

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 petroliun, 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 wraming. 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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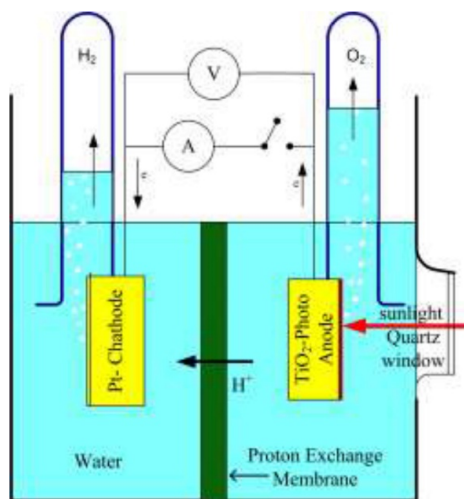
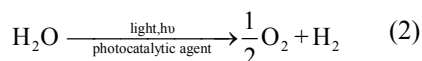


Figure 1. Configuration of PEC cells with TiO₂ photoanode for photoelectrolysis

The photocatalytic evolution of H₂ and O₂ from water can be represented by the following equation,



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 TiO₂ 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, TiO₂ and modified structure TiO₂ are widely used because they are highly photocatalytic, stable, abundant, and environmentally sound (Nowotny *et al.*, 2007). However, the wide band gap of TiO₂ 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 TiO₂ can be reduced by metal-doping and this will result in exploiting more solar spectrum. The photoanodes were in TiO₂ thin films (Mishra

et al., 2003), Metal-doped TiO₂ (Peng *et al.*, 2004), TiO₂ nanotubes (Mor *et al.*, 2006). It is also agreed that photoactivity of TiO₂ depends on its crystal structure. The suitable crystal for photocatalysis is anatase TiO₂. 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 TiO₂ thin films as a working electrode (Jun and Shahed., 2002). Previous work shows that Fe-doped TiO₂ nanorod clusters and monodispersed nanoparticles absorb more UV spectrum than undoped TiO₂ (Tang *et al.*, 2014) and Fe-doped TiO₂ 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 TiO₂ nanotubes for working electrodes of photoelectrochemical cells (PEC) for hydrogen production and performed photocatalysis test.

Experimental

The Pure and Fe-doped TiO₂ 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

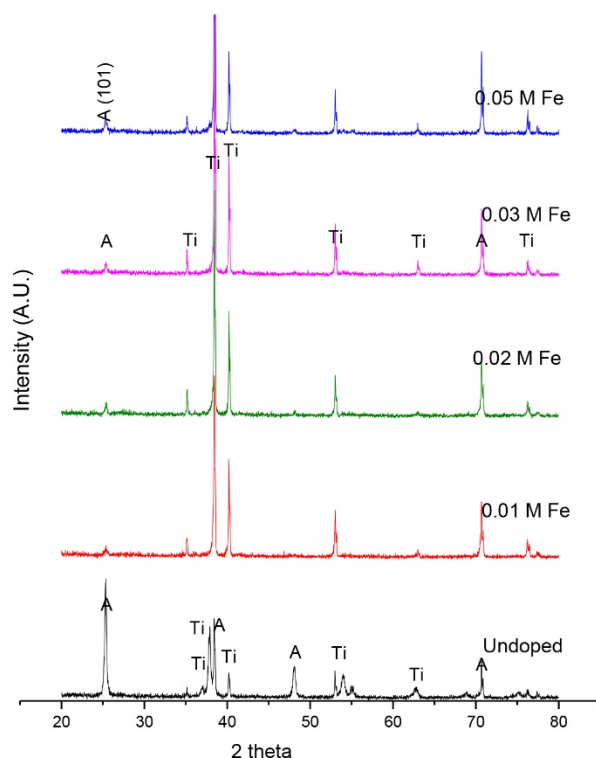


Figure 2. XRD patterns of post annealed TiO₂ NTs grown in Titanium substrates; The letter A peaks belong to Anatase phase of TiO₂ crystal structure and Ti peaks belong to Titanium metal

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

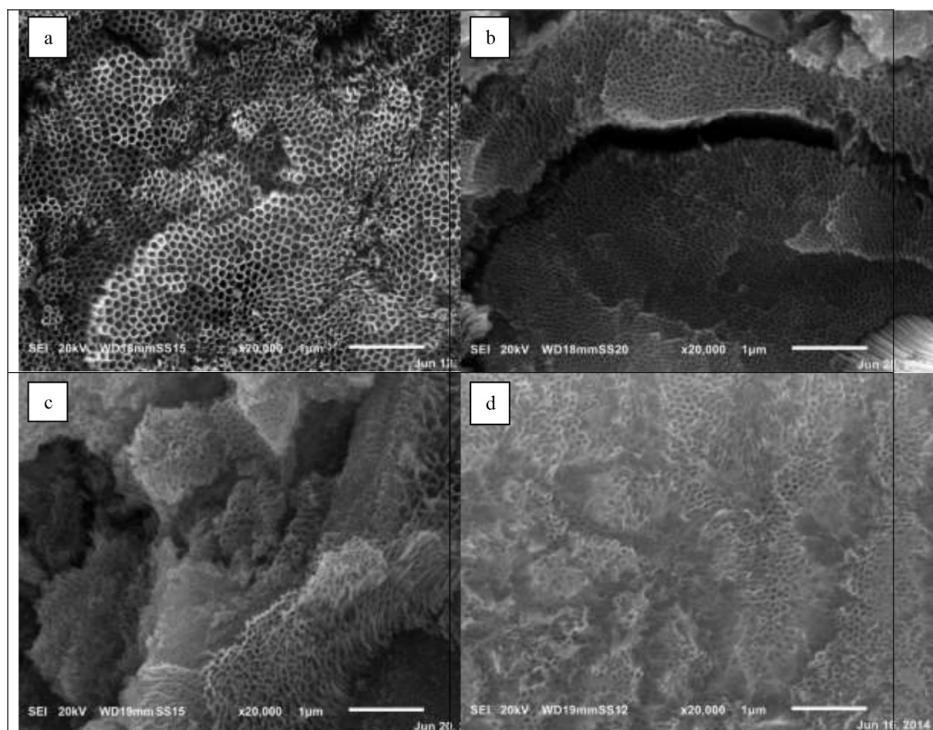


Figure 3. SEM images of anodized TiO_2 NTs with different concentrations of the dopant Fe and anodization time for 2 h; (a) with undoped, (b) with 0.01 M, (c) 0.02 M, (d) 0.03 M of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

between 0-0.05 M is not altered. Figure 3 shows SEM image of the resultant samples of TiO_2 NTs grown in with different concentrations of dopant $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The morphology of the TiO_2 was found to be influenced by the dopant. The prepared samples were the titania films with anatase phase. Anatase phase of TiO_2 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 TiO_2 NTs, 60 nm for 0.01 M of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 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, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, increases. It was observed that the nanotubes cracked and are not well arranged when the amount of the

dopant increased. The nanotubes were broken when the dopant 0.10 M of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 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 terms 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 % NH_4F) and deionized water (2 Vol % H_2O) with the concentrations of dopant 0.01 M of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

Photoconversion efficiency of TiO_2 NTs was measured by a standard three-electrode cell at room temperature under the illumination of 100 mW/cm^2 in a 1 M KOH solution. The photocurrent response measurement was tested without external applied potential to investigate the photoinduced charge separation efficiency

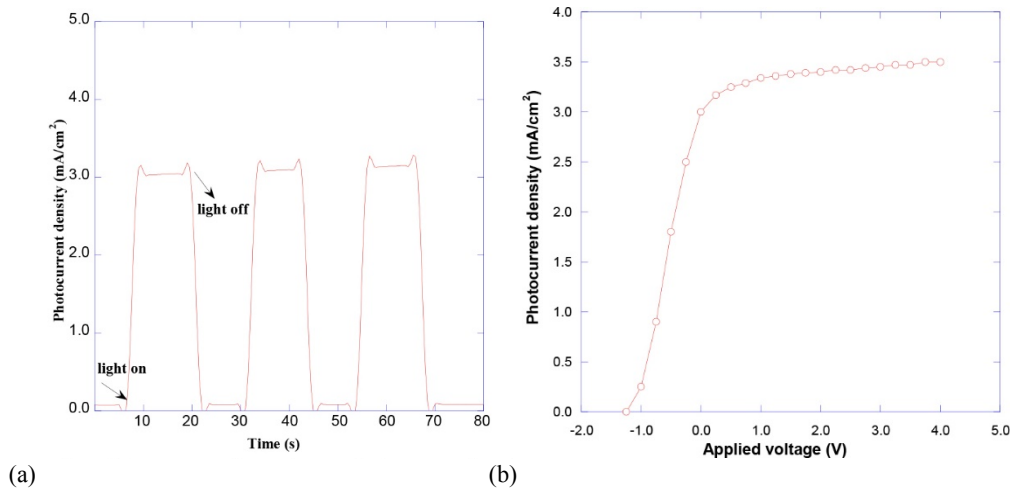


Figure 4. (a) Photocurrent densities as a function of time under interrupted illumination of light of 0.03M Fe-doped TiO₂ nanotube array working electrode
(b) The photocurrent density-voltage (J-V) characteristic of the best cell with 0.03M Fe-doped TiO₂ nanotube array working electrode

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_{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 TiO₂ was used as a working electrode. With out an external bias voltage, the photocurrent density after the switch was turned on was

about 3.0 mA/cm² corresponding with the photocoverage efficiency of 3.7 %.

This photoconversion efficiency (3.7%) of TiO₂ NTs photoanode is larger than that of nano-TiO₂ 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 TiO₂ NTs are larger than those of nano-TiO₂ films due to the agglomeration of the small spherical crystals of nano TiO₂ crystals by nature (Tipparach *et al.*, 2008).

The experiment showed that under the illumination of 75 mW/cm², PEC produced hydrogen by electrophotolysis at the rate of 0.74 ml/h cm² corresponding to experimental photoconversion efficiencies of 3.47 % as shown as follows:

$$\eta(\%) = \frac{237,000(\text{J/mol}) \times \left(\frac{0.74 \times 10^{-3} \text{ l/h}}{22.4 \text{ l/mol}} \right)}{(75 \times 10^{-3} \text{ W/cm}^2) \times (60 \text{ min/h}) \times (60 \text{ s/min})} \times 100 = 3.03\%$$

provided that hydrogen yields energy of 273000 J/mol (Liao *et al.*, 2012; Matsuoka *et al.*, 2007). The experimental efficiency

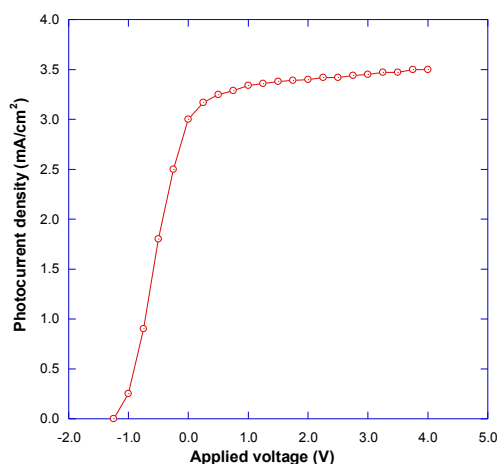


Figure 5. The photocurrent density-voltage (J-V) characteristic of the best cell with 0.03M Fe-doped TiO₂ nanotube array working electrode.

(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 TiO₂ NTs optical bandgap energy because nitrogen from NH₄F used for making the electrolyte may incorporate the structure of TiO₂ NTs. It is well known that Fe-doped TiO₂ lowers the bandgap energy of TiO₂ (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 TiO₂ NTs by X-ray photoelectron spectroscopy (XPS).

Conclusions

We have synthesized pure and Fe-doped TiO₂ 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 % NH₄F) and deionized water (2 Vol % H₂O) with the different concentrations of dopant, Fe(NO₃)₃·9H₂O. 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 TiO₂ NTs was used as a working electrode for PEC.

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