International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.5, No.4, pp 1641-1645, April-June 2013

Novel Anodizing Procedure To Grow TiO_2 Nanotubes Successfully Employed In Ethanol Photolysis

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Abstract: Qualitative determination of acetaldehyde produced by oxidation of ethanol in a photoelectrochemical cell is reported as an indicator of the effectiveness of a nanotubular titanium dioxide thin film for hydrogen production by photolysis in separate chambers. The titanium dioxide thin film was grown using a novel anodizing procedure on a 2cm2 titanium foil, varying the anodizing voltage between 80V and 20V during one and five minutes, respectively, for two hours in a 0.10%wt. NH_4F solution in ethylene glycol and using a 4cm2 titanium foil as cathode. The photoelectrochemical cell was formed by two borosilicate glass-chambers separated by a salt bridge of agar-agar and LiCl, UVA lamps, a Ti cathode and the anodized foil as anode, submerged in ethanol 93vol.% and connected by a copper wire in series with a voltmeter. For acetaldehyde determination, two qualitative methods were used: first, the reaction of the ethanol-water solution, after 4 hours of photolysis, with NaOH and heating; the second test was the reaction of a different solution with 2,4-dinitrodiphenyl hydrazine dissolved in methanol. Both assays were positive for aldehyde.

Keywords: Anodizing, Thin Film, Titanium Cathode, Titanium Dioxide, Photolysis, Hydrogen Production.

Introduction

Global warming, increasing energetic demand and sustainability of a healthy environment have lead to modern society to pursue alternatives to fossil fuels [1], one of the most promising energy sources is solar-produced hydrogen [2]. However, around 95% of hydrogen produced nowadays comes from non-renewable sources, and only 5% comes mainly from water electrolysis [3], even though hydrogen production from light and water has been studied since the 1970's from the pioneering work of Fujishima and Honda[4], who used a photoelectrochemical cell consisting of a titania photoanode, under UV light, and platinum as cathode.

Research on titania for hydrogen production by water photolysis is broad and several alternatives have been studied [3]. Among these alternatives, titania thin layers have been successfully used as photoanode in photoelectrochemical cells where electrodes are separated in two chambers, hydrons are exchanged through membranes and electrons through copper cables. Such set solves one of the main issues regarding to hydrogen production: the reverse reaction in the absence of light [5]. Preparation of the thin layer has been extensively studied using magnetron sputtering [12], chemical vapor deposition [13], electrophoric deposition [14], chemical bath deposition [15] and anodizing [16]. The simplest technique, which also have some of the best results [6], is anodizing, where a voltage is applied to a Ti anode against a metallic cathode in an electrolytic solution. Under appropriate conditions, anodizing results in highly ordered nanotubes, whose morphology and efficiency depend on voltage, temperature, time, material and

shape of cathode, and composition of the electrolytic solution [6], [16]-[20].

As an attempt to produce more effective titania thin layers, we explore a novel anodizing procedure based on Ji et al [7] and report its use in ethanol photolysis to confirm its photocatalytic activity aiming at its use in water photolysis. Assays are conducted using ethanol instead of water due to its sharper redox potential and the simpler detection of its oxidation products, which are produced in the photoanode chamber as hydrogen in the other, by qualitative chemical analysis techniques.

Photolysis Mechanism

Photocatalytic hydrogen production from any substance requires a semiconductor material which conductive band must be more negative than its reduction potential and have a valence band greater than its oxidation potential [3], i. e., band gap of the semiconductor should be greater than the redox potential of the substance, so electrons from valence band migrate to conductive band when they are excited by light, leaving holes that will be filled with electrons produced by oxidation, then, electrons reaching the conductive band are used in reduction reactions to produce hydrogen. Summarily, light provides energy to take electrons from the oxidized specie to the reduced one, and, thus, the necessary redox potential. Mechanism is shown for ethanol in Fig.1.

A comprehensive review of this topic is reported by Ji et al (2007) [3]; the fast electron/hole recombination and occurrence of backward reaction in the dark as two of the major drawbacks of water photolysis. Electron donors, such as ethanol are added to the solution during photolysis to hinder electron/hole recombination [3]. In order to avoid reverse reaction, separate chambers are used so oxidation takes place in a different compartment than reduction, that way reaction products will not meet nor even in the dark [5]. In such scheme, performance is improved by applying voltage and chemical bias, i.e., a different pH for each chamber [11].

Main reaction in ethanol photolysis is its direct oxidation to acetaldehyde, as seen in eq. 1. Other reactions take place, for example ethanol reforming, free radicals formation, and acetaldehyde mineralization to acetic acid and methane.

$$CH_3CH_2OH \rightarrow CH_3CHO + 2H^+ + 2e^- \quad (1)$$

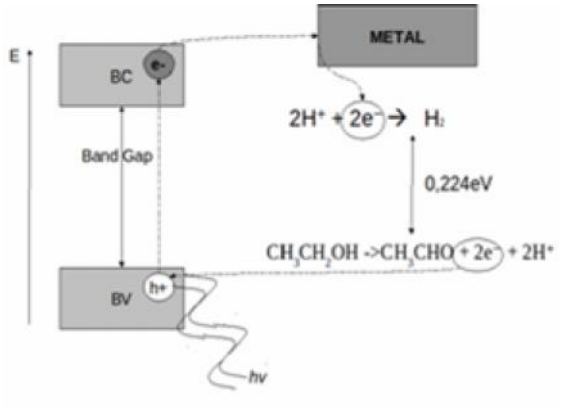

Figure 1. Schematic representation of ethanol photolysis mechanism.

The band gap of titanium dioxide varies usually between 3.0eV and 3.2eV depending on its crystalline phase, rutile or anatase [8], respectively. Such band gap is greater than redox potential for water, 1.2eV [9] and ethanol to acetaldehyde redox potential, making titania suitable to produce hydrogen from both of these substances by means of photolysis. However, because of its big band gap, electrons require great amounts of energy to go from valence band to conductive band, hence UV light is needed, which is inconvenient. To reduce TiO_2 band gap, several dopants have been tested, but Radecka et al, (2008) [10] found that photolysis was not necessarily improved when band gap was reduced.

The couple of electrons released fills the holes and then go to cathode to react with hydrogen ions producing molecular hydrogen, as seen in eq. 2.

$$2H^+ + 2e^- \rightarrow H_2 \quad (2)$$

At pH 7, the redox potential for the ethanol cell is -0,22V [9], so the reaction is not spontaneous and requires additional energy to proceed. As said above, UV radiation provides the energy necessary to complete the oxidation in the photoanode. From this reaction hydrogen is produced in the cathode chamber and acetaldehyde in the other, meaning that presence of acetaldehyde in the first chamber will prove hydrogen production in the other.

Thin Film Synthesis

Two Ti foils (99,6% purity, 0,05 mm width from Gallium Source) were cut, washed with methanol and air-dried. Geometric area of the anodized foil was 2 cm², a half of the geometric area of the cathode. Both foils were connected to DC power and submerged into a solution of NH_4F (Rhodaquímicos) 0,10 wt% in ethylene glycol (Limpic). Alternating

voltage was applied beginning with 20V for 5 min and followed by 80V for 1 min repeatedly for two hours. After anodizing, foils were washed with distillated water and dried in air stream. Then, anodized foil was annealed at 500°C with a heating rate of 2°C/min in air atmosphere using a tubular furnace (Lindberg/Blue M 1100 tube furnace Thermo Scientific).

This procedure is based on Ji et al, 2011 [7], whom obtained double walled, bamboo like anatase nanotubes. Originally they washed the foils in several steps prior to anodizing, used platinum gauze instead of titanium as cathode and oxygen atmosphere in the annealing. Material of the cathode is an important variable, and there are a few reports of materials different from platinum, but it has been found that using titanium as cathode can reduce costs producing highly ordered nanotubes [6], unlike Fe, Co or C cathodes [21].

Characterization

Thin films were morphologycally characterized by SEM using a NeoScope JCM-500.

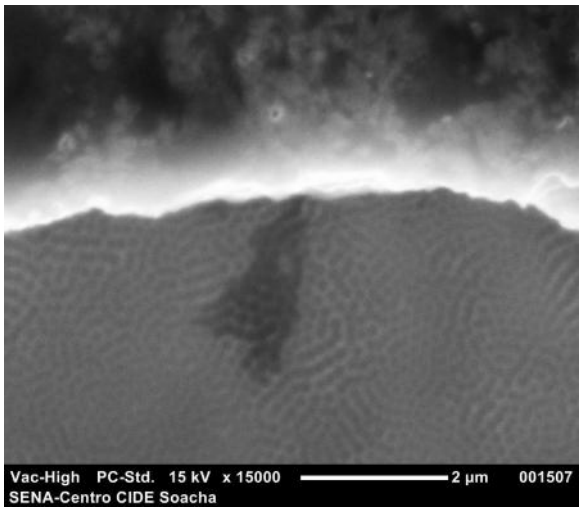

Figure 2. SEM top view of synthesized film.

Microscopy confirmed the growth of two layers, the upper one was almost completely removed during washing and drying after anodizing. Appearance of superficial layer was opaque while nether seems brighter. Fig 2 is a top view where both layers can be seen. Upper region of the image corresponds to the superficial layer which is clearly irregular in contrast to the lower part of the image where uniform, circular openings are evident. Diameter of the openings is 110nm approximately and 70nm thick walls separate neighbors. Fig. 3 shows cracks on the border of the nether layer created intentionally to get a lateral view of it and confirm the formation of highly ordered nanotubes which length is greater than 1µm.

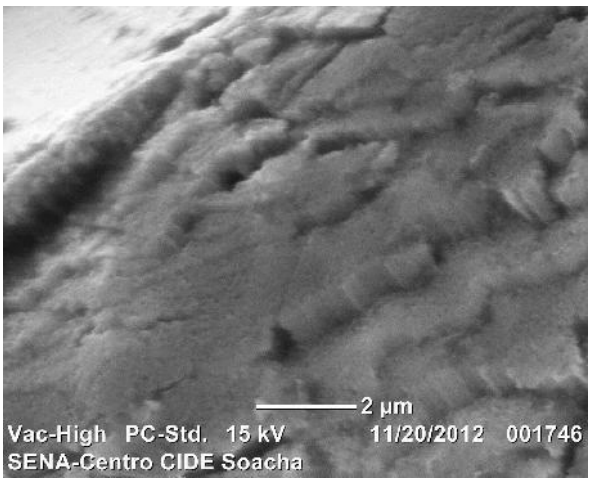

Figure 3. SEM side view of synthesized film.

Photolysis Experiments

A photoelectrochemical cell consisting of two separate chambers made of borosilicate glass was used for photolysis experiments. Instead of a nanofiltration membrane, a salt bridge with Agar-Agar and LiCl filled the 1 cm long, 3 cm wide glass bridge that connects the chambers as seen in Fig. 4. Each tubular chamber was 8 cm high, 3 cm wide. Both chambers were filled with 93Vol.% ethanol, electrodes were submerged in each camera and connected to a voltmeter and a UVA lamp was placed 4cm distant from the photoanode chamber. Photolysis assays were conducted for 4 hours under UVA radiation.

Since it is a first approach to establish whether or not the new material can be used in photolysis, it is convenient to evaluate its performance qualitatively. Techniques used were NaOH followed by heating, and 2,4-dinitrofenyl hydrazine reaction, because these methods can detect presence of aldehydes and ketones, such as acetaldehyde which, even being volatile, is easier to identify than hydrogen and prove its production as discussed above.

For the alkali test, 5ml from the final solution from the anodic chamber were added to a NaOH 30wt.% aqueous solution and then heated [22]. For the 2,4-dinitrofeyl hydrazine test, a solution was prepared according to [23] and a few drops of the photolysed solution were added and left to stand.

The two tests were applied to two different solutions from the anodic chamber after photolysis with the same photoanode. Results of both tests were positive for the two assays. In the case of the first determination technique, a yellow coloration and characteristic odor evolved from the solution tested, which is a positive result for aldehydes. For the second test, small crystals were found after settling. According to Fieser et al (1992) [24] the crystals are a hydazone formed in the reaction of acetaldehyde and the hidrazine.

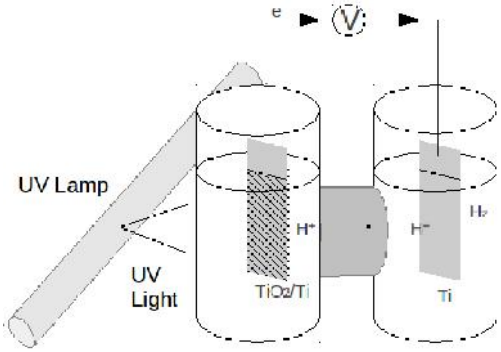

Figure 4. Experimental setup for the photolysis tests.

Conclusions

A novel procedure was used to grow highly ordered titania nanotubes by anodizing with alternating voltage in ethylene glycol with NH_4F 0,10wt.% and no addition of water. This is the first report, to the best of our knowledge, of the use of Ti as cathode for anodizing in organic medium under alternating voltage. Raw materials were commercial grade and yet the resulting material successfully oxidized ethanol into acetaldehyde, as determined qualitatively, by photolysis under UVA radiation in a separated chambers photoelectrochemical cell with a salt bridge consisting of agar-agar and LiCl.

Acknowledgments

We would like to thank to the Electrochemistry and Catalysis Laboratory of the Chemical Engineering Department at National University of Colombia, and to the Tecnoparque Nodo Cazucá of the SENA for their support in the characterization of the material. This project was also supported financially by Ujsek Quintero.

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