Zhang, and Sun 2011).

To put it simply, 0D nanomaterials contains spheres or clusters which are considered as point-like particles. While 1D nanomaterials are inclusive of tubes, porous, wires, rods and fibers. For 2D structures, films, plates, multilayers or networks are identified. In this work, 1D titania nanotubes will be studied as this structure compliments outstanding features in comparison to another structure of metal oxide for such applications. The examples of the implementation of TiO_2 nanotubes are shown in Figure 2.7.