Fabrication Of TiO_2/Ti Nanotube Electrode By Anodizing Method And Its Application On Photoelectrocatalytic System

Muh. Nurdin, Maulidiyah

Abstract: Fabrication of TiO_2/Ti nano tube electrodes along with its characteristics and application on photoelectrocatalytic system has been conducted. The formation of TiO_2/Ti thin film on the surface of Ti metal was carried out through anodizing method. The results of data analysis on XRD spectroscopic indicated that the TiO_2 crystal formed is anatase crystal type. Degradation test of photoelectrocatalytic reactor to Acid Orange 7 dye showed a decrease of the organic dye concentration with the greatest degradation activity was generated by TiO_2/Ti electrode with 4 hours anodizing time compared with anodizing time of 1 hour, 2 hours, 8 hours, and 10 hours.

Keywords: Photocatalyst, photoelectrocatalytic, anodizing, nano tube, electrode, acid orange 7, Ti metal

1 INTRODUCTION

TEXTILE industry is one of industries producing non-biodegradable organic pollutants from the use of dye. Textile dyestuffs are generally made from azo compound and its derivatives which belongs to benzene chain and known difficult to be degraded and even if they can, it takes long period of time. The existence of azo compound in environment in long period of time is dangerous due to its nature which is carsinogenic and mutagenic. In addition, when the water body is polluted by azo compound, it will be difficult for sunlight to enter the body of water that it impedes the process of photosynthesis . As a result, oxygen level in the water body decreases. Photocatalytic process is one of technologies that plays an important role in degrading perfectly organic pollutants into carbon dioxide, one of them is in the water [1], [2] ,[3], [4]. However, for the purification of water or wastewater treatment, this technology still faces some challenges, among which is relatively low efficiency [1], [2], [3], [4], [5]. Therefore, several attempts have been made by researchers to improve the efficiency such as by combining the photocatalytic process with electrochemical process known as photoelectrocatalytic. Photoelectrocatalytic process is proven to be a very effective method to degrade organic pollutants in water [6], [7], [8], [9]. Oxidation efficiency can be improved by bias potential application to flow electrons through an external circuit, so that it prevents the recombination of electrons and positive holes. This is the principle of photoelectrocatalytic [10]. In order to use photoelectrocatalytic process for wastewater treatment, an easy and cheap method for preparation of TiO_2 film electrodes is needed that it's possible to be applied on a large scale.

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There are currently several methods of preparation of TiO_2 films, such as sol - gel, hydrothermal, solvothermal , chemical vapor deposition, electrodeposition, direct oxidation and others [11]. The most inexpensive and easy method is a direct oxidation method. Direct oxidation can be conducted by thermal and electrochemical oxidation (anodizing) [12]. The fabrication of TiO_2/Ti nano tube with electrochemically direct oxidation method (anodizing) was first reported by Gong, et al, 2001[13]. Further study then focused on the extent and quality of the nano tube morphology [14] , length and pore size of nano tube [15], and the thickness of nano tubes wall [16]. Anodizing method was conducted by using platinum cathode (Pt) known as highest quality type of cathode used in the electrochemical process. However, to be applied on a large scale to degrade organic pollutants, the use of Pt cathode is relatively less profitable due to its high price. Therefore, this research was conducted by replacing the Pt cathode with copper cathode (Cu) which has a more favorable economic value yet having similar quality with the Pt cathode that making it possible to be applied on a large scale. Based on the elaboration above, there has not been any report on the use of Cu as an alternative replacing Pt cathode in anodizing methods on fabrication of TiO_2 nano tube by anodizing method. Therefore, it is necessary to fabricate TiO_2/Ti nano tube electrode with anodizing method by using Cu cathode as well as degradation test toward textile dyes.

2 EXPERIMENTAL

2.1 Chemicals and Materials

The materials used in this study were Titanium plate with the level of purity is 99 % and 1 mm thickness, woven wire platinum (Pt), plate Copper (Cu), Nitric Acid (pa), Acid Fluoride (pa) , Ammonium Fluoride (pa), Sodium Nitrate, Glycerol (pa), Aqueous distillate, and Acid Orange 7 (AO7) textile dye.

2.2 Preparation of TiO_2/Ti Electrode

TiO_2/Ti electrode preparation was conducted by cutting the titanium plate with level of purity 99 % and 1 mm thickness with size of 4 cm x 2 cm then it was sanded by using fine sand paper to the size of the 1200 until the surface was clean and shiny. It was then washed with solution of detergent, water, and aqueous distillate to make sure that the Ti plate is clean of impurities. After dried in the air, the Ti plate (etching) was then immersed by using a mixed solution of HF, HNO_3, and

Aqueous distillate in ratio 1:3: 6 for 2 minutes. This treatment was aimed to remove grease and the remaining oxide layer on the surface of the Ti metal because metal is easy to react with oxides. The final stage of the preparation was rinsing the Ti plate with aqueous distillate to remove the etching residual solvent on the surface, and then it was dried in air.

2.3 Formation of TiO_2 layer with Anodizing Method

The prepared titanium plate was put in a probe filled with an electrolyte solution of NH_4F 0, 27M and 4 % aqueous distillate glycerol (pa) 99.5 %. Anodizing process was carried out by placing the Ti plate as anode and Cu plate as the cathode by giving potential bias of 25 V. The anodizing process was carried out by using time variation of 1 hour, 2 hours, 4hours, 8 hours, and 10 hours. The final stage was furnishing Ti plate for 3 hours at a temperature of 500^{o}C to evaporate the residual electrolyte solution found on the surface of the Ti plate as well as to obtain anatase TiO_2 crystals which photodegradation activity is better than other types of crystals.

2.4 Characterization of Catalyst

a. Cyclic voltammetry

Characterization of catalysts by cyclic voltammetry method was conducted to test the activity photoelectrocatalytic of TiO_2 by placing the TiO_2 plate as anode and wire Pt as cathode in a probe filled with an electrolyte solution of $NaNO_3$ 0,1 M. Response was obtained by using potential of -100 mV to 1000 mV and a scan rate of 100 mV/s with and without UV light irradiation. Measurement was made on all plates with anodizing time variations.

b. Difuse Reflectance UV-Visible

Measurements with *Difuse Reflectance* UV-*Visible was conducted* to determine the wavelength of absorption of the catalyst in the wavelength range from 200 nm to 900 nm. Based on the obtained spectrum, band gap representing semiconductor identity of TiO_2 obtained can be determined.

c. X-Ray Diffraction (XRD)

Measurement by XRD was conducted to see the characteristics of anatase TiO_2 crystals formed. XRD characterization results in the form of X-ray diffraction pattern will show a specific peak in the spectrum result of the XRD characterization which is the identity of anatase TiO_2 crystals obtained.

d. Scanning Electrone Microscope (SEM)

Measurement with *Scanning Electrone Microscope* (SEM) was conducted to determine the condition of TiO_2 thin film formed. The formation of nano tube on the surface of TiO_2 thin film with a certain size can be obtained from the result of SEM image.

2.5 The Fabrication of Photoelectrocatalytic

TiO_2/Ti electrode obtained through subsequences of anodizing process was then used in the fabrication of photoelectrocatalytic reactor. Schema and drawing of TiO_2/Ti photoelectrocatalytic reactor is shown in Fig. 1.

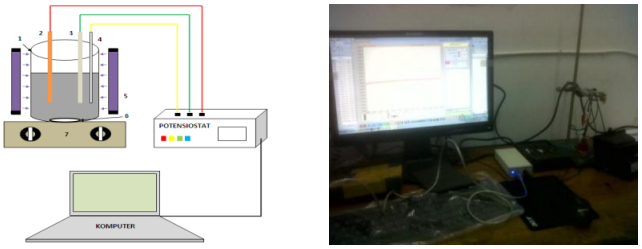


Fig. 1. Schema and picture of TiO_2/Ti photoelectrocatalytic reactor. (1) A tubular probe , (2) Pt counter electrode, (3) working electrode TiO_2/Ti, (4) a Ag/AgCl reference electrode, (5) UV light, (6) magnetic bar, (7) magnetic stirrer.

a. Dye degradation test

Degradation test of Acid Orange 7 (AO7) 10 ppm (+ 0.1 M $NaNO_3$)dye was conducted by using the Multi Pulse Amperometry in the duration of 10 minutes and the potential bias of 500 mV in UV irradiation. In each 10 minutes within 1 hour absorbance measurement by using UV-Vis Spectrometer was measured to determine the decrease of dye concentration. Measurement was made on all plates with anodizing time variations.

b. The comparison of electrocatalytic, photocatalytic, and photoelectrocatalytic in degrading dyes

The comparison of electrolytic, photocatalytic, and photoelectrocatalytic in degrading dye was conducted to determine the difference of degradation level produced by the process of electrocatalytic, photocatalytic, and photoelectrocatalytic. Theoretically, the process of electrocatalytic will show the lowest degradation activity in which the decrease of the concentration occurs not due to the presence of the degradation process , yet by the process of absorption by the catalyst surface toward the molecules of the Acid Orange 7 (AO7) dye. While photoelectrocatalytic process is essentially not too different from the photocatalytic process, there is the addition of electrons (electric current) that would prevent the electron - hole recombination when light illumination is conducted. This will lead to the formation of higher active species in the catalyst and theoretically the degradation process and the molecules of the Acid Orange 7 (AO7) dye will be much more efficient than electrocatalysis and photocatalysis.

3 RESULTS AND DISCUSSION

3.1. Preparation of Electrode TiO_2/Ti

Preparation of TiO_2 thin film on the surface of the Ti plate with anodizing method used time variation of 1 hour, 2 hours , 4 hours, 8 hours, and 10 hours (Fig.2) . The time variation was aimed to vary the thickness of TiO_2 thin film formed on the surface of the Ti plate. The longer the time of anodizing, the thicker the TiO_2 thin layer formed. Plate which had been anodized then calcinated with furnace at 500^{o}C temperature for 3 hours. Calcination was aimed to evaporate the organic solvents trapped in the titanium plate. Calcination is also required to oxidize the chelate ligands bound to the titanium plate so that the result of the calcination is only the metal oxide as expected. In addition, the calcination process was carried out to obtain anatase TiO_2 crystalline whose photocatalytic activity is better than the other types of crystals with the temperature range between 120^{o}C to 500^{o}C . There are two

common crystal structures used in the photocatalytic reaction, they are rutile and anatase. However, anatase crystals has better activity than rutile crystal types. This is because crystal of anatase has a greater surface area and greater active side to absorb light better than any type of rutile crystals. When viewed from the energy of band gap, the structure of anatase is more photoactive than the rutile structure. The band gap energy states how much energy is required for the transition of electrons from the valence band to the conduction band.

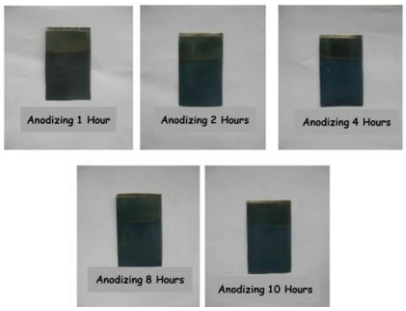


Fig. 2. Photo of TiO_2 thin film prepared by anodizing method at time variation

3.2 Characterization of Catalysts

a. Cyclic Voltametry

Measurement of cyclic voltammetry used the same principle with the potentiometric method that emphasizes the relationship between the current generated with the relative electrode potential. This measurement was aimed to find out the TiO_2/Ti plate anodizing that has the highest activity. Measurements were made by placing the TiO_2/Ti plate as the working electrode, woven wire Pt as the counter electrode, and Ag / AgCl as reference electrode. $NaNO_3$ 0,1 M was used as electrolyte solution. The combination of cyclic voltammetry TiO_2/Ti electrode measurement results with different time variations can be seen in Fig. 3. The results of the measurements shows that the TiO_2/Ti electrode made by anodizing method for 4 hours had greater photocatalytic activity than the electrode with anodizing time of 1, 2, 8, and 10 hours observed from the high currents generated when UV light irradiation is given as the source of photons . Therefore, it can be concluded that 4 hours anodizing time is the optimum time to produce TiO_2 with the highest activity.

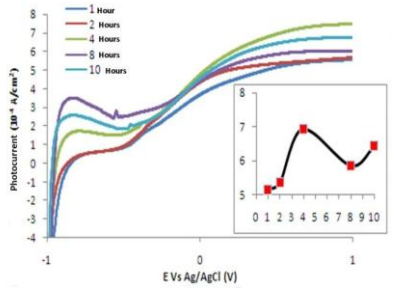


Fig. 3. The combination of cyclic voltammetry TiO_2/Ti electrode measurement result with anodizing method

b. Spektrofotometer Difuse Reflectance UV-Visible

The measurement of the absorption TiO_2/Ti layer that had been made with Spectrometer of *Difuse Reflectance* UV-*Visible* in the wavelength range from 200 nm to 900 nm and produces a spectrum pattern is shown in Fig. 4. It can be seen that the coating gives absorption at λ around 350-400 nm. The absorption character represents the identity of TiO_2 semiconductor with anatase structure that has band gap energy of 3.2 eV which is equivalent to wavelength of 388 nm. The absorption of UV light will cause some pair of e^- and h^+ will recombine, while others will maintain the situation until it reaches the surface of the particles.

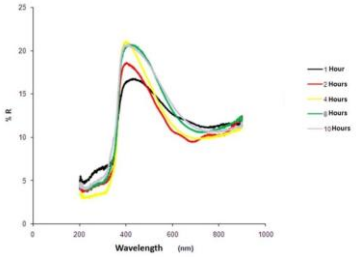


Fig. 4. UV-Vis spectra of TiO_2/Ti thin layers.

Based on the obtained spectrum, the energy gap can be determined by using the following two Kubelka - Munk equations

$$F(R) = \frac{K}{S} = \frac{(1-R)^2}{2R} \qquad (1)$$

where : F(R) = Kubelka-Munk factor
K = Absorption Coefficient
S = Scattering Coefficient
R = reflectance value measured

$$F(R) = A(h\upsilon - Eg)^{m/2} \qquad (2)$$

where : A = Proportionality Constant
Eg = Energi Gap
m = 1 for a direct transition allowed

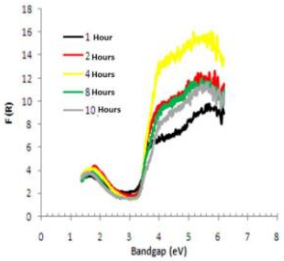


Fig. 5. The combination of band gap curve of TiO_2 plate anodizing according to Kubelka - Munk equation

Fig. 5 shows the band gap curve of the TiO_2 plate from anodizing time variation according to the Kubelka – Munk equation. By plotting the value of F(R) toward hu and extrapolating the linear region, the hu value in F(R) = 0 can be determined, which is nothing but the value of the TiO_2 plate bandgap. Bandgap values obtained from the value plot of F(R) toward hu and the extrapolating of the linear region on the Kubelka–Munk curve is presented in Table 1

TABLE 1.
BANDGAP VALUES FOR ANODIZING TIME VARIATION

Anodizing time (hour)	*Bandgap*(eV)
1	3,17
2	3,28
4	3,18
8	3,21
10	3,17

c. X-Ray Diffraction (XRD)

The result of XRD characterization in the form of X-ray diffraction pattern in Fig. 5 shows no crystalline other than anatase crystal of TiO_2 on the surface of Ti plate made by anodizing method with time variation. This was shown by the formation of specific peaks on the spectrum of XRD characterization results. Diffraction pattern indicates the presence of five peaks which are the spectrum generated by the anatase TiO_2 crystalline. The five peaks are each presented in the fields 101, 112, 200, 105, and 211.

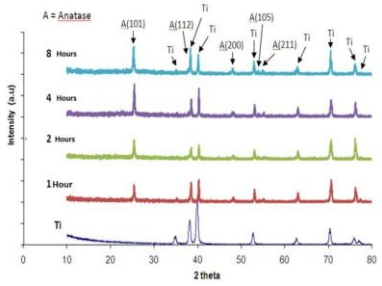
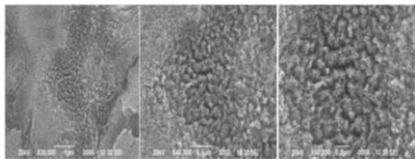


Fig. 6. The anodizing XRD diffraction pattern of TiO_2 thin film

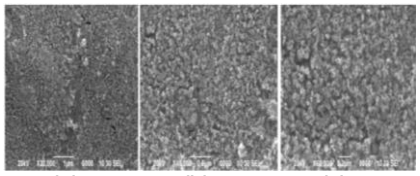
d. Scanning Electron Microscope (SEM)

The result characterization with SEM for anodizing plate with the time variation of 1 hour, 2 hours, 4 hours, and 8 hours can be seen in Fig. 7 to Fig. 10. The result of SEM image on the surface of film layer, the formation of nano tube with an inside diameter is approximately 10-60 nm.



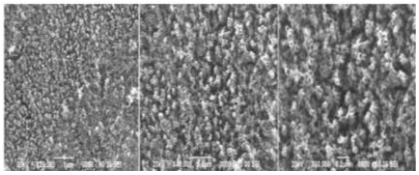
(a) (b) (c)

Fig. 7. The result of SEM characterization of TiO_2 thin film *anodizing* of 1 hour at a magnification of (a) 20 thousand times , (b) 40 thousand times , and (c) 60 thousand times



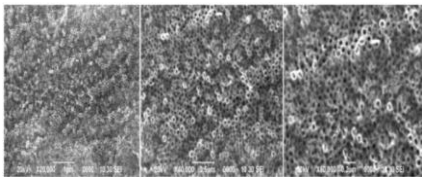
(a) (b) (c)

Fig. 8. The result of SEM characterization of TiO_2 thin film *anodizing* of 2 hours at a magnification of (a) 20 thousand times , (b) 40 thousand times , and (c) 60 thousand times



(a) (b) (c)

Fig. 9. The result of SEM characterization of TiO_2 thin film *anodizing* of 4 hours at a magnification of (a) 20 thousand times , (b) 40 thousand times , and (c) 60 thousand times



(a) (b) (c)

Fig. 10 . The result of SEM characterization of TiO_2 thin film *anodizing* of 8 hours at a magnification of (a) 20 thousand times , (b) 40 thousand times , and (c) 60 thousand times.

a. The degradation of the Acid Orange 7 (AO7) dye

The degradation of the acid orange 7 dye which was conducted by using 10 ppm (+ 0,1 M $NaNO_3$), with a given potential bias of 0.5 V. Degradation results are presented in Fig. 11, which shows that the TiO_2 plate with anodizing time of 4 hours has the highest activity in degrading dye of AO7 as well as shown in the measurement of cyclic voltammetry.

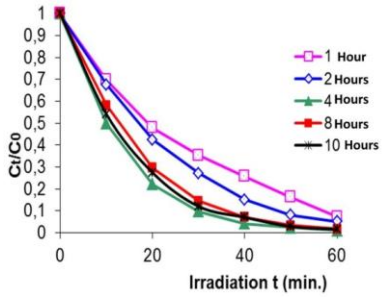


Fig. 11. Photoelectrocatalytic degradation of *Acid orange* 7 dye with different anodizing time, plot C_t/C_0vs. irradiation time

c. The comparison of electrocatalytic, photocatalytic, and photoelectrocatalytic in degrading dyes

Fig. 12 shows the high degradation activity of photoelectrocatalytic process (with UV irradiation and the potential bias of 0.5 V) toward AO7 dye compared with the electrocatalytic process (with a potential bias of 0.5 V without irradiation of UV) and photocatalytic processes (with UV irradiation without the potential bias). The experiment was conducted by using TiO_2 plate with anodizing time of 4 hours which has the highest activity in degrading organic dye.

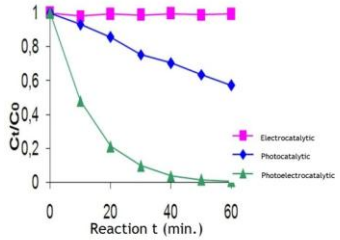


Fig. 12. The comparison of the degradation test results on electrocatalytic, photocatalytic , and photoelectrocatalytic on Acid Orange 7 dye, plot C_t/C_0 *vs*. reaction time.

Based on Fig. 12, it is clearly visible the difference of degradation level produced by the process of electrocatalytic, photocatalytic, and photoelectrocatalytic. The process of electrocatalytic showed the lowest degradation activity in which the concentration decrease occurs not due to the presence of the degradation process, but due to the process of absorption by the catalyst surface to the molecules of the Acid Orange 7 (AO7) dye. The process of photocatalytic has shown better degradation activity although not as good as photoelectrocatalytic process. This is because the process is sometimes encountered resistance due to electron-hole recombination so that the active species will decrease which is affect to the low activity of degradation. Photoelectrocatalytic process which basically is not too different from the photocatalytic process has the addition of electrons (electriccurrent) that would prevent the electron-hole recombination when light illumination was conducted. This led to the formation of the higher active species in the catalyst and theoretically the degradation process and the molecules of the Acid Orange 7 (AO7) dye will be much more efficient than the method of electrocatalytic and photocatalytic.

4 CONCLUSIONS

TiO_2 films prepared by anodizing method produces the optimum time with the highest degradation efficiency level of organic dye when it is at 4 hours anodizing time compared with other time variation such as 1 hour, 2 hours, 8 hours, and 10 hours. The result of XRD Spectroscopic characterization showed that the TiO_2 crystalline solids formed on the top surface of the Ti plate is a type of crystalline anatase characterized by the diffraction pattern showed peak ofanataseTiO_2 crystals in fields 101,112 , 200 , 105 , and 211

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REFERENCES

[1]. Linsebigler, A. L., Guangquan, L., Yates, J.T., "Photocatalysis on TiO_2 surface: principles, mechanism and selected results", *Chem. Rev*, 95, 735-758. 1995

[2]. Hoffman, M.R., Martin, S.T., Choi, W., Bahnemann, D.W.," Environmental Application of Semiconductor Photocatalysis" *Chem. Rev*., 95, 69-96. 1995

[3]. Hallmann, M.M.,"Photodegradation of water pollutants", CRC Press, Florida. 1996

[4]. Serpone, N., Pelizzetti, E., Hidaka, H.,"Photocatalytic purification and treatment of water and air", Edited by D.F. Ollis and H. Al-Ekabi, Elsevier Sci. Pubs, Amsterdam. 1993

[5]. Galves, J.B.,"Solar detoxification", UNESCO WSP Program. 1999

[6]. Kim, D.H., Anderson, M.A.,"Photoelectrocatalytic degradation of formic acid using a porous TiO_2 thin-film electrode". *Environ. Sci. Technol.*, 28, 479–483. 1994

[7]. Li, X.Z., Liu, H.L., Yue, P.T., Sun, Y.P.,"Photoelectrocatalytic oxidation of rose bengal in aqueous solution using a Ti/TiO_2 mesh electrode". *Environ. Sci. Technol.*, 34, 4401–4406. 2000

[8]. Li, X.Z., Liu, H.S.," Development of an $E\text{-}H_2O_2/TiO_2$ photoelectrocatalytic oxidation system for water and wastewater treatment". *Environ. Sci. Technol.* 39, 4614–4620. 2005

[9]. Quan, X., Yang, S., Ruan, X., Zhao, H.,"Preparation of titania nanotubes and their environmental applicationsas electrode", *Environ. Sci. Technol,* 39, 3770-3775. 2005

[10]. Xu, Y., He, Y., Cao, X., Zhong, D., Jia, J.,"TiO_2/ Ti rotating disk photoelectrocatalytic (PEC) reactor: a combination of highly effective thin-film PEC and convensional PEC processes on a single electrode", *Environ. Sci. Techno.l*, *42* (7*)*, 2612–2617. 2008

[11]. Chen, X., Mao, S.,"Titanium Dioxide Nanomaterial: Synthesis, Properties, Modification and Aplication", *Chem Rev*, 107, 2891-2959. 2007

[12]. Nurdin, M., Wibowo, W., Supriyono, Febrian, M.B., Surahman, H., Krisnandi, Y.K., dan Gunlazuardi, J.," Pengembangan metode baru penentuan *Chemical Oxygen Demand* (COD) berbasis sel fotoelektrokimia: Karakterisasi elektroda kerja lapis tipis TiO_2/ITO", *Makara, Sains*, 3 (1), 1-8. 2009

[13]. Gong, D., Grimes, C.A., Varghese, O.K., Hu, W., Singh, R.S., Chen, Z., Dickey, E.C., , "Titanium oxide nanotube arrays prepared by anodic oxidation", *J. Mater Res*, 16:3331–3334. 2001

[14]. Mor, G.K., Varghese, O.K., Paulose, M., Mukherjee, N., Grimes, C.A.,"Fabrication of tapered, conical-shaped titania nanotubes", *J. Mater Res*, 18:2588–2593. 2003

[15]. Cai, Q., Paulose, M., Varghese, O.K., Grimes, C.A.,"The effect of electrolyte composition on the fabrication of self-organized titanium oxide nanotube arrays by anodic oxidation", *J. Mater Res*, 20:230–236. 2005

[16]. Mor, G.K., Shankar, K., Paulose, M., Varghese, O.K., Grimes, C.A."Enhanced photocleavage of water using titania nanotube arrays", *Nano Lett*, 5:191–195. 2005