Tungsten trioxide (WO$_3$) possesses a small band gap energy of 2.4–2.8 eV and is responsive to both ultraviolet and visible light irradiation including strong absorption of the solar spectrum and stable physicochemical properties. Thus, controlled growth of one-dimensional (1D) WO$_3$ nanotubular structures with desired length, diameter, and wall thickness has gained significant interest. In the present study, 1D WO$_3$ nanotubes were successfully synthesized via electrochemical anodization of tungsten (W) foil in an electrolyte composed of 1 M of sodium sulphate (Na$_2$SO$_4$) and ammonium fluoride (NH$_4$F). The influence of NH$_4$F content on the formation mechanism of anodic WO$_3$ nanotubular structure was investigated in detail. An optimization of fluoride ions played a critical role in controlling the chemical dissolution reaction in the interface of W/WO$_3$. Based on the results obtained, a minimum of 0.7 wt% of NH$_4$F content was required for completing transformation from W foil to WO$_3$ nanotubular structure with an average diameter of 85 nm and length of 250 nm within 15 min of anodization time. In this case, high aspect ratio of WO$_3$ nanotubular structure is preferred because larger active surface area will be provided for better photocatalytic and photoelectrochemical (PEC) reactions.

1. Introduction

Design and controlled growth of nanostructure semiconductor assemblies has gained significant attention in recent years due to the scientific interests and potential applications [1, 2]. In this manner, WO$_3$ is one of the famous electrochromic inorganic materials since Deb’s discovery in 1969 [3]. WO$_3$ film exhibits a broad range of functional properties, such as small band gap energy (2.4–2.8 eV), deeper valence band (+3.1 eV), stable physicochemical properties, and strong photocorrosion stability in aqueous solution [4–10]. The characteristics of WO$_3$ film make them suitable for electrochromic layers in a smart window [11]. Many studies pertaining to WO$_3$ nanostructures are mainly aimed at the formation of high active surface area in view of their use in electrochromic applications [9, 10]. However, several studies have reported that growth of well-aligned and uniformity of anodic WO$_3$ nanotubular structure was a difficult task and most of the studies were only able to grow anodic WO$_3$ into nanoporous instead of nanotubular structure [7–10, 12, 13]. In the present study, we describe the synthesis of well-aligned anodic WO$_3$ nanotubes using electrochemical anodization technique in a fluorinated-based electrolyte. To the best of our knowledge, literatures on optimization of the geometrical features of regular anodic WO$_3$ nanotubular structures are still lacking. Thus, such mechanistic studies and understanding are very important to tailor the desired length, pore size, and wall thickness of ordered WO$_3$ nanotubular structures for high surface area to volume ratio. In this study, a comprehensive experiment was conducted to control the one-dimensional nanostructure of anodic WO$_3$ using electrochemical anodization to achieve effective photocatalytic degradation of MO dye and H$_2$ gas generation via PEC water splitting process.

2. Experimental Procedure

The high purity (99.95% purity with 0.1 mm in thickness) tungsten (W) foils from Alfa Aesar USA were used in
this study. Prior to anodization, W foils were degreased in ultrasonic bath containing ethanol for 30 minutes. The foils were then rinsed in deionized water and dried in nitrogen stream. Then, anodization was performed in a two-electrode configuration bath with W foil served as the anode and the platinum electrode served as the counter electrode. The electrolyte is composed of 100 mL of 1 M of sodium sulfate (Na₂SO₄, Merck, USA) solution with ammonium fluoride (NH₄F, Merck, USA) at 40 V with sweep rate of 1 V/s. In the present study, different content of NH₄F (0.3, 0.5, and 0.7 wt%) will be added into 1 M Na₂SO₄ solution for several anodization duration (15, 30, and 60 min) in order to investigate the formation of anodic WO₃ nanotubular structures. As-anodized anodic WO₃ samples were cleaned using acetone (J.T. Baker, Nederland) and dried in nitrogen stream after anodization process. The morphologies of anodic WO₃ nanostructures were observed by field emission scanning electron microscopy (FESEM), using a FEI Quanta 200 (FESEM model, USA) at a working distance of around 1 mm. The cross-sectional observation was carried out on mechanically bent samples to get the thickness of the oxide layer. The chemical stoichiometry of the sample was characterized using energy dispersive X-ray (EDX) analysis, which is equipped in the FESEM. In order to assess the photocatalytic performance of the anodic WO₃ nanostructure formed, anodized W foil of 25 mm × 25 mm was prepared and placed in 200 mL of 30 ppm MO dye in a customized photoreactor made of quartz glass. Two different surface morphologies of anodic WO₃ nanostructure were selected for MO dye degradation purpose (e.g., oxide layer and nanotubular structure). In the present study, both samples were left in the photoreactor for 30 min in a dark environment to achieve adsorption/desorption equilibrium. Then, both samples were photo-irradiated at room temperature by using a 150 W Xenon solar simulator (Zolix LSP-X150) with intensity of 800 W/m². A 5 mL solution was removed at an interval of 1 h from the photoreactor, and concentration of the solution was measured using a UV spectrophotometer (PerkinElmer Lambda 35). Next, the photoelectrochemical properties of the selected samples were further characterized using a three-electrode water splitting cell, with WO₃ nanotubes as the working electrode, platinum rod as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. The bath with electrolyte composed of 0.5 M sulfuric acid aqueous solution was selected in this experimental work. The H₂ gas generated at platinum rod was collected using the water displacement technique. As the H₂ gas was produced in counter electrode in water splitting chamber, it was bubbling up into inverted burette. The volume of H₂ gas was determined by reading the gas level on the side of burette.

3. Results and Discussion

In the present study, the effect of fluoride content and anodization time on the morphology of anodic WO₃ layer was investigated. Figure 1 to Figure 3 showed the surface morphologies of anodic WO₃ layer in different fluoride content electrolyte from 15 min up to 60 min of anodization time. As shown from the FESEM images, the appearance of anodic WO₃ layer was strongly dependent on the fluoride content and anodization times. Then, the EDX analysis was employed to investigate the composition of element of W and O from the anodic WO₃ layer. Based on the results obtained, the atomic percentage of W element was about 55 at% and O element was about 45% at%. During electrochemical anodization, fluoride content played an important role in controlling the chemical dissolution rate at the interface of W/WO₃ [14]. Figure 1 exhibited variations of WO₃ surface morphology under low 0.3 wt% fluoride content electrolyte for different anodization times. It could be observed that formation of oxide layer on W foil was incomplete at 15 min of anodization time (Figure 1(a)). Interestingly, only thin compact oxide layer with randomly pits was formed after prolonging the anodization time to 30 min and 60 min (Figures 1(b) and 1(c)). The resultant thickness of oxide layer was approximately 100 nm. These results indicated that low fluoride concentration was insufficient in forming the deep and large pore size on the oxide layer due to the inactive chemical dissolution reaction [15]. In this case, oxygen ions within the electrolyte through the W surface towards the W/WO₃ interface induce further growth of the oxide layer under applied potential. The high electric field across the oxide layer of WO₃ and subsequently induce the polarization of W–O bonding, which is able to transfer the W⁶⁺ ions from the pores and leave behind random pits [14, 15]. By further increasing the content of fluoride to 0.5 wt%, the irregular anodic WO₃ nanoporous structure with thickness of approximately 200 nm could be observed from Figures 2(a) to 2(c). However, it could be noticed that the pore diameter on the oxide layer was increasing up to 70 nm when prolonging the anodization time to 60 min. The uniform anodic nanoporous WO₃ layer could be achieved in 1 M Na₂SO₄ electrolyte composed of 0.5 wt% fluorides content. When the fluoride content was further increased to 0.7 wt%, a hollow cylinder oxide nanostructure was observed as shown in Figure 3(a), which indicated that the amount of fluoride in the electrolyte was sufficient to increase the chemical dissolution rate. This condition led to further acidification reactions to develop the nanoporous structure into nanotubular structure [16–18]. In this case, tungsten fluoro-complex ions within the electrolyte playing an important role in inducing chemical dissolution to enlarge and deepen pores and eventually transforming to nanotubular structure [14]. It is noteworthy to mention that the WO₃ nanotubes with diameters of approximately 85 nm and lengths of 250 nm were successfully formed when the fluoride content was increased to 0.7 wt%. However, nanotubular structure disappeared when further the anodization time increased to 30 min and 60 min and eventually resulted in irregular nanoporous structure (Figures 3(b) and 3(c)). The reason might be attributed to the excessive chemical etching on the wall surface of nanotubes during the chemical dissolution reactions. Thus, optimization of fluoride content identified in our electrolyte was 0.5 wt% in order to grow the well-aligned one-dimensional WO₃ nanotubes for 15 min electrochemical anodization duration. Figure 4 presented a simple schematic illustration of formation of...
The photocatalytic removal ability of the selected sample of anodic WO$_3$ oxide layer was compared with that of anodic WO$_3$ nanotubular structure by exposing the samples to MO dye under solar illumination. The initial MO dye concentration in the solution was fixed at 30 ppm. The changes in MO dye concentration were investigated within 5 hours and the result was shown in Figure 5. The degradation rates of MO dye concentration for sample “anodic WO$_3$ oxide layer” and sample “anodic WO$_3$ nanotubular structure” was decreased from 30 ppm to 13.5 ppm and 8.5 ppm, respectively. When anodic WO$_3$ nanotubular structure exposed to the $h\nu$ illumination that solar photonic energy is higher than its band gap energy (2.4–2.8 eV), the anodic WO$_3$ itself will generate pairs of photo-induced electrons ($e^-$) and holes ($h^+$). In this manner, the $e^-$ and oxygen molecule (O$_2$) will combine to form super oxide anion ($O_2^{2-}$), whereas the $h^+$ of anodic WO$_3$ and water molecule (H$_2$O) will generate hydroxyl radical (‘OH). These powerful oxidizing agents (“OH and $O_2^{2-}$”) will then decompose the MO dye (organic dye) into CO$_2$ and H$_2$O. This cycle will continue when the $h\nu$ illumination is available. A simple schematic illustration of basic principal in photocatalytic degradation of MO dye is shown in Figure 6. In theoretical perspectives, the photocatalytic degradation performance of anodic WO$_3$ can be related on the ability to generate pairs of charge carriers, which will release powerful oxidizing agents (“OH and $O_2^{2-}$”) that are able to undergo the secondary reactions. In other words, anodic WO$_3$ nanotubular structure with larger surface area of active reaction sites (inner and outer wall surface of nanotubes) has better photon absorption under $h\nu$ illumination. The distance of light scattering inside the nanotubes extends and provides more photon absorption to trigger the photocatalytic degradation reaction.

On the other hand, the evolution rate of H$_2$ gas generated from the photoelectrochemical (PEC) water-splitting process under solar illumination was measured. The H$_2$ evolution as a function of time is shown in Figure 7. H$_2$ generation rate from water splitting reaction increased linearly with increasing exposure time. The sample (anodic WO$_3$ nanotubular structure) achieved a maximum evolution of approximately 1 mL/cm$^2$ within 1 hour, which is relatively higher compared with the anodic WO$_3$ oxide layer. The H$_2$ production completely stopped after the termination...
of \( hv \) illumination. This observation clearly shows that \( \text{H}_2 \) is only produced photocatalytically. A constant production rate of \( \text{H}_2 \) gas could be observed in the present study. In theoretical perspectives, PEC water splitting process is the general term for a chemical reaction in which water is separated into \( \text{O}_2 \) and \( \text{H}_2 \) using anodic \( \text{WO}_3 \) film that catalyze the water splitting reaction. A basic schematic diagram of such overall water splitting reaction using a semiconductor photocatalyst is presented in Figure 8. The water splitting reaction can be summarized as follows: \( 2\text{H}_2\text{O(l)} \rightarrow \)
Figure 4: Schematic illustration of formation and mechanistic studies of anodic WO$_3$ nanostructured film with and without fluoride content during electrochemical anodization stage.

Table 1: Photodegradation of MO dye: (a) anodic WO$_3$ nanostructures obtained in 1 M Na$_2$SO$_4$ electrolyte containing 0.7 wt% NH$_4$F for 15 min at 40 V, (b) anodic WO$_3$ nanostructures obtained in 1 M Na$_2$SO$_4$ electrolyte containing 0.3 wt% NH$_4$F for 15 min at 40 V.

Table 2: Water splitting performance of anodic WO$_3$ nanostructures.

Figure 5: Photodegradation of MO dye using WO$_3$ nanostructured film under solar illumination.

Figure 6: The overall mechanism of the photocatalytic degradation of MO dye using WO$_3$ nanostructured film under solar illumination.

Figure 7: H$_2$ evolution under solar illumination of (a) anodic WO$_3$ nanostructures obtained in 1 M Na$_2$SO$_4$ electrolyte containing 0.3 wt% NH$_4$F for 15 min at 40 V and (b) anodic WO$_3$ nanostructures obtained in 1 M Na$_2$SO$_4$ electrolyte containing 0.7 wt% NH$_4$F for 15 min at 40 V.

O$_2$(g) + 2H$_2$(g). The overall water splitting reaction is considered as a thermodynamically uphill reaction with a large Gibbs free energy of $\Delta G^0 = +237.2$ KJ mol$^{-1}$. This reaction indicates that photon energy is required to overcome the large positive change in Gibbs free energy through PEC water splitting process [19, 20]. The light-driven water splitting process is triggered when anodic WO$_3$ film absorbs photons from $hv$ illumination with energies greater than its band gap energy. This light absorption generates negative $e^-$ in the conduction band and positive $h^+$ in the valence band. The $h^+$ performs work at the anodic WO$_3$ electrolyte interface oxidizing water molecules to create O$_2$ and H$^+$ ions within the electrolyte. Then, the $e^-$ will move through the external circuit to the platinum electrode (counter electrode) where they reduce H$^+$ ions creating H$_2$ molecules due to the electric field or under external bias [20]. The PEC water splitting performance is consistent with the photocatalytic degradation. In summary, the self-organized WO$_3$ nanotubular structure has strong ability to release much more photo-induced e$^-$/h$^+$ pairs than that of compact layer structure. Thus, it is crucial to maximize the active surface area of photocatalyst (anodic WO$_3$) for better photocatalytic and photoelectrochemical performance.

4. Conclusion

In conclusion, complete transformation of W foil to one-dimensional WO$_3$ nanotubes with an average diameter of 85 nm and length of 250 nm could be achieved within 15 min in an electrolyte composed of 1 M of Na$_2$SO$_4$ and 0.7 wt% of NH$_4$F. The main reason attributed to the sufficiency of tungsten fluoro-complex ions induced chemical dissolution to enlarge and deepen pores and eventually transform to nanotubes. The ability to grow large active surface area
of anodic WO$_3$ nanostructures demonstrated a substantial enhancement in the degradation of MO dye and H$_2$ generation via water splitting process, as compared to the anodic WO$_3$ oxide layers.

**Conflict of Interests**

The author declares that there is no conflict of interests regarding the publication of this paper.

**Acknowledgments**

This research is supported by High Impact Research Chancellory Grant UM.C/625/1/HIR/228 (155001-73873) from the University of Malaya. In addition, authors would like to thank University of Malaya for sponsoring this work under University of Malaya Grant UM.C/625/1/HIR/228 (J55001-73873) from the cell orly Grant. This research is supported by High Impact Research Channel Fund Grant UM.C/625/1/IR/228 (J55001-73873) from the University of Malaya. In addition, the authors would like to thank University of Malaya for sponsoring this work under the University of Malaya Grant UM.C/625/1/HIR/228 (J55001-73873) from the Government of Malaysia.

**References**


