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# A Review on $Tio_2$ Nanotube Based Free Standing Membrane: Synthesis Mechanism and Structur Modification

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## Abstract

The $TiO_2$ semiconductor material with nanotube morphology has a wide application due to its high effectiveness in responding to light on the surface as well as having a wide band gap energy. Related studies of $TiO_2$ nanotubes were developed based on previous studies that have examined and tested the effectiveness of photoelectrocatalytic $TiO_2$ nanotube films grown on titanium foil substrate for corrosion prevention applications (Misriyani et al., 2015). However, the presence of titanium substrate on $TiO_2$ nanotubes precludes light absorption because it is opaque. This affects the activity of $TiO_2$ in responding to light. The development of $TiO_2$ nanotube films through the manufacture of film based free standing membrane becomes very important to do. Transparent film coatings in addition to improving light absorption on the surface of $TiO_2$ also make it easy to integrate with other substrates. This paper reports the review of all the preparation technologies as well as the optimum conditions of synthesis of $TiO_2$ nanotube based free standing membrane.

**Keywords:** $TiO_2$ Nanotube, Free standing membrane, Synthesis, Characterization

## 1.INTRODUCTION

Study of $TiO_2$ attracted much attention of many researchers for several decades because it can increase the rate of oxidation or reduction induced by light, has optical and electronic properties, highly photoreactive, non-toxic, chemical stability in the long term and low cost (Xu et al., 2014); (Mun et al., 2010) and (Huichao He, 2012). The surface of $TiO_2$ plays an important role in responding the light. Therefore, the $TiO_2$ surface morphology becomes important to investigated by many research. In order to obtain wide applications, has a specific size and shape depending on the desired characteristics through the synthesis parameter control. $TiO_2$ nanotube morphology were introduced as a material that has many benefits in photoelectrochemical properties. $TiO_2$ nanotubes have a high surface area so that they can receive more light exposure in every pore tube wall (Nah et al., 2010) and (El Ruby Mohamed and Rohani, 2011). Design and synthesis of materials with the nanotubes morphology have attracted many attention of researchers. Several methods performed to establish the morphology of $TiO_2$ nanotubes, such as hydrothermal method (Ou and Lo, 2007); (Yang et al., 2008) and (Li et al., 2009), the synthesis by using template (Qiu et al., 2007) and anodizing with electrochemical techniques (Ye et al., 2014); (Tsui and Zangari, 2014); (Passalacqua et al., 2015) and (Xue et al., 2015). Electrochemical anodization chosen as the best method because $TiO_2$ nanotube films have a strong bond with titanium substrate, quite effective with low cost and easy to manufacture (Robin et al., 2014); (Li et al., 2012); (Zhou et al., 2015). Misriyani et al (2015) has successfully synthesize $TiO_2$ nanotubes grown on the surface of the titanium substrate. The most simple process in $TiO_2$ nanotubes formation by electrochemical anodization method is electrochemical anodizing of titanium metal in electrolyte solution containing fluoride followed by thermal treatment (Chen et al., 2012); (Li et al., 2013) and (Kapusta-Kołodziej et al., 2014).

$TiO_2$ nanotubes has been studied intensively as a good photocatalyst because it has a uniform tubular structure that gives advantages on photoelectrochemical properties. However, the the presence of a titanium substrate becomes a barrier to the light response. Morphology nanotubes on titanium substrate is opaque, thereby limiting the amount of light entering the surface of $TiO_2$, and decrease the photocatalytic activity. This paper report reviews the synthesis and modification of $TiO_2$ nanotube films to a membrane form that stands alone without the presence of a titanium substrate as well as optimization of the synthesis conditions of $TiO_2$ nanotube based free standing membrane. The advantages of $TiO_2$ nanotubes with free standing membrane form (free standing TNT membrane) are the disappearance of the barrier layer on the bottom of the tube, can transfer electrons directly, stable against vibration and easy to integrate with other substrates. With the ideal structural shapes, causing the free standing TNT membrane has wider applications in the energy production and environment field (Perillo, 2016).

## 1.ELECTROCHEMICAL MECHANISM

The $TiO_2$ nanotube Material conducted by using two electrodes in an electrolyte solution system with electrochemical anodization method, wherein titanium foil acts as an anode and Pt metal as the counter electrode. Electrochemical anodization is a simple method, hence and involve lower costs to obtain $TiO_2$ nanotube array that easy to combined with another substrat because of flexible support as reported by (Perillo, 2016); (Lv et al., 2016) . Formation of $TiO_2$ nanotube membrane starts from oxidation of metal surface, release $Ti^{4+}$ ions and electrons. While the oxide form on the metal surface obtained from chemical dissolution involving the release of $Ti^{4+}$ ions and $O^{2-}$ or $OH^-$ ion from water molecules. Titanium oxide obtained from anodizing through a condensation reaction on the surface of Pt cathode indicated by the emergence of hydrogen gas (Roy et al., 2011).

The initial stage anodizing process is the electrochemical oxidation on the surface of titanium and establish uniform array $TiO_2$ nanotubes on the surface of titanium according to the equation (1) and (2) (Robin et al., 2014):

$$Ti(s) + 2H_2O(l) \rightarrow TiO_2(s) + 4H^+(g) + 4e^- \text{ (anode axidation)} \quad (1)$$

$$TiO_2(s) + 4H^+(aq) + 6F^-(aq) \rightarrow TiF_6^{2-}(aq) + 2H_2O(l) \text{ (chemical dissolution)} \quad (2)$$

The growth of titania nanotube caused by competition of anode oxidation and chemical dissolution in the electrolyte solution containing fluoride (Sreekantan et al., 2011). Complex formation of titanium hexafluoride occurs in the presence of an electric field, which causes the fluoride ion (F-) moves toward the metal and $TiF_6^{-2}$ move to the electrolyte according to the equation (3).

$$Ti^{4+}(s) + 6F^-(aq) \rightarrow TiF_6^{-2} (aq) \quad (3)$$

Barrier layer on the interface metal/oxide of nanotube films plays a role as a barrier of the flow of ions such as $Ti^{4+}$ and $O_2$, which is required to move through the film to maintain the anodic oxidation process. Ti-O bonding polarized and weakened, causing the dissolution of metal cations. $Ti^{4+}$ ions migrate from metal to the oxide/electrolyte interface and dissolved in the HF electrolyte solution. Free anion $O^{2-}$ migrate toward the metal/oxide interface and further interact with metals. The larger barrier can be overcome by increasing the anodization voltage. The length of the nanotubes increases until oxidation rate at the interface metal/oxide reaches equilibrium with the chemical dissolution rate at the top of the tube (the oxide/electrolyte). After equilibrium, the length of the tube is no longer dependent on anodization time.

## 1.Fabrication of free standing $TiO_2$ nanotube membrane

The $TiO_2$ nanotube layer with membrane-shaped successfully built on the surface of the titanium foil substrate. The presence of titanium substrate becomes a barrier to

$TiO_2$ in response the light. Nanotubes morphology on titanium substrate is opaque, thereby limiting the amount of light entering the surface of $TiO_2$ photocatalytic reactions result in a decrease in many applications (Lin et al., 2010).

Physical properties and morphology of free standing $TiO_2$ nanotube membrane depends on several parameters specific processes. Detachment method of $TiO_2$ nanotube membrane becomes free standing membranes have been developed by methanol evaporation, ultrasonic agitation and voltage pulse method which discussed in following section:

**1.1 Methanol evaporation**

The liquid used for rinsing and solvent is methanol and water. Detachment mechanism is possible through solvent evaporation and induces the formation of free standing membranes. Nanotube membrane surface is rinsed and stored in organic bath after electrochemical anodization. Slowly etching occurs due to the presence of $H^+$ and $F^-$ ions cause structural defects. Further samples were rinsed with methanol which diffuses towards the pores in and wetting defect structure. Then evaporated slowly at structure defects area induce layer detachment controlled by surface tension.

After rinsing with solvents, ultrasonic treatment in methanol was agreed for cleaning nano fibers on the membrane surface. Clean membrane then dried in air with the surface facing up. Brownish membrane further detached from titanium foil during the methanol evaporation process. Perfect exfoliation can be assisted by slowly bending the membrane (Liu et al., 2014).

**1.1Ultrasonic agitation**

The $TiO_2$ nanotube layer removed from the titanium foil by ultrasonication has reported as beneficial method to formation the ordered free standing $TiO_2$ nanotube membrane (Lv et al., 2016). Ultrasonic vibrations cause exfoliation the membrane by a high frequency in the liquid. During ultrasonic vibration, abrasion cavities occur or vibration with high pressure will accumulate thereby increasing tension on the surface of solids.

Additions $H_2O$ increase the dissolution of $TiO_2$ on the interface metal/oxide leads to formation of defect area. Some parameters have been reported appear during the ultrasonic process such as frequency, temperature, static pressure, vapor pressure and surface tension. Surface tension and vapor pressures are the main factors that can be defined from the ratio of water and organic solvent in the ultrasonic bath.

Vibration treatment in water and ethanol solution with volume ratio of 1: 4 followed by drying in the atmosphere produces a thin free standing membrane $TiO_2$ nanotubes detached from the Ti foil. Ultrasonic for several minutes in lower water concentration of 95% ethanol causes the membrane peeling thicker because of its low acidity.

### 1.1 Voltage pulse method

Preparation of free standing $TiO_2$ nanotube membrane with a larger voltage pulse has been reported. In this method, a higher voltage is applied at the end of the anodizing process in a short time (Liao et al., 2012). The elevating the anodizing voltage can damage the membrane layer of $TiO_2$ nanotubes adhesion out of the surface of the titanium substrate and simultaneously open the bottom layer of the membrane (Perillo, 2016); (Liao et al., 2012). $TiO_2$ nanotube based free standing membranes widely successfully performed using anodization technique. $TiO_2$ nanotube grown on the surface of titanium subsequently released from the substrate. Thermal treatment during process have also been reported as an important step in preparation of free standing TNT membrane (Lin et al., 2010). High pressure also introduced give an effect. High pressure on membrane surface causes the accumulation high amounts of energy voltage. When the rate of release energy stress exceeds the interfacial strength of membrane, the membrane layer peeling occurs on the surface of substrat.

## 1.MEMBRANE OPTIMIZATION

Optimization of membrane thickness of $TiO_2$ controlled by adjusting parameters such as composition of electrochemical solution (Albu and Schmuki, 2013); (Nischk et al., 2014); (Tsui and Zangari, 2014), optimization anodizing voltage in the range of 40-100 V (Liao et al., 2012b); (Ratnawati et al., 2015), time and temperature anodizing (Alsamuraee and Al-Ittabi, 2011)); (Nischk *et al*., 2014); (Omidvar et al., 2011); (Regonini and Clemens, 2015); (Li *et al*., 2011); (Acevedo-Peña and González, 2014); (Kim et al., 2013) and (Li *et al*. 2013).

Length of free standing membrane $TiO_2$ nanotubes have been reported between 20 nm – 1000 μm. The competition between the chemical dissolution of nanotube layers and barrier increasing the rate of length membrane formation. The tube length increased with longer initial stage while the thickness is no longer increase at steady state.

High voltage accelerating with migration of $O^{2-}$ and contribute in the formation of a tube length. Increasing the tube length accordance with the increasing in voltage between 1 – 25V. But in certain conditions increasing the tube length is at voltage between 20 - 80 V. The HF strong acid solution (pH <3) produce a tube length less than 500 nm, and up to 6,4 μm in a fluoride solution with a pH of 3-6. The tube length in 1000 μm was achieved in the organic electrolyte solution. High thickness of nanotubes can prepared by adjusting the concentration of electrolytes $F^-$. High concentrations accelerate the ion transport and push up the barrier layer, whereas at low concentrations contribute to shortening the length of membrane tube.

## 1.NANOTUBE DIAMETER CONTROL

The $TiO_2$ nantube diameter depends on several factors, are the $F^-$ concentration, $H_2O$ content and temperature of the electrolyte. Nanotube wall thickness increases equivalent with a decrease in the diameter of the nanotubes along the tube from top to bottom. The voltage is an important parameter to control the diameter of the tube. The higher applied voltage the stronger the electric field on the substrate. Diameter pores enlarged quickly before forming the hole. Generally $TiO_2$ nanotube diameter depending on the voltage worked during anodizing and the high voltage rate at the initial of electrochemical process led to diameter expanded (Yoriya, 2012)(Omidvar et al., 2011). The low pH value and high concentrations of $F^-$ cause an increase in the intensity of chemical dissolution, which expands tube diameter. Water content in organic electrolytes are the parameters necessary since the the involvement $O^{2-}$ and $H^+$ for nanotube growth and dissolution of the water (Albu and Schmuki, 2013).

## CONCLUSION

The development of synthesis and modification of $TiO_2$ nanotube material into free standing membrane form led to extensive study. The high-surface area of $TiO_2$ nanotube (TNT) supported by the design of the material with a free standing membrane form enhancing the response to light because the substrate as a barrier layer is removed from the bottom of the tube so it can transfer electrons directly, stable against vibration and easy to integrate with the other substrate. Currently, the synthesis of $TiO_2$ nanotube composites with metal doping inspires researchers to explored, not only to obtain good morphology, but also to provide high response properties in visible light and increase the separation of electrons and holes, thus increasing photocatalytic reactions.

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