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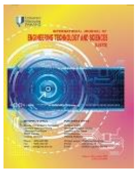

Synthesis and Characterization of TiO_2 Nanotube Using Electrochemical Anodization Method

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Abstract - In this study, Titaium dioxide (TiO2) nanotubes (TNTs) were synthesized by a simple electrochemical anodization method. TNTs were characterized by Field Emission Scanning Electron Microscope (FESEM), Transmission Electron Microscope (TEM), UV-Vis Diffuse Reflectance Spectra and Photoluminescence (PL) Spectra to identify the morphology, crystalline phase and photocatalytic activity under the visible light. . The morphological analyses revealed that the inner diameter, and tube length of the synthesized TNTs has an average value of 60 nm, and 900 nm, respectively. The wall thickness of the TNTs is of 11 nm. The observed TNTs have nanotubular shape. The absorption edge in the visible range at around 400-460 nm obtained from UV-Vis Diffuse Reflectance Spectrum analysis. In addition, the PL spectral peak identified at around 400nm and 590 nm. The finding shows that the synthesized TNTs made by electrochemical anodization method has photocatalytic properties and can be used as a photocatalyst for further photocatalytic application.

Keywords: TNTs, Crystalline phase, Photocatalytic activity, visible light, photocatalyst

I. INTRODUCTION

Energy and environmental problem are being extensively increasing due to the depletion of fossil fuel and rising amount of greenhouse gases [13; 16] . The photocatalytic technology using semiconductor can convert solar energy into other chemical energy which creates a great hope to overcome such dilemma [15; 27]. Photocatalysis process can be defined as the acceleration of a photo-reaction by the presence of a catalyst [20]. As the catalyst plays important function during photocatalysis, researches focused on the development of various photocatalyst. Metal oxide semiconductors are the most investigated materials for the photocatalytic application, various semiconductors are used as a photocatalyst such as Zinc Oxide (ZnO) [18], Magnesium Oxide (MgO) [2], Cadmium Sulfate (CdS) [14], Zirconium Oxide (ZrO_2) [28] and TiO_2 [10] . Among these TiO_2 is the most widely used photocatalyst due to its non-toxicity, stability, inexpensive and high photoactivity [24; 32] . In 1972, the photocatalytic properties of TiO_2 were discovered by Fujishima and Honda [5]. However, TiO_2 has its own drawbacks, it is only active when irradiated by UV light and not so effective under visible light due to its wide band gap (3.2 eV for anatase and 3for rutile), that also creates rapid recombination of photogenerated electron-hole (e^+/h) pairs [8]. Researchers, now trying to modify the simple TiO_2 to various nanofiber [30], nanorod [6], nanowires [35], nano-flowers [29], nanotube [7; 34] form, self organized TNTs are of great interest for being used as a photocatalyst due to their larger surface area, long term stability to photo and chemical corrosion, cost-effective construction and higher surface-to-volume ratio [17].

Several methods are available for the development of TNTs that involves template-assisted method [4], sol-gel method [22], hydrothermal method [3] and anodization method [33]. By using electrochemical anodization method Jankulovska, Lana-Villarreal, and Gómez [11] fabricated TNTs that exhibited admirable features, Kaneco, Chen, Westerhoff, and Crittenden [12] also reported the inner diameter of the TNTs can be increased by controlling the anodic current and also showed that the density increased of the TNTs with larger surface area. According to literature, anodization method is widely used due to its controllable reproducible results, easily handled anodization parameters (applied voltage, electrolyte, electrodes ,time and annealing temperature) and also considered simple process [9] . Among various anodization parameters, annealing temperature has a great effect to construct crystalline nanotube since the different temperature can show the rutile and anatase phase of TiO_2 [21; 31]. However, anodization method has its own limitations. The formation of TNTs depends on the selection of electrolyte during anodization and the high cost apparatus [1]. The objective of this study is to make visible light effective TNTs via electrochemical anodization method as well as overcome the drawbacks of the anodization method by preparing low cost apparatus. Self-organised and highly ordered TNTs with average length, diameter and wall thickness can be made from the anodization method rather than other methods. This study presents a simple electrochemical anodization method for preparing the TNTs that has effect under visible light and could contribute for further photocatalytic activity especially on carbon dioxide (CO_2) gas reduction.

II. EXPERIMENTAL

2.1 Reagents and Materials

Ethylene Glycol (EG, 99.5%), Ammonium Floride (NH_4F, 98.0%), were brought from Sigma-Aldrich Chemical Co. All chemical reagents were of analytical grade and used as received and stored at room temperature (25℃) for further use. Titanium foils (.25mm thickness, 99.99% purity) were also purchased from Sigma-Aldrich. The pure water (18 MΩ. cm at 25 ℃) were used to prepare all the solutions during the experiment was purified with the Nanopure ® water system. A power supply (Laboratory DC Power Supply, GPS- 3030DD) (30Voltage) were used as the source of power.

2.2 Preparation of TNTs

In this study, TNTs were prepared based on electrochemical anodization method [26]. TNTs layers were fabricated directly on Ti foil (12.5mm× 12.5mm×.25mm) through electrochemical anodization in EG that containing 0.56g NH_4F and 1 ml pure water. The foil was ultrasonically cleaned with acetone for 20 min then cleaned with ethanol and pure water for 20 min each before anodization. A power supply (30V) is being used as a source of power, Ti foil used as working electrode and connect with the positive (+) (Red) portion of the source, platinum (Pt) used as counter electrode and connect with the negative (-) (Black) portion of the power supply. To make proper anodization, 1cm distances between the electrodes were maintained. The electrolyte colour turns into light purple from its natural water colour after 1h of continuous anodization. The anodized samples were rinsed with pure water after 3 hr and annealed at 550 ℃ for 1h and denoted as sample TNTs. To remove the unwanted debris from the surface of the sample, it was ultrasonically cleaned with ethanol for 30 min and continued annealing for 2hr at 450℃.

2.3 Experimental Set Up

Fig 1 represents the experimental set up for electrochemical anodization. During anodization the formation of nanotubes is the result of electrochemical oxidation of Ti at the surface of the metal and chemical dissolution TiO_2 layer formed by fluorides (F^-) in electrolyte according to the Equations (1), (2) and (3) [9].

$$\mathbf{Ti \rightarrow Ti^{4+} + 4e^{-}} \quad (1)$$

$$\mathbf{Ti^{4+} + 2H_2O \rightarrow TiO_2 + 4H^{+}} \quad (2)$$

$$\mathbf{TiO_2 + 6F^{-} + 4H^{+} \rightarrow [TiF_6]^{2-} + 2H_2O} \quad (3)$$

The F^- ions are essential to the formation of tubular structure due to its ability to form soluble hexafluoro titanium complex ($[TiF_6]^{2-}$) and the nanotube formation mechanism also shown in Fig 1.

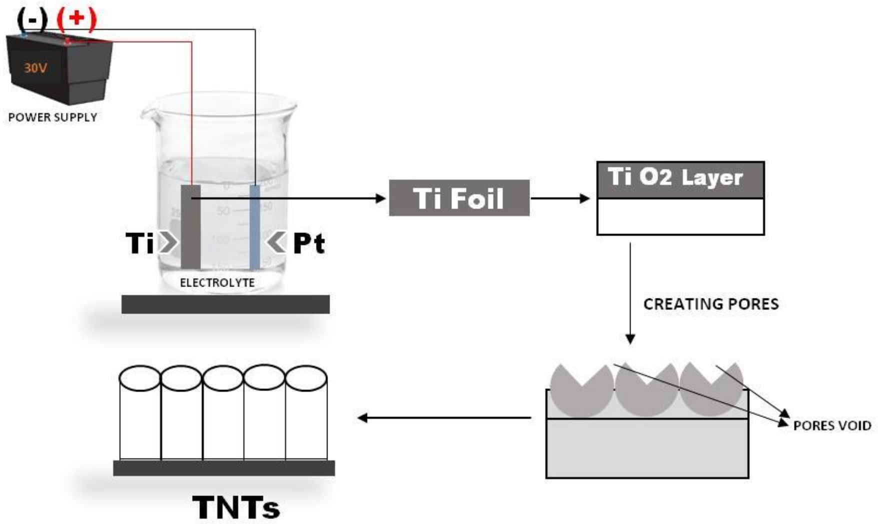

Fig 1: Schematic diagram of anodization set up and formation mechanism of TNTs

2.3 Characterization

The morphologies of samples were examined by a Field Emission Scanning Electron Microscope (FESEM, JEOLUSA). The images were taken at an accelerating voltage of 20 kV. Transmission Electron Microscope (TEM, Brand: FEI, Model: Tecnai–G2–20–Twin), operated at an acceleration voltage of 200kV was used to identify the lattice fringe images, length and the width of the synthesized sample. The UV-visible-diffuse reflectance spectra (UV-DRS), were measured using UV-visible spectrophotometer (UV 2600-230V, SHIMADZU) A Photoluminescence (PL) spectra (EDINBURGH INSTRUMENTS,NIR 300/2) was used to acquire PL spectra with the excitation wavelength at 400nm and 590nm, respectively.

III. RESULT AND DISCUSSION

3.1 Structural and Morphological Characterization

The morphologies of the TNTs were characterized by FESEM; (Fig. 1) represents the nanotubular structure of the pure TNTs with inner diameter ranging between 50 nm and 60 nm. The length of the TNTs obtained from the FESEM, which are 800 nm and 900 nm. Moreover, 11 nm of wall thickness also obtained. These results agreed with the literature value [19]. In this study, the diameter and wall thickness of the TNTs can be compared to the 80 nm diameter of the TNTs where the applied time was 6h. Within half time the similar characteristics of TNTs were grow rapidly and also these characteristics can be used in photocatalytic process. Similarly, the synthesized TNTs length can be compared to the photocatalytic responsive TNTs reported by Sim, Leong, Saravanan, and Ibrahim [25]. The synthesized TNTs characteristics show that this can be used as a photocatalyst during the photocatalytic process.

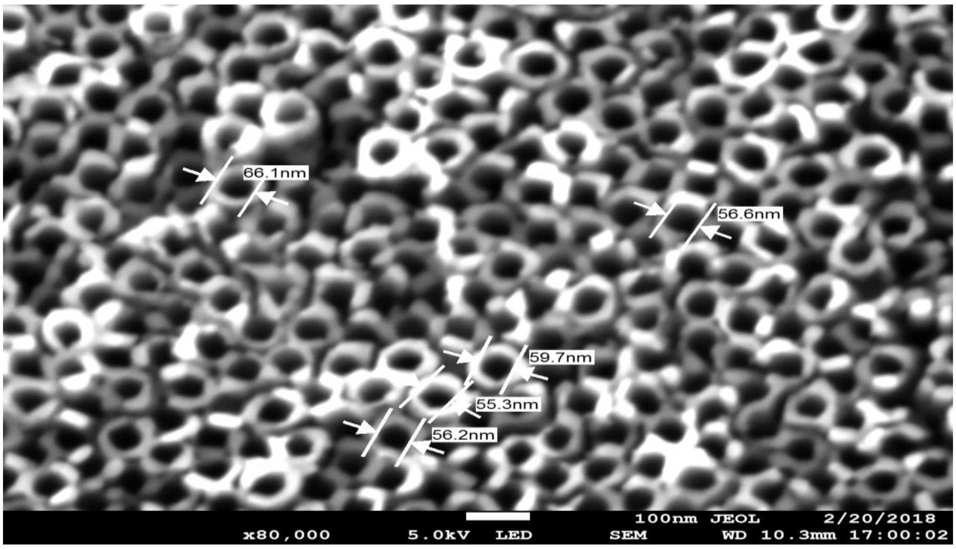

Fig 2: FESEM images of the top view of the pure TNTs

Fig. 3 represents the crystalline nanotubular formation of TNTs from the TEM image. The width of the nanotube is 11 nm observed by TEM analysis. The lattice space was identified from the crystalline phase which is 0.33nm. The lattice spacing of two lattice planes with spacing 0.35 nm was obtained from Sim et al. [26] which corresponded to the (1 0 1) plane of the anatase TiO_2, this result is similar and the synthesized nanotubes represent the anatse TiO_2.

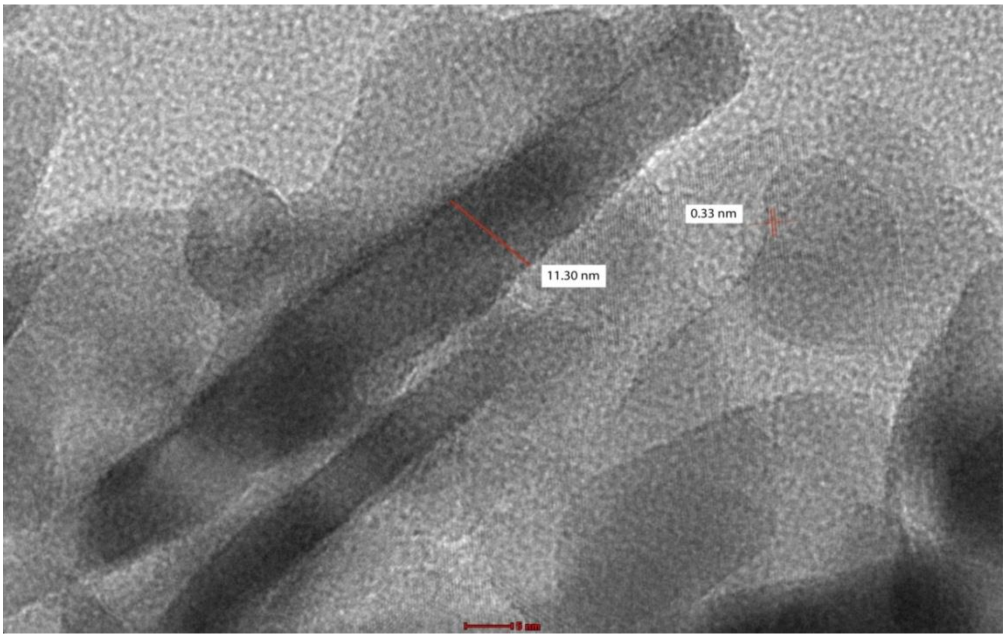

Fig 3: TEM image of TNTs

3.2 UV-Vis Diffuse Reflectance Spectra and Photoluminescence

The UV-visible diffuse reflectance spectra that support the visible light responsiveness characters of the TNTs are shown in Fig 4. TNTs exhibit an absorption band around 360 nm which is in the UV region and an absorption edge in the visible range of 400-460 nm was also observed. Similar phenomenon reported from Low et al. [19] that TNTs exhibit an absorption of 387 nm due to its radical band gap (3.2 eV) absorption of pure anatase TiO_2. TNTs absorption in the visible region happened because the titania can absorb the visible light as it contains a lot of defects reported from Sher Shah, Park, Zhang, Park, and Yoo [23].

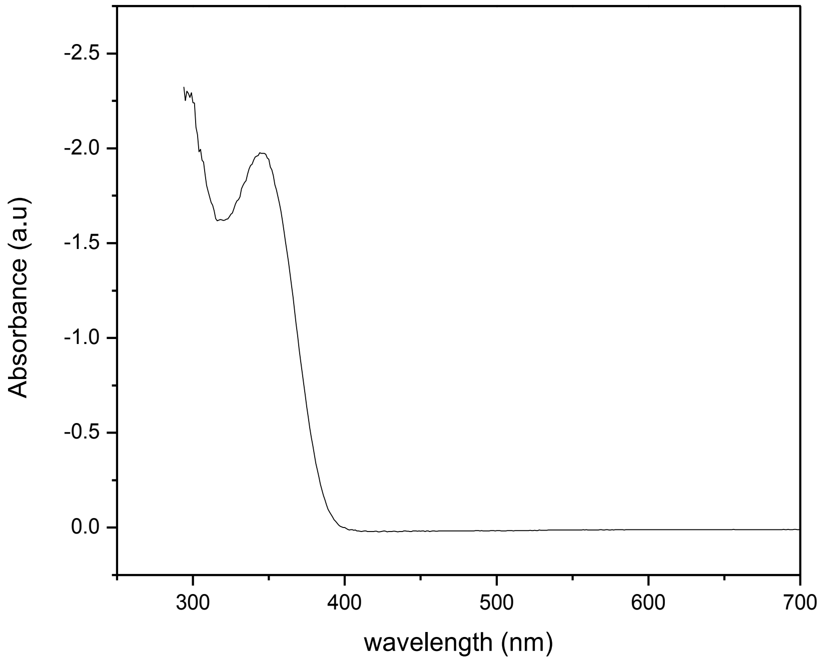

Fig 4: UV-Vis Diffuse Reflectance Spectra of pure TNTs

Fig 5 shows that, TNTs exhibited a wide PL signals in the range of 370-600 nm with the excited wavelength of 350 nm. The spectral peak located at around 400 nm and 590 nm, respectively. These characteristics represents the light emission spectra that is used to identify the separation and recombination properties of photoinduced charge carriers in the photocatalytic process.

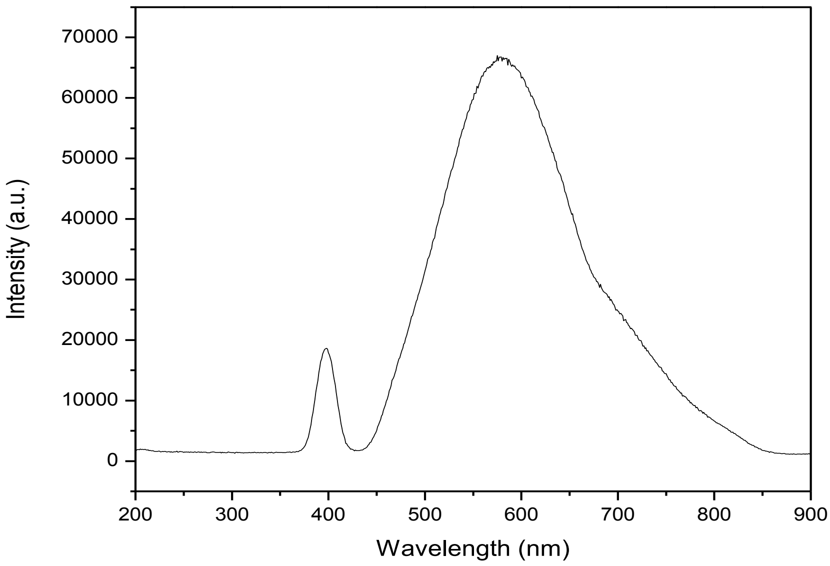

Fig 5: Photoluminescence Spectra of TNTs

IV. CONCLUSION

In summary, a simple electrochemical anodization method was used to synthesize the self-organised TNTs. The morphological characteristics of the TNTs exhibit the rapid growth of the TNTs. Moreover, this feature of the nanotube focused that the low voltage did not make any changes as well as we can use it instead of high voltage. The synthesized nanotubes possess an absorption band under visible light. Moreover, the nanotubes rapid growth and characteristics obtained from FESEM, TEM, UV-Vis Diffuse Reflectance Spectroscopy and PL spectra make it worth use for further photocatalytic applications.

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