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Research Article

Surface Morphology and Growth of Anodic Titania Nanotubes Films: Photoelectrochemical Water Splitting Studies

Chin Wei Lai

Nanotechnology & Catalysis Research Centre (NANOCAT), Institute of Postgraduate Studies (IPS), University of Malaya, 3rd Floor, Block A, 50603 Kuala Lumpur, Malaysia

Correspondence should be addressed to Chin Wei Lai; cwlai@um.edu.my

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Design and development of one-dimensional nanoarchitecture titania (TiO) assemblies have gained significant scientific interest, which have become the most studied material as they exhibit promising functional properties. In the present study, anodic TiO_2 films with different surface morphologies can be synthesized in an organic electrolyte of ethylene glycol (EG) by controlling an optimum content of ammonium fluoride (NH_4F) using electrochemical anodization technique. Based on the results obtained, well-aligned and bundle-free TiO_2 nanotube arrays with diameter of 100 nm and length of 8 μm were successfully synthesized in EG electrolyte containing ≈5 wt% of NH_4F for 1 h at 60 V. However, formation of nanoporous structure and compact oxide layer would be favored if the content of NH_4F was less than 5 wt%. In the photoelectrochemical (PEC) water splitting studies, well-aligned TiO_2 nanotubular structure exhibited higher photocurrent density of ≈1 mA/cm^2 with photoconversion efficiency of ≈2% as compared to the nanoporous and compact oxide layer due to the higher active surface area for the photon absorption to generate more photo-induced electrons during photoexcitation stage.

1. Introduction

At present, one of the crucial steps taken by many countries to aid our mother earth [1–3] and minimizing environmental problems is applying sustainable development [4–8]. It seems that sustainable development to create an alternative clean and renewable energy [3, 5] to sustain the present level of population and economic development is a strategic goal of modern society reflecting contemporary demand for economic, social, political, and environmental development [9, 10]. To date, hydrogen (H_2) has been established as a potential future energy carrier [7–9] and possibly the best substitute for fossil fuel to secure the future supply of a clean and sustainable energy [11–14]. This probable supply of energy in the future is by trapping the solar energy to split the water into hydrogen and oxygen gases within a PEC water splitting cell [10–16]. The controlled reaction of hydrogen and oxygen gases within a fuel cell will generate electricity [17–19]. However, the cost effective generation of H_2 with sunlight via water splitting process is a critical breakthrough needed to transition to a renewable energy based hydrogen economy [14–16].

In fact, a suitable candidate as a photoelectrode for H_2 production via water splitting process must have three basic criteria as shown below [7, 8].

(i) Stability. The semiconductor must be photochemically stable in aqueous solution, in which it will not be photocorroded during the water splitting process.

(ii) Band Gap. The semiconductor must have a band gap of about 1.7–2.0 eV considering the overpotential losses and energy required for water splitting process.

(iii) Energy Level. For spontaneous water splitting process, the oxidation and reduction potential must lie between the valence and conduction band edges of the semiconductor.

Since 1972, PEC water splitting using TiO_2 as photoelectrode was successfully reported by Fujishima and Honda [4, 5]. Since then, TiO_2 has been extensively used as an efficient

photoelectrode in PEC water splitting system for H_2 generation [11–16] because of its unique characteristics, such as high active surface area, strong oxidation ability, active at room temperature, outstanding charge transport property, and high stability against corrosion [20, 21]. This breakthrough has triggered the subsequent interests in photocatalysis research by scientists and researchers from all over the world on TiO_2 and made TiO_2 an important component in photocatalysis field [6, 7]. However, bundling problem (disorder arrangement of nanotube arrays) and weak adherence of the nanotubes on Ti substrate remains as a great challenge for synthesizing high quality of one-dimensional (1D) TiO_2 nanotubes film [12–16]. Thus, considerable efforts have been conducted to the development of more efficient photoanode materials, especially well-aligned and ordered arrangement of 1D TiO_2 nanotubes [20–22]. Nowadays, synthesis of TiO_2 nanostructures can be achieved by various approaches, such as sol-gel methods [23–25], hydrothermal synthesis [26–28], and anodization technique [22, 29, 30]. Among all of these methods, electrochemical anodization technique has been seen as an effective and economical way in the formation of well-aligned TiO_2 nanotubes [31–34]. Moreover, anodization technique is relatively simple and can be adopted for large-scale industrial production for creating self-organized anodic oxides in the form of nanotubular structures with almost perfect vertical alignment.

In order to obtain the right dimensions and morphologies, a controlled synthesis procedure for the production of well-aligned and ordered arrangement of 1D TiO_2 nanotubes must be investigated and optimized [35–37]. In principles, three different morphologies of Ti anodic oxide layer could be achieved via anodization technique, which are compact oxide layer, nanoporous structure, and self-organized nanotube arrays [38, 39]. The most important point ought to be mentioned is that anodization technique is a versatile technique to form self-organized nanotubular thin film with controllable dimension, such as tubular's diameter, length, and wall thickness [35–40]. Therefore, well understanding regarding the formation of highly ordered and bundle-free nanotubular structure on anodized Ti surface is important in order to obtain the right dimensions and morphologies in PEC water splitting studies. In this work, a study has been performed to evaluate the morphology of the anodized Ti foil in different contents of NH_4F and determine the best morphology for high efficient PEC water splitting performance.

2. Experimental Procedure

Ti foil (99.7% purity) with a thickness of 127 μm from STREM Chemicals, USA, was selected in this experimental work. Before the anodization process was conducted, Ti foils were degreased by sonication in ethanol for 30 minutes. Then, Ti foils were rinsed in deionised water and dried in a nitrogen stream. Next, anodization process was conducted in a two-electrode configuration bath, where Ti foil served as anode and the platinum foil served as counter electrode. The anodic oxidation was conducted in EG electrolyte containing 5 wt% of H_2O_2 with different amounts of NH_4F (1 wt%, 3 wt%, and 5 wt%) for 1 hour at a constant potential of 60 V. In the present study, H_2O_2 was maintained at 5 wt% and applied potential was fixed at 60 V because smooth and highly ordered nanotubes arrays could be synthesized when they are maintained around this value according to our preliminary study [29, 41]. The current density transient was recorded using a computerized Keithley DC Power Supply. The sweep rate was maintained at 1 V/min. After the anodization process, the anodic samples were cleaned using acetone and dried in nitrogen stream. The as-prepared anodic samples were then annealed for 4 h at 400°C in argon atmosphere. It was anticipated that the formation of the single crystalline anatase phase would result in enhanced PEC performance [37, 42].

The morphologies of the TiO_2 nanotubes were characterized through field emission scanning electron microscopy (FESEM) using a Zeiss SUPRA 35 VP at working distances down to 10 mm. To obtain the thickness of the nanotube layer, cross-sectional measurements were carried out on mechanically bent samples. The actual length of the nanotube arrays was fixed on a 45° sample stage to view the cross-sectional morphologies. Then, actual length was determined by dividing the observed length by cos 45°. The PEC water splitting properties of the samples were characterized using a three-electrode PEC water splitting cell with TiO_2 nanotube arrays as the working photoelectrode, platinum rod as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. A solution of 1 M KOH with addition of 1 wt% of EG was used as the electrolyte in the PEC cell. In this study, ethylene glycol was used as sacrificial agent to reduce electron-hole recombination losses, which could improve the photocurrent density [7]. All three electrodes were connected to a potentiostat (μAutolab III). A 150 W xenon lamp (Zolix LSP-X150) with an intensity of 800 W/m^2 was used to produce a largely continuous and uniform spectrum. The light was transmitted by the quartz glass as the xenon lamp shone on the working electrode (photoanode). The xenon lamp was switched on after the three electrodes were connected to the potentiostat and the photocurrent was measured during the voltage sweeping (5 mV/s).

3. Results and Discussion

An optimum content of NH_4F has significant influence on the morphology of anodic TiO_2 nanotubes film. Figure 1 shows FESEM images of the surface of the anodized Ti foils formed in EG electrolyte containing 5 wt% of H_2O_2 with different contents of NH_4F from 1 wt% to 5 wt%. The insets are the cross-sectional morphology of the oxide layers. From those FESEM images, the morphology of the Ti anodic oxides was dependent on the contents of NH_4F in the electrolyte. Anodization of Ti foil in a bath containing 1 wt% NH_4F resulted in a thin TiO_2 compact oxide layer with small random pits on the surface of Ti foil as shown in Figure 1(a). The overall thickness of the oxide is approximately 500 nm. This result indicates that a low fluoride (F^-) concentration can only form small pits over the TiO_2 foil. The reason is attributed to the inactive chemical dissolution reaction, which is induced by the low content of F^- ions.

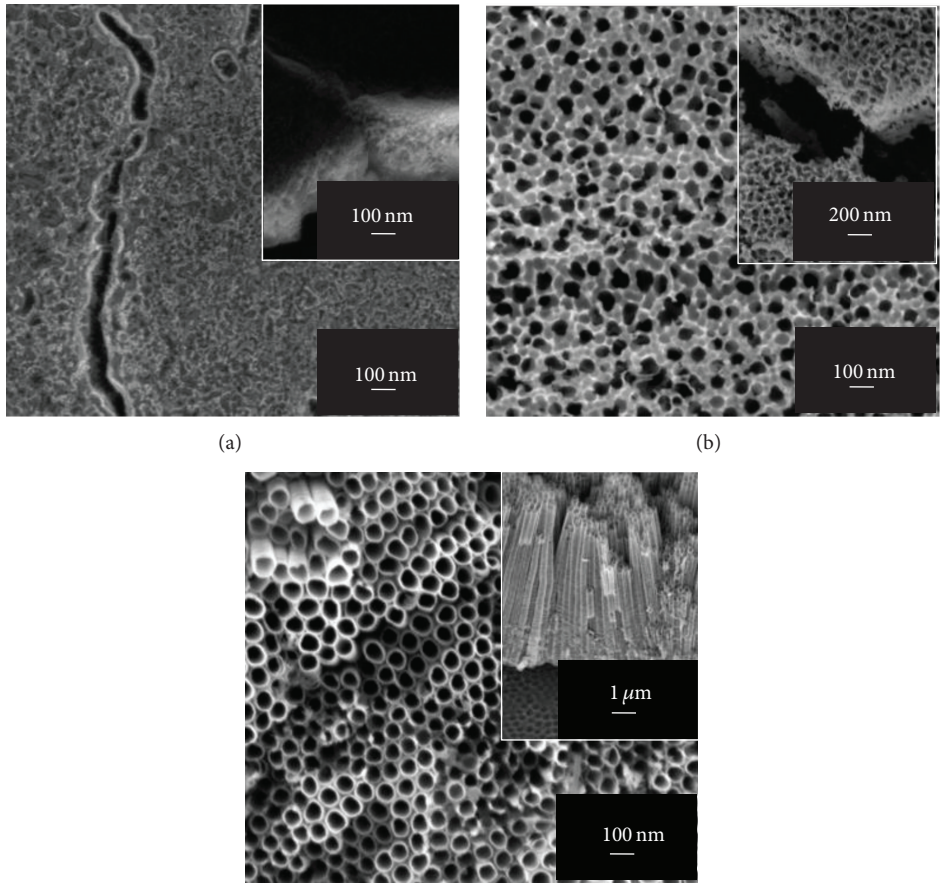

FIGURE 1: FESEM images of the TiO_2 anodic oxide film anodized at 60 V for 1 h in EG electrolyte containing 5 wt% of H_2O_2 and different contents of NH_4F, (a) 1 wt%, (b) 3 wt%, and (c) 5 wt%.

When the amount of NH_4F in the electrolyte was increased to 3 wt%, Ti surface contained irregular features and a porous oxide instead of ordered nanopores was observed (Figure 1(b)). The irregular pore sizes are in the range of 25 nm–100 nm and the thickness of this porous oxide layer is approximately 800 nm. The insufficient F^- content in the electrolyte probably caused incomplete chemical dissolution and oxidation at the interface between Ti and the barrier layer. Thus, the irregular features and nanoporous oxide layer formed. For the 5 wt% NH_4F, self-organized and well-aligned TiO_2 nanotube arrays were successfully synthesized. This indicates that sufficient F^- content is able to increase the chemical dissolution reaction during electrochemical anodization process. This led to further acidification to develop a nanotube structure, as shown in Figure 1(c). The TiO_2 nanotube arrays with diameters of approximately 100 nm and lengths of 8 μm were formed when the F^- concentration was increased up to 5 wt%. Based on the results obtained, NH_4F plays an important role in the formation of the nanotubular structure of Ti anodic oxide films and an optimum F^- content was identified as ≈5 wt% in the EG electrolyte in order to synthesize well-aligned nanotube arrays.

A simple schematic illustration explaining the TiO_2 nanotube arrays formation is exhibited in Figure 2. First of all, an oxide layer was formed on Ti surface and then turned into TiO_2 due to the electrochemical oxidation process [43, 44]. In the presence of F^- ions, the oxide layer dissolves locally and small pits are formed on the oxide layer (Figure 2(a)). These random pits react with the F^- ions to produce $[TiF_6]^{2-}$ complex ions as shown in the following [43–45]:

$$TiO_2 + 4H^+ + 6F^- \longrightarrow [TiF_6]^{2-} + 2H_2O \quad (1)$$

The porous structure is formed as a result of the localized chemical dissolution of the oxide by $[TiF_6]^{2-}$ complex ions during electrochemical anodization process (Figure 2(b)) [34]. The chemical dissolution reduces the thickness of the oxide layers and allows electrochemical etching process to continue at the bottom of the pits [44, 46]. Meanwhile, the high applied potential during anodization process will lead to the field-assisted dissolution, where Ti metal ions (Ti^{4+}) dissolve into electrolyte. The growth of pores is due to the competition between electrochemical oxide formation and chemical dissolution by sufficient content of F^- ions [43–47]. Finally, the nanotube structure will grow inwards

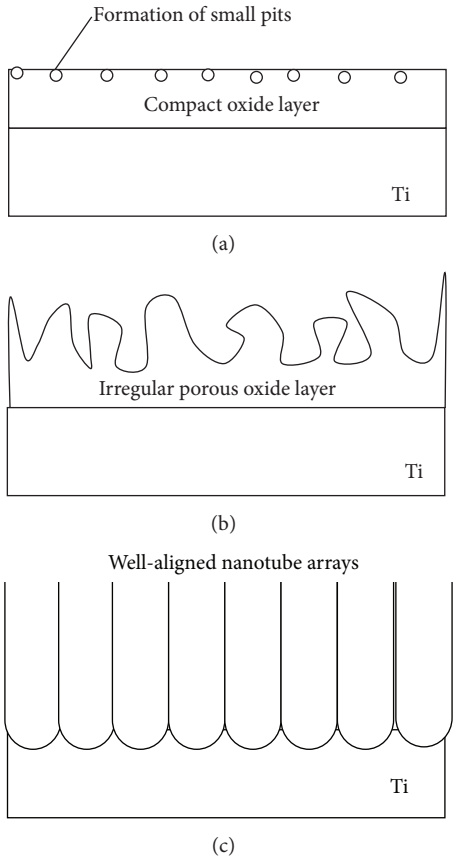

Figure 2: Schematic illustration explaining the TiO_2 nanotube arrays formation: (a) growth of compact oxide layer and small pits formation; (b) growth of irregular porous oxide layer; and (c) well-aligned nanotube arrays.

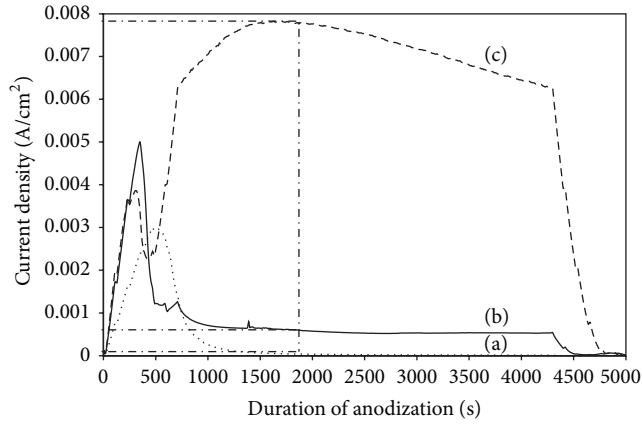

Figure 3: The current density-time behavior during the anodization of Ti foils at 60 V in EG electrolyte containing 5 wt% H_2O_2 and different amounts of NH_4F, (a) 1 wt%, (b) 3 wt%, and (c) 5 wt%.

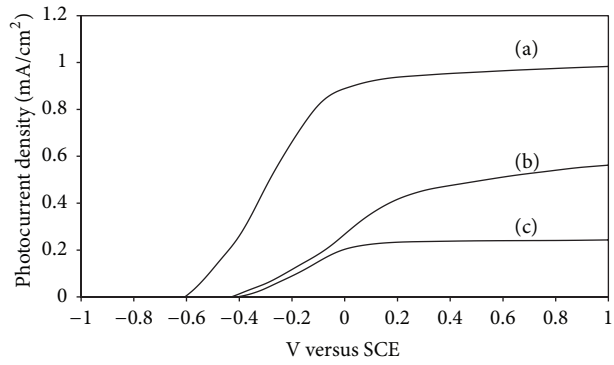

Figure 4: The *I-V* characteristics of different surface morphologies of anodic TiO_2 photoanode in 1 M KOH solution with 1 wt% of EG, (a) nanotubes, (b) nanoporous, and (c) compact oxide layer.

(Figure 2(c)). In summary, formation of TiO_2 nanotube arrays in fluorinated electrolyte was the result of three simultaneously occurring processes: (1) field-assisted oxidation of Ti metal to form TiO_2, (2) field-assisted dissolution of Ti^{4+} ions into electrolyte, and (3) chemical dissolution of Ti and TiO_2 in the presence of F^- ions [38, 39]. From the results obtained, it could be concluded that optimum amount of NH_4F is one of the important factors for the formation of well-aligned TiO_2 nanotubes.

The difference in morphology of the TiO_2 nanotube arrays under different amounts of NH_4F can be explained by referring to the current density profile, as shown in Figure 3. It was found that current density increased up to 7.8 mA/cm^2 when increasing the NH_4F up to 5 wt% (Figure 3(c)). The reason is attributed to the high diffusivity of the F^- ions concentration in the electrolyte, which led to enhanced conductivity of the solution [48, 49]. The higher current density in the electrolyte indicates that the higher chemical etching process induces by the $[TiF_6]^{2-}$ complex ions [50].

In order to evaluate the effect of the various morphologies of anodic TiO_2 layer on the PEC water splitting performance, the above-discussed samples were used as photoelectrode in the PEC water splitting cell. The *I-V* characteristics of the samples were recorded under illumination by a 150 W xenon lamp, with a light intensity of approximately 800 W/m^2. Based on the *I-V* characteristic curves, the photocurrent density was increased when the voltage was increased from −1 V to 1 V under solar illumination. A maximum photocurrent density of approximately 1 mA/cm^2 was observed from the anodic TiO_2 nanotube arrays as compared to the nanoporous and compact oxide layer as exhibited in Figure 4(a). Meanwhile, the TiO_2 nanoporous structure and TiO_2 compact oxide layer exhibited decrease of photocurrent densities, which are approximately 0.55 mA/cm^2 (Figure 4(b)) and 0.25 mA/cm^2 (Figure 4(c)), respectively.

TiO_2 nanotube arrays exhibited higher photocurrent density among the samples. The reason is mainly attributed to the larger specific surface area. It is noteworthy to point out that larger specific surface area of well-aligned nanotube arrays can greatly increase the density of active sites available for the photon absorption to generate more photo-induced electrons. The highly ordered, vertically oriented tubular structure is suitable for a high degree of electrons mobility along the tube axis and perpendicular to the Ti

substrate, which will greatly reduce interface recombination. As a matter of fact, nanotubular structure offers a preferred dimensionally to the TiO_2 back contact, which can improve the transportation of charge carriers due to the less grain boundaries in the one-dimensional nanotube arrays system [16, 35, 36, 38, 39, 42]. In addition, both sides of the nanotube walls and the entire tube sidewalls can act as large number of reaction sites for chemical reactions to occur and allow more photo-induced electrons generated for the hydrogen reduction process during illumination. The larger active surface area proximal to the electrolyte solution enhances the generation of photo-induced electrons from nanotube arrays towards to the back contact of the TiO_2 and eventually these photo-induced electrons move to counter electrode (platinum electrode) through the external circuit where they reduce H^+ ions creating H_2 molecules ($2H^+ + 2e^- \rightarrow H_2$) under external bias [51, 52]. This statement was further confirmed by the more negative values of photopotential for the TiO_2 nanotube arrays (−0.65 V) compared to TiO_2 nanoporous structure (−0.45 V) and TiO_2 oxide layer (−0.4 V) as shown in Figure 4. The more negative values of photopotential or open circuit potential indicated that more photo-induced electrons were generated from valence band to the conduction band when the terminal was left open (no bias voltage was applied).

The drawback of the used irregular nanoporous TiO_2 structure in PEC studies is most probably due to the numerous defect sites and trapping sites, which results in more recombination losses of charge carriers and reduces the photo-induced collection at the TiO_2 back contact [53]. Thus, the photocurrent density was decreasing significantly. On the other hand, the use of TiO_2 compact oxide layer showed the lowest photocurrent density among the samples. The compact oxide layer generally will have less specific surface area compared to the nanotubular and nanoporous structure. Thus, the number of photo-induced electrons generated from the photoelectrode will significantly reduce. Based on the results obtained, it is crucial to maximize the specific surface area of TiO_2 photoelectrode in the PEC water splitting studies.

Next, the TiO_2 response with different surface morphologies towards the interruption of light was studied with a potentiostatic (photocurrent density versus time) at a fix bias voltage of 0.6 V. The photocurrent density of the samples was measured and plotted in Figure 5. All samples showed good photoresponses under light pulse illumination. The photo-induced electrons can effectively transfer from TiO_2 photoelectrode to counter electrode and eventually generate the photocurrent response during illumination. The photocurrent drastically dropped to approximately 0 mA under dark conditions. This indicates that TiO_2 is a good photo-response semiconductor for the transfer and decay of the photo-induced electrons [13, 42]. It is noteworthy to point out that the photocurrent reverted back to the original state within a couple of seconds under illumination. This photocurrent pattern was highly reproducible for several on-off cycles. The results from the potentiostatic curves are in good agreement with the results in photocurrent density curves.

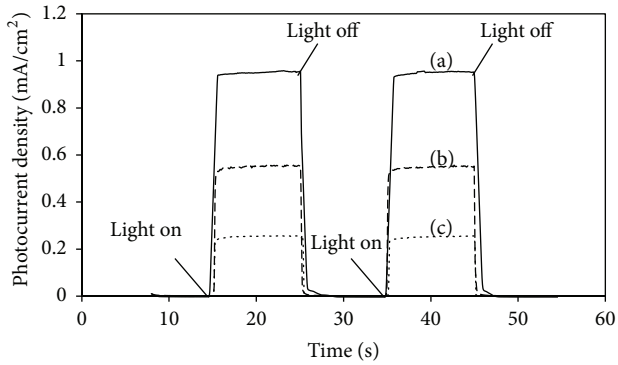

Figure 5: Potentiostatic plot of photocurrent density for different surface morphologies of anodic TiO_2 photoanode in 1 M KOH solution with 1 wt% of EG under interrupted illumination, (a) nanotubes, (b) nanoporous, and (c) compact oxide layer.

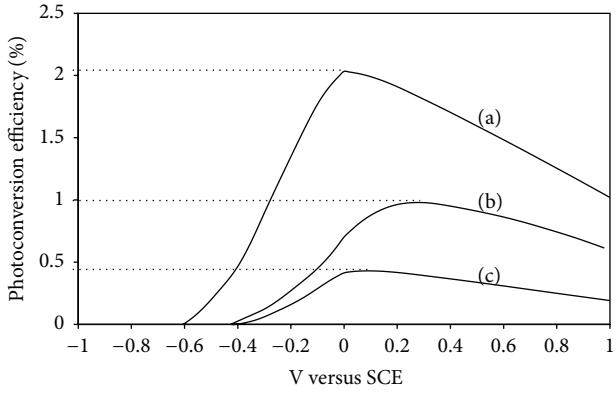

Figure 6: Photoconversion efficiency versus potential applied to the different surface morphologies of anodic TiO_2 photoanode (a) nanotubes, (b) nanoporous, and (c) compact oxide layer.

The photoconversion efficiency (η) for the water splitting reaction was calculated based on the following equation:

$$\eta\,(\%) = \left[\frac{\text{total power output} - \text{electrical power output}}{\text{light power input}}\right] \times 100\% = j_p\left[\frac{E^0_{\text{rev}} - \left|E_{\text{app}}\right|}{I_o}\right] \times 100, \quad (2)$$

where j_p is the photocurrent density (mA/cm^2); $j_p E^0_{\text{rev}}$ is the total power output; $j_p|E_{\text{app}}|$ is the electrical power input; I_o is the power density of the incident light (mW/cm^2); E^0_{rev} is the standard reversible potential (1.23 V/SHE); $E_{\text{app}} = E_{\text{mean}} - E_{\text{aoc}}$; E_{mean} is the electrode potential (versus SCE) of the working electrode where the photocurrent was measured under illumination; and E_{aoc} is the potential (versus SCE) of the working electrode at open circuit condition.

The highest visible spectrum efficiency (about 2%) was obtained from TiO_2 nanotube arrays from the photoconversion efficiency curves shown in Figure 6. The decrease in

photocurrent efficiency was as follows: 1% and 0.5%, which correspond to nanoporous and compact oxide structure, respectively. These results clearly indicate that the PEC performance is dependent on the specific surface area of the TiO_2 anodic film.

4. Conclusion

The formation mechanism of self-organized and well-aligned TiO_2 nanotube arrays in the fluorinated-based electrolyte was investigated and discussed. The present study demonstrated that bundle-free TiO_2 nanotube arrays film was successfully synthesized in EG electrolyte containing ≈5 wt% of H_2O_2 and ≈5 wt% of NH_4F. It is shown that anodic TiO_2 synthesized in EG electrolyte containing less than 5 wt% of NH_4F will result in the formation of nanoporous structure and compact oxide layer. The high specific surface area of anodic TiO_2 nanotubes generated a good photocurrent response of 1 mA/cm^2 with photoconversion efficiency of 2%. The main reason could be attributed to the better light absorption for the PEC water splitting reaction sites by generating more photo-induced electrons under illumination. In summary, it is crucial to maximize the specific surface area of TiO_2 anodic films in order to achieve maximum photocurrent generation and photoconversion efficiency.

Conflict of Interests

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

Acknowledgments

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