Development of Titania (TiO_2) Nanotube Photoanodes of Photoelectrochemical Cells for Hydrogen Production using Anodization and Hydrothermal Method

Pakawat Wongwanwattana [a, *], Sert Kiennork [a], Ronariddh Nakhowong [a], Buagun Samran [b], Udom Tipparach [c]

[a] *Faculty of Science, Ubon Ratchathani Rajabhat University, Ubon Ratchathani, 34000 Thailand*
[b] *Facuty of Science, Nakorn Phranom University, Nakorn Phranom, 48000 Thailand*
[c] *Department of Physics, Ubon Ratchathani University, Ubon Ratchathani, 34190 Thailand*

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Abstract

Titania nanotube (TiO_2) based photoanodes of electrochemical cells were fabricated to generate hydrogen by water splitting through solar energy. The anodization was used to synthesize TiO_2 nanotubes. The nanotube arrays were ultrasonically cleaned at different extensions of times of as anodized samples for 0 – 50 min and followed by annealing at 450 °C for 2 h. The suitable period of time for ultrasonic cleaning of the surface was 30 min. The ultrasonic cleaning was used to perform to obtain the suitable to be subjected to hydrothermal process. The samples were then subjected to hydrothermal. The hydrothermal was carried out different solutions: acid, neutral, and base. After being treated by hydrothermal process, the samples were annealed at 180 °C for 18 h. The samples were characterized by several techniques including XRD, SEM UV-vis Spectroscopy. The results show that TiO_2 nanotubes were longer when compared with the anodized samples. The samples also show main phase of TiO_2 and the energy gaps of the samples were reduced. The TiO_2 nanotubes can serve as working electrodes and generate hydrogen. The highest efficiency of solar energy conversion to hydrogen was the samples subjected to neutral solution treatments in hydrothermal process.

KEYWORDS: Anodization; Titania nanotubes; Hydrogen production; Hydrothermal; Ultrasonic cleaning

* Corresponding authors; e-mail: pakawat.w@ubru.ac.th

Introduction

The conversion of sunlight to chemical energy in the form of hydrogen is an ultimate goal of scientific and technological interest which solution may be an feasible importance as a renewable source of sustainable and environmentally energy for next generations. Photoelectrolysis of water to produce hydrogen (H_2) has attracted great attention due to the depletion of fossil fuels and global warming. The photocatalytic evolution of H_2 and O_2 from water occurs when a photocatalytic agent with appropriate band gap is illuminated by sufficiently energetic light. Honda and Fujishima [1] demonstrated the process of electrochemical photolysis of water using semiconductor TiO_2 as a working anode. Since then, a large number of semiconductor materials have been employed for photoanodes, also called working anodes for hydrogen production. TiO_2 and modified TiO_2 are widely used because they are highly photocatalytic, stable, abundant, and environmentally safe [2].

A great deal of recent research in science and technology attempts to focus on nanostructured titania such as nanoparticles [3], nanoflims [4], and nanotubes [5 – 6] to increase water photo-splitting efficiency due to their high surface-to-volume ratios and size-dependent properties to increase the energy conversion efficiecy. Nanostructured titania may be synthesized by many methods [3 – 8] such as sol-gel, and anodization. Anodization has been one of the most popular in making titania nanotubes because it is simple and cheap. We have recently prepared nanotube arrays for working electrodes by anodization [8]. It is believed that ability to control the structures of titania nanotubes can be expected to positively impact a variety of important technologies and the structure of titania nanotubes depends largely on many preparation parameters such as a

temperature, electrolyte, anodic voltage, dopant, and ultrasonic clearning of the nanotubes.

In this paper, we present the effect of ultrasonic cleaning of the nanotubes and additional hydrothermal process afther anodization on the structures, surface morphology, and conversion efficiency of titania nanotubes for hydrogen production.

Materials and Methods

Titania nanotube arrays were grown by anodization method at a room temperature and followed by hydrothermal process. Titanium sheet with 0.25 mm thick, 99.7% purity purchased from Sigma Aldrich were polished by various abrasive papers. After polishing, polished titanium substrates were ultrasonically cleaned in the mixture of acetone and ethanol. Then, anodized titanium substrates were rained by distilled water and dried in the flow of N_2 gas. The electrolytes were NH_4F solution which was made from the mixtures of ethylene glycol (10% EG), ammonium fluoride (0.30 %wt NH_4F) and deionized water (2 Vol % H_2O). The anodization system consists of a two-electrode configuration. The anode was titanium substrate mounted onto a home-made housing apparatus to be anodized and the counter electrode was highly pure platinum. The configuration of the apparatus is shown in Fig. 1. This apparatus allows only one face of the titaniun substrate contacts with the electrolyte. The anodization process was carried on under a constant dc potential 50 V for 2 h. To study the effect of ultrasonic cleaning, As anodized samples were ultrasonically cleaned with different periods of time ranging from 0, 10, 30, and 50 min to get rid of debris on the surface of the samples. The samples were also subjected to hydrothermal treatment. The hydrothermal treatments were carried out under solutions: acid, neutral, and base. The acid solution was made from hydrochloric acid of 10% while the base solution was 6 molar of sodium hydroxide and was mixed with titanium(IV) isopropoxide then heated at 180 °C for 18 h. After being treated by hydrothermal process, the samples were annealed at 450°C for 1 h.

To investigate the surface morphology and microstructure of titania nanotube arrays, all resultant samples were characterized by scanning electron microscopy (SEM, JSM 6010LV, JEOL, USA) and X-ray diffraction (XRD, Phillip 2000 X'pert-MPD, Natherland) using CuKα radiation (λ = 1.5406 Å). The optical properties of titania nanotube arrays were obtained by UV-Vis spectroscopy (T90+, PG instruments, UK). The hydrogen production using titania nanotube arrays as catalyst in water splitting was examined using photoelectrochemical cell (PEC) where the titania nanotube array samples were used as photoanode and a platinum rod as a cathode (Fig.1).

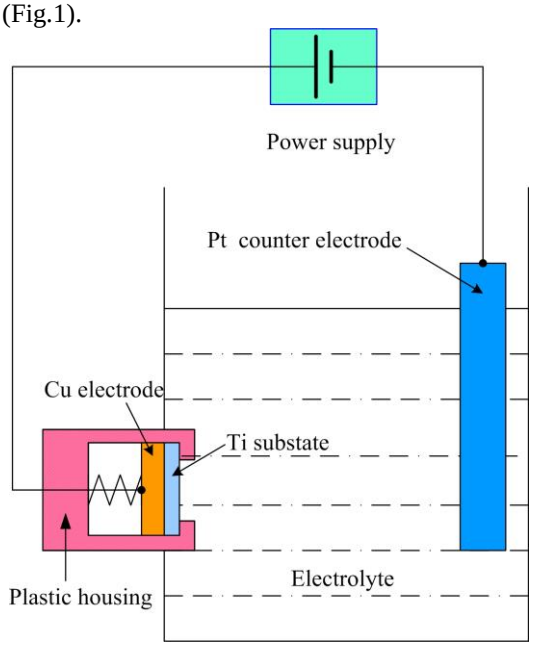

Fig. 1 Experimental equipment diagram of one-face anodization for titania nanotubes [8]

Results and Discussion

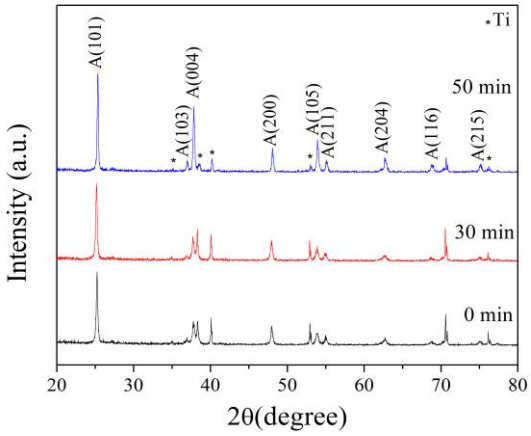

Fig. 2 The XRD patterns of titania nanotubes with different cleaning time.

The XRD patterns of titania nanotube samples annealed at the temperature of 450 °C are shown in Fig. 2. The main diffraction peaks were well agreement with standard diffraction data of pure Ti metal and anatase phase TiO_2. The Ti peaks still exist in the obtained XRD patterns due to the pure Ti substrate on which titania

nanotubes were formed. After ultrasonic cleaning, it was found that the diffraction intensity increase as the increasing of the cleaning time. The XRD results indicate that ultrasonic cleaning time had effect on the improve the crystallinity of the samples due to removal of debris on the surface of the samples. Fig. 3 shows as anodized titania nanotubes with different periods of time of ultrasonic cleaning. SEM images show that as anodized samples are nanotube arrays. The nanotubes were covered with debris if they were not ultrasonically cleaned see Fig. 3(a). They can be seen if they were ultrasonically cleaned for 10 min see Fig. 3(b) and even much better if cleaned for 30 min see Fig. 3 (c). However, the nanotubes were broken or shorter if they were ultrasonically cleaned longer 30 or 50 min see Fig. 3 (d). For this reason, we conclude that the best titania nanotubes can be obtained when ultrasonically cleaned longer for 30 min.

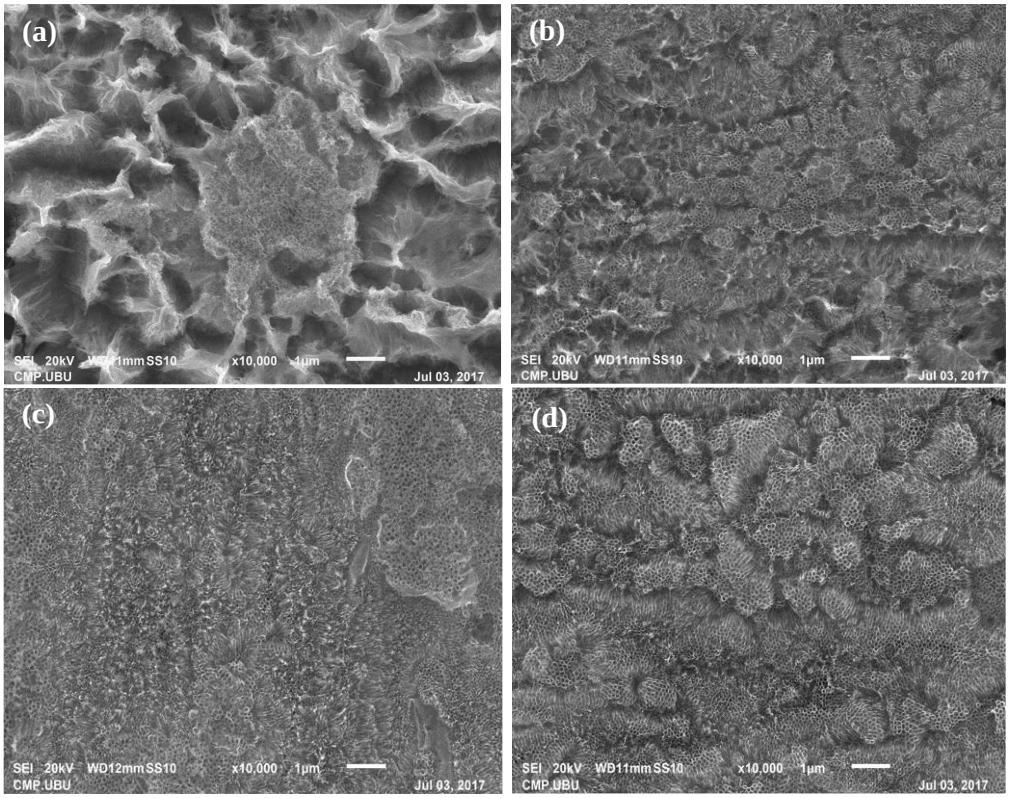

Fig. 3 SEM images of titania nanotubes after anodization followed by different ultrasonic cleaning with different periods of time: (a) 0 min, (b) 10 min, (c) 30 min, and (d) 50 min.

The optical energy band gap of titania nanotubes was calculated from the relation [11]:

$$F(R)h\upsilon = A\left(h\upsilon - E_g\right)^n \qquad (1)$$

where $F(R)$ is the Kubelka-Munk function ($F(R) = (1-R)^2 / 2R$, R is the refelctance data), h is the Planck's constant, υ is the frequency of light, A is a proportionality constant, E_g is the band gap energy and n is the parameter of the direct transition or indirect transition of the semiconductor. The optimal time for ultrasonic cleaning was 30 min was used to prepare for hydrothermal titania nanotubes. After being treated with hydrothermal process, UV-vis data analysis was carried out and the data shown in Fig. 4. The optical energy band gaps of titania nanotubes with treatment with acid, neutral, and base were 3.20 eV, 3.23 eV, and 3.24 eV (Fig. 4(a-c), respectively.

The efficiency of solar energy conversion to hydrogen was performed by measuring current-voltage characteristics and was converted sunlight energy to hydrogen energy using equation [9],

$$\eta(\%) = \frac{(1.23 - |V_{bias}|)\, j}{I_0} \times 100 \qquad (2)$$

where V_{bias} is a bias potential (V), j is current density (mA cm^{-2}), and I_0 is intensity of the light source (I_0 = 77 $mWcm^{-2}$).

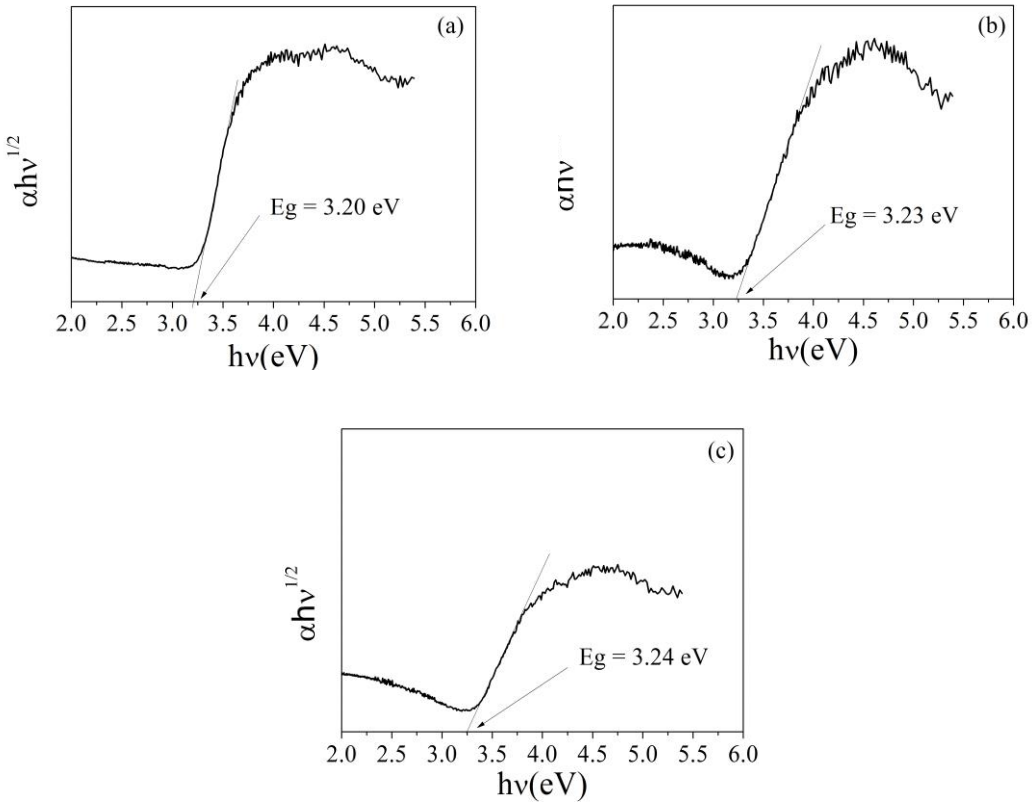

Fig. 4 The determination of optical band gaps by the absorption as a function of light energy for titania nanotubes after hydrothermal process in different solutions: (a) acid, (b) neutral, and (c) base.

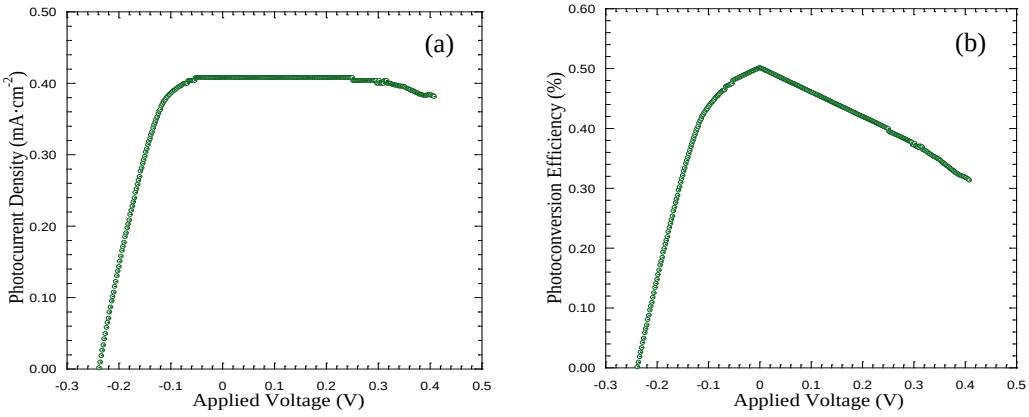

Fig. 5 Performance of the photoelectrochemical cells for hydrogen production with photoanode of hydrothermal titania nanotubes treated with neutral solution (a) IV curve and (b) Photoconversion efficiency as a function of an applied voltage.

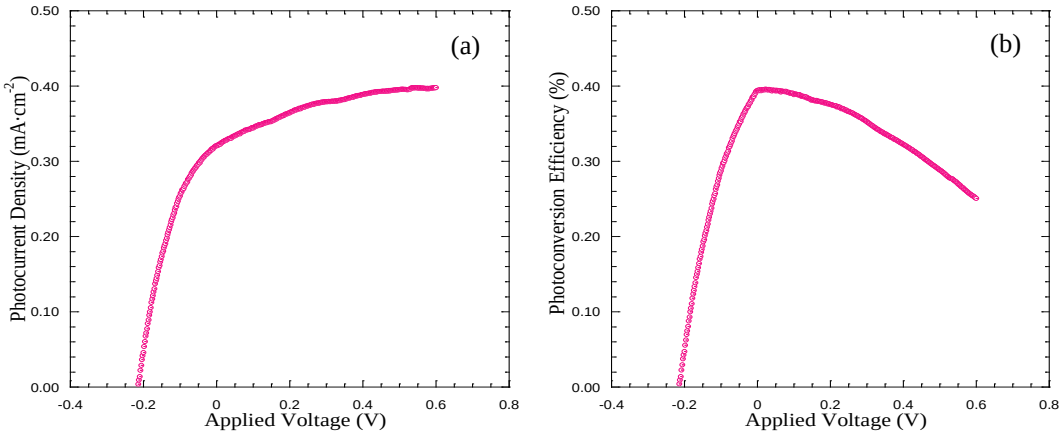

Fig. 6 Performance of the photoelectrochemical cells for hydrogen production with photoanode of hydrothermal titania nanotubes treated with acid solution (a) IV curve and (b) photoconversion efficiency as a function of an applied voltage.

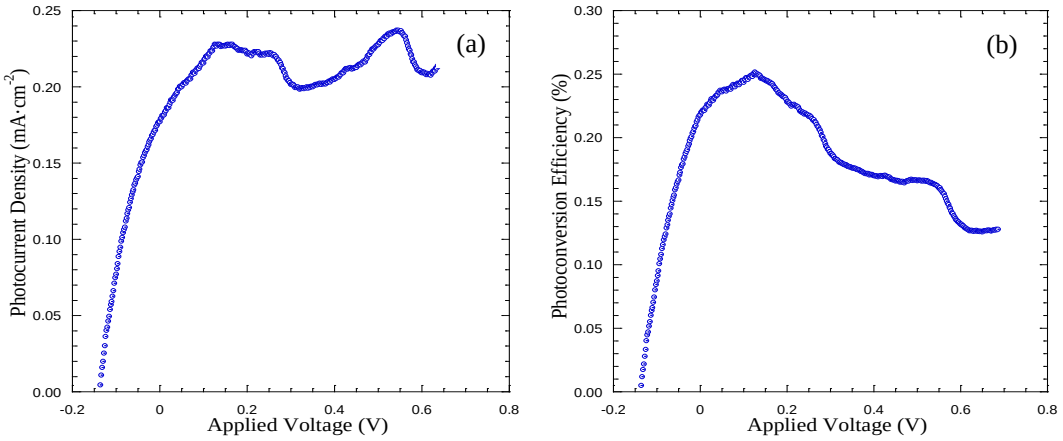

Fig. 7 Performance of the photoelectrochemical cells for hydrogen production with photoanode of hydrothermal titania nanotubes treated with base solution (a) IV curve and (b) photoconversion efficiency as a function of an applied voltage.

The photoconversion from sunlight to hydrogen energy of the photoelectrochemical cells for hydrogen production with different photoanodes of hydrothermal titania nanotubes treated with neutral, acid and base solutions are shown in Figs. 5 – 7. It was showed that all samples can generate hydrogen. Fig. 5 (a) shows the photocurrent density-voltage ($J-V$) characteristic of titania nanotubes treated with a neutral solution. It can be seen that the photocurrent begins rising approximately -0.21 V and then increase to the maximum value of 0.415 mA cm^{-2}. The photocurrent density was further stable after the applied voltage of – 0.06 V and then further constant, indicating the good stability of the samples. Fig. 5 (b) revealed that the maximum efficiencies of the photoelectrochemical cells with photoanodes treated with a neutral solution was 0.50%. Fig. 6 and 7 shows the photocurrent density and the photoconversion efficiency of acid and base, respectively. It was seen that the photocurrent density of titania nanotube treated with acid and base solutions exhibit the photocurrent density and efficiencies were lower than a neutral solution. The efficiencies of acid and base solution of 0.40%, and 0.25% were obtained which is lower a neutral solution. The efficiency was close to that of nanoparticles working electrodes photoelectrochemical cells done by Wongwanwattana et al. [10]. It was revealed that titania nanotube treated with a neutral solution shows the highest activity with the photocurrent density and efficiencies, indicating its benefit to hydrogen evolution reaction.

Conclusion

We have successfully fabricated titania nanotube (TiO_2) photoanodes of electrochemical cells for hydrogen generation by water splitting via solar energy. The working electrodes were made out of anodization followed by hydrothermal process. The optimal period of time for ultrasonic cleaning was 30 min in order to eliminate debris out of the surface of as anodized titania nanotube samples. The neutral solution was the best to treat titania nanotubes in hydrothermal process. The highest efficiency of photoconversion of 0.50% was achieved with neutral solution treatment for thetitania nanotube photoanode.

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