FABRICATION AND CHARACTERIZATION TITANIA NANOTUBES BY ANODIZATION FOR HYDROGEN GENERATION

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Abstract

Titania nanotubes (TiO₂ NTs) were synthesized by an anodization method. The electrolytes were the mixtures of oxalic acid (H₂C₂O₄), ammonium fluoride (NH₄F), and sodium sulphate (VI) (Na₂SO₄) with different ratios. A constant dc power supply at 50 V was used in anodization. The samples were annealed at 450°C for 2 h. Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) were used to characterized TiO₂ NTs. TiO₂ NTs with diameter of 100 nm were obtained when the electrolyte of 0.08 M oxalic acid, 0.5 wt% NH₄F, and 1.0 wt% Na₂SO₄ was used. The maximum photocurrent density was 4.2 mA/cm² under illumination of 100 mW/cm². Hydrogen was generated at an overall conversion efficiency of 3.7%.

Keywords: Titania nanotubes, TiO₂, anodization, hydrogen production, renewable energy

Introduction

Fossil fuel energy in forms of petroleum, coal and natural gas is limited but the demand is unlimited. The use of fossil fuel also causes environmental problems such as air pollution and global warming. Human has sought for environmentally sound source of energy. The conversion of sunlight to energy in the form of electricity or hydrogen is an ultimate goal of scientific and technological interests which solution may be feasible importance as a renewable source of sustainable and environmentally friendly energy for next generations. Photoelectrolysis of water to produce hydrogen (H₂) have attracted attention because it is renewable and environmentally friendly.

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The photocatalytic evolution of $\text{H}_2$ and $\text{O}_2$ from water can be represented by the following equation,

$$\text{H}_2\text{O} \xrightarrow{\text{light, h\nu}} \text{photocatalytic agent} \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2 \quad (2)$$

This reaction occurs when a photocatalytic agent with appropriate band gap is illuminated by sufficiently energetic light. Honda and Fujishima (1972) demonstrated the process of electrochemical photolysis of water using semiconductor TiO$_2$ as a working anode as shown in Figure 1. Since then, a large number of semiconductor materials have been employed for photoanodes, also called working anodes for hydrogen production. All of semiconductor materials, TiO$_2$ and modified structure TiO$_2$ are widely used because they are highly photocatalytic, stable, abundant, and environmentally sound (Nowotny et al., 2007). However, the wide band gap of TiO$_2$ limits the absorption of sunlight to the high energy portion in UV of solar spectrum which contains about 4 percent of whole solar energy (Bak et al., 2002).

It is believed that the band gap of TiO$_2$ can be reduced by metal-doping and this will result in exploiting more solar spectrum. The photoanodes were in TiO$_2$ thin films (Mishra et al., 2003), Metal-doped TiO$_2$ (Peng et al., 2004), TiO$_2$ nanotubes (Mor et al., 2006). It is also agreed that photoactivity of TiO$_2$ depends on its crystal structure. The suitable crystal for photocatalysis is anatase TiO$_2$. However, the revolution of hydrogen may not increase as expected due to electron-hole recombination (Ni et al., 2007). To overcome the recombination of electron-hole pairs, Jan and Shahed introduced Pt-loaded TiO$_2$ thin films as a working electrode (Jun and Shahed., 2002). Previous work shows that Fe-doped TiO$_2$ nanorod clusters and monodispersed nanoparticles absorb more UV spectrum than undoped TiO$_2$ (Tang et al., 2014) and Fe-doped TiO$_2$ films also absorb more visible light than undoped one (Liu et al., 2011) which led to increase photocatalytic activity. In this work, we fabricated Fe-doped TiO$_2$ nanotubes for working electrodes of photoelectrochemical cells (PEC) for hydrogen production and performed photocatalysis test.

**Experimental**

The Pure and Fe-doped TiO$_2$ nanotube array films on Ti substrate were prepared directly by using an anodization process. The electrolytes were HF solution which was made from the mixtures of ethylene glycol (EG), ammonium...
fluoride (0.3 wt % NH₄F) and deionized water (2 Vol % H₂O) with different concentrations of dopant Fe(NO₃)₃·9H₂O. The concentration of Fe dopant was varied from 0.01M, 0.02M, and 0.03M of Fe(NO₃)₃·9H₂O to 0.5% HF electrolyte solution. The system consists of a two-electrode configuration. The anode was Ti substrate mounted onto a home-made housing apparatus to be anodized and the counter electrode was highly pure platinum. This apparatus allows only one face of the titanium substrate contacts with the electrolyte. The anodization process was carried on under a constant dc potential 50 V for 2 h. All substrates were annealed at 450°C for 2 hrs in air to obtain anatase crystalline phases of TiO₂. The current and anodization time data were collected computer-controlled apparatus equipped by LabVIEW programming. To investigate the surface morphology and microstructure of TiO₂ NTs, all resultant samples were characterized by SEM, XRD and techniques. PAR 173 Potentiostat/Galvanstat was used to measure the photocurrent of PEC cells.

**Results and Discussion**

Figure 2 shows XRD patterns of Ti sheet and post annealed TiO₂ NTs. The experimental XRD patterns agree with the JCPDS card no. 84-1284 (anatase TiO₂) and card no. 44-1288 (Ti metal). The XRD patterns show that the phase of TiO₂ NTs is anatase. The anatase (101) peak shows prominently when the anodization was carried out. The samples with different amounts of the dopant have the same crystal structure. The lattice parameters are also constant. These results indicate that the crystal structure of Fe doped TiO₂ NTs
between 0-0.05 M is not altered. Figure 3 shows SEM image of the resultant samples of TiO₂ NTs grown in with different concentrations of dopant Fe(NO₃)₃·9H₂O. The morphology of the TiO₂ was found to be influenced by the dopant. The prepared samples were the titania films with anatase phase. Anatase phase of TiO₂ NTs were reduced when the Fe dopant was added to the electrolyte. The SEM images indicate that our titania nanotubes are well arranged with diameters of about 60-120 nm. The diameters of the nanotubes are about 120 nm for undoped TiO₂ NTs, 60 nm for 0.01 M of Fe(NO₃)₃·9H₂O doped. When the concentration of the dopant increases, the density of the nanotubes decreases. On the other words, the sizes or the diameters of the nanotubes are bigger when the concentration of Fe dopants, Fe(NO₃)₃·9H₂O, increases. It was observed that the nanotubes craked and are not well arranged when the amount of the dopant increased. The nanotubes were broken when the dopant 0.10 M of Fe(NO₃)₃·9H₂O was added to the electrolyte. These titania nanotubes can be used as materials for energy conversion such as photoanodes for producing hydrogen and working electrodes for dye-sensitized solar cells. The best samples in tern of high density and arrangement is the nanotubes prepared by using the electrolyte of the mixture of ethylene glycol (EG), ammonium fluoride (0.3 wt % NH₄F) and deionized water (2 Vol % H₂O) with the concentrations of dopant 0.01 M of Fe(NO₃)₃·9H₂O. Photoconversion efficiency of TiO₂ NTs was measured by a standard three-electrode cell at room temperature under the illumination of 100 mW/cm² in a 1 M KOH solution. The photocurrent response measurement was tested without external applied potential to investigate the photoinduced charge separation efficiency.
of the prepared photanodes and are shown in Figure 4. The photocurrent density-voltage (J-V) characteristic is shown in Figure 5. When the light was turned on and irradiated the photoanode, the photocurrent rose up and kept constant during the light was on while the light was turned off, the photocurrent abruptly disappeared. This evident showed that the current came from the illumination. The photoconversion efficiency ($\eta\%$) of water electrolysis was calculated based on the following relations (Kelly and Gibson 2006; Sang et al., 2012),

$$\eta\% = \left(\frac{J \times E_{\text{rev}}^0}{P_{\text{in}}}\right) \times 100 \quad (2)$$

where $J$ is the photocurrent density, $J \times E_{\text{rev}}^0$ is the total power output and $I_0$ is the power density of incident light and $E_{\text{rev}}^0$ is the standard reversible potential which is 1.23V. The highest photocurrent density was obtained when the photoanode with 0.03 M Fe-doped TiO$_2$ was used as a working electrode. Without an external bias voltage, the photocurrent density after the switch was turned on was about 3.0 mA/cm$^2$ corresponding with the photocurrent efficiency of 3.7%.

This photoconversion efficiency (3.7%) of TiO$_2$ NTs photoanode is larger than that of nano-TiO$_2$ film photoanode made by sol-gel dip coating (Tipparach et al., 2008; Wongwanwattana et al., 2012). The increase of photoconversion efficiency may be resulted from the fact that the surface areas of TiO$_2$ NTs are larger than those of nano-TiO$_2$ films due to the agglomeration of the small spherical crystals of nano TiO$_2$ crystals by nature (Tipparach et al., 2008).

The experiment showed that under the illumination of 75 mW/cm$^2$, PEC produced hydrogen by electrophotolysis at the rate of 0.74 ml/h cm$^2$ corresponding to experimental photoconversion efficiencies of 3.47 % as shown as follows:

$$\eta(\%) = \frac{237.00 \text{(J/mol)} \times \left(0.74 \times 10^{-3} \text{l/h}\right)}{(75 \times 10^{-2} \text{W/cm}^2) \times (60 \text{min/h}) \times (60 \text{sec/min})} \times 100 = 3.03\%$$

provided that hydrogen yields energy of 273000 J/mol (Liao et al., 2012; Matsuoka et al., 2007). The experimental efficiency
(3.03%) is slightly lower than theoretical efficiency (3.7%) due to irreversible processes related to the recombination of electron-hole pairs, ohmic resistivity, and over potential occurring interface between electrolyte and electrodes. Another reason may be due to the reduction of TiO$_2$ NTs optical bandgap energy because nitrogen from NH$_4$F used for making the electrolyte may incorporate the structure of TiO$_2$ NTs. It is well known that Fe-doped TiO$_2$ lowers the bandgap energy of TiO$_2$ (Tang et al., 2014) and absorbs more UV spectrum (Liu et al., 2011) leading to increase the utilization of sunlight spectrums and also increase photoactivity. This may be possible to identify the existence of iron in the structure of TiO$_2$ NTs by X-ray photoelectron spectroscopy (XPS).

**Conclusions**

We have synthesized pure and Fe-doped TiO$_2$ NTs on Ti sheet by anodization method in the mixture electrolyte. The post anodization process was carried out by annealing in air at 450°C for 2 h. The mixtures electrolyte was ethylene glycol (EG), ammonium fluoride (0.3 wt % NH$_4$F) and deionized water (2 Vol % H$_2$O) with the different concentrations of dopant, Fe(NO$_3$)$_3$∙9H$_2$O. The nanotubes are well arranged and the diameters are about 60-120 nm. The photocurrent response indicated that the photocurrent was the contribution of light irradiation on photoanode. The hydrogen can be produced with overall the photoconversion efficiency of 3.7 % when 0.03 Fe-doped TiO$_2$ NTs was used as a working electrode for PEC.

**References**


