Synthesis of TiO$_2$ Nanotubes Electrode for Photo Electrochemical cells Application

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Abstract. In this research propose a synthesis and study characteristics of electrode for photoelectrochemical cells using TiO$_2$ nanotubes electrode. The fabrication of electrode for photoelectrochemical cells using TiO$_2$ nanotubes which made from anodization process at size area 2x2 cm$^2$ and counter electrode used platinum pastes coated on fluoride-doped tin oxide (FTO) glass at size area 2x2 cm$^2$. The solar simulation was used as the light source for the photoelectrochemical cells at 100mW/cm$^2$. The morphological properties of TiO$_2$ electrode was confirmed by X-ray diffraction (XRD) and scanning electron microscope (SEM). We measure the sheet resistance, open circuit voltage and short circuit current for analyse the photoconversion efficiency. The photoconversion efficiency was 5.78%, open circuit voltage was 0.72V and short circuit current was 2.87mA.

1. Introduction
The Photo Electrochemical Cell (PEC) is the part of thin film solar cell technology that can convert the solar energy to electricity energy. Electricity energy is the importance energy to develop the technology. The solar cell is an interested application due to it has enormous advantage such as clean energy during electricity generation with solar cell panels there are no harmful greenhouse gas, neutral energy it is thus free and abundant, the solar cell panels are silent, no motion part, easy to install on roof or on ground and generate directly electricity energy. The PEC has attracted much attention in the academic and commercial due to a trend that is produced in commercially available, the price is lower than the P-N junction type of silicon semiconductor solar cell (at currently manufactured), and can be produced in large quantities [1-6]. In present, the mostly material that used for made the solar cells device were silicon which used in electronic device. In addition, the materials used for made solar cells device were gallium arsenide and cadmium telluride which those materials have high price. The PEC is mainly composed of working electrode, electrolyte and counter electrode. The working electrode consists of n-type semiconductor metal oxide films such as titanium dioxide (TiO$_2$), zinc oxide (ZnO), and tin oxide (SnO). In the counter electrode material is used platinum (Pt), graphene and carbon (C) electrode, can show previous a reported [7-10]

TiO$_2$ is the interested material science and most studied. It is used for dye-sensitized solar cells and biomedical device. In the recent research was used titanium powder or TiO$_2$ for dye-sensitized solar cell
device [11]. But in this research used TiO_2 nanotubes by anodization process due to the nanoparticle has affect to efficiency of photocatalyst process.

In this work, we focused to study the characteristic of Photo Electrochemical Cell with TiO_2 nanotubes and TiO_2 electrode. The TiO_2 nanotubes was confirmed the morphological by X-ray diffraction (XRD) and scanning electron microscope (SEM). The working electrode of Photo Electrochemical Cell used TiO_2 nanotubes which made from titanium foil under size 2x2 cm^2 by anodization process. The counter electrode of Photo Electrochemical Cell used FTO glass size 2x2 cm^2 coated with platinum pastes. Working electrode and counter electrode were sealed with sealing material then injected the electrolyte. The Photo Electrochemical cell with TiO_2 nanotubes and platinum electrode was tasted by applied the light source which used solar simulator 100mW/cm^2.

2. Experimental setup

2.1. Synthesis TiO_2 nanotubes

The synthesis of the titanium nanotubes was prepared by anodization process. The titanium foil (thickness 0.25 mm, 99.7% trace metals basis, Sigma-Aldrich) at 2x2 cm^2 area size was used as the substrate. The substrate was degreased by acetone and ethanol in ultrasonic cleaner (JAC4020, Ultrasonic) for 30 min then dried. The electrolyte for anodization process was prepared by ethylene glycol contained 0.3wt% ammonium fluoride (NH_4F) and deionized water. The titanium foil was connected to the positive of power supply and the Pt plate (gauze, 100 mesh, 99.9% trace metals basis, Sigma-Aldrich) was connected to negative. The voltage of power supply for anodization process was constant at 30 V for 240 min then annealed at 450°C for 180min. The TiO_2 nanotubes electrode was investigated by X-ray diffraction (XRD; Rigaku D/max 2100H), the morphological property was measured by field emission scanning electron microscope (FE-SEM; Hitachi S-3000H)[12].

![Figure 1](image_url)

**Figure 1.** The structure of Photo Electrochemical Cell with TiO_2 nanotubes electrode

2.2. Preparation of platinum electrode

FTO glass (resistance sheet: ~7 Ω/sq, Pilkington) at size area 2x2 cm^2 was degreased by acetone and ethanol in ultrasonic cleaner for 30 min then dried. After the FTP glass dried, the platinum pastes (Platisol T/SP, Sloaronix) was coated on FTO glass by doctor-blade technique then annealed at 450°C for 30min.

2.3. Fabrication of Photo Electrochemical Cell with TiO_2 nanotubes electrode and Platinum electrode

The TiO_2 nanotubes was set as the photoanode of the Photo Electrochemical Cell and the platinum electrode was set as the cathode. The two electrodes were overlap and sealed with sealing film thickness 60 µm (Meltonix 1170-60, Solaronix) the structure of photo electrochemical cell is show in figure1. Then annealed at 125°C for 15min. After annealed, The Photo Electrochemical Cell was injected the electrolyte into the gap between electrodes. The Photo Electrochemical Cell was applied
the light source by solar simulator at 100mW/cm$^2$ then measure the voltage and current for analyze. The process of fabrication of photo electrochemical cell is show in figure 2.

**Figure 2.** The block diagram for fabrication of Photo Electrochemical Cell and experimental

3. Results and Discussion

Figure 3(a) shows the XRD pattern of TiO$_2$ and TiO$_2$ nanotubes. The strong peaks of TiO$_2$ nanotubes shown at (100), (002), (101), (102), (110), (103), (112) and anatase peaks shown at (101) and (200). The strong peaks of TiO$_2$ shown at (100), (002), (101), (102), (110), (103), (112). We found that the strong peaks of TiO$_2$ didn’t shown the anatase peaks different from the TiO2 nanotubes. Figure 3(b) shows the SEM image of TiO$_2$ nanotubes.
Figure 3. (a). The XRD pattern of TiO$_2$ and TiO$_2$ nanotubes and (b) SEM image of TiO$_2$ nanotubes

Figure 4 shows the I-V curve of Photo Electrochemical Cell which tasted under the light source by solar simulator at 100mW/cm$^2$. The parameters which measure in this experimental was open circuit voltage ($V_{oc}$), short circuit current ($I_{sc}$) and fill factor (FF) was obtained from I-V curve. The parameters of Photo Electrochemical Cell with TiO$_2$ nanotubes electrode was $V_{oc} = 0.72$V, $I_{sc} = 2.87$mA, FF = 1.13 and conversion efficiency was 5.78% which higher than the conversion efficiency of TiO$_2$ electrode. The parameters of Photo Electrochemical Cell with TiO$_2$ electrode was $V_{oc} = 0.715$V, $I_{sc} = 2.4$mA, FF = 1.05 and conversion efficiency was 4.53%. The both counter electrodes show that the $I_{sc}$ increased significant with change a counter electrode. However, the conversion efficiency of TiO$_2$ nanotubes was more than that the TiO$_2$ due to the charge transfer resistance of TiO$_2$ nanotubes was higher than that the TiO$_2$.

Figure 4. I-V curve of Photo Electrochemical Cell with TiO$_2$ and TiO$_2$ nanotubes electrode under testing by solar simulator at 100mW/cm$^2$
Figure 5 shows electrochemical impedance spectroscopy of TiO$_2$ nanotubes and TiO$_2$. The two semicircles can be observed from Nyquist plots. The high frequency semicircle shows a charge transfer resistance ($R_{CT}$) at counter electrode (CE)/electrolyte interface, and the higher frequency represents the series resistance ($R_S$)[14].

![Electrochemical impedance spectroscopy Nyquist plots of Photo Electrochemical Cell with TiO$_2$ nanotubes and TiO$_2$ electrode](image)

**Figure 5.** Electrochemical impedance spectroscopy (EIS) Nyquist plots of Photo Electrochemical Cell with TiO$_2$ nanotubes and TiO$_2$ electrode

### 4. Conclusions
The Photo Electrochemical cell with TiO$_2$ nanotubes electrode from anodization process which was compared with TiO$_2$ electrode. The energy conversion efficiency of PEC with both electrode samples was investigated with under the solar simulation at AM 1.5 (100 mW/cm$^2$). The PEC using TiO$_2$ nanotubes showed a conversion efficiency of 5.78% which better than the TiO$_2$ electrode that the conversion efficiency was 4.53% due to the effective electron transfer on the large surface of TiO$_2$ nanotubes electrode. The TiO$_2$ nanotubes electrode can be replaced another electrode, and it also can increase efficiency.

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### Reference
[1] B. O'Regen and M. Grätzel 1991 A low-cost, high-efficiency solar cell on dye-sensitized colloidal TiO$_2$ films Nature, 353 (1991) 737-740
[2] G. Smestad, C. Bignozzi and R. Argazzi 1994 Testing of dye sensitized TiO$_2$ solar cells I: Experimental photocurrent output and conversion efficiencies Sol. Energy. Mater. Sol. Cell. 32(3) (1994) 259-272.
[3] N. Papageorgiou, W.F. Maier and M. Grätzel 1997, J. Electrochem. Soc., 144 (1997), pp. 876–884
[4] K. Tennakonea, P.K.M. Bandaranayakea, P.V.V. Jayaweerab, A. Konnob, G.R.R.A. Kumarab 2002 Dye-sensitized composite semiconductor nanostructures Physica E: Low-dimensional Systems and Nanostructures. 63 (2002) 1-7.

[5] N. Meng, K.H.L. Michael, Y.C.L. Dennis and K. Sumathy 2006 An analytical study of the porosity effect on dye-sensitized solar cell performance Sol. Energy. Mater. Sol. Cell. 90 (9) (2006) 1331-1344.

[6] Y. Chiba, A. Islam, R. Komiya, N. Koide and L. Han 2006 Conversion efficiency of 10.8% by a dye-sensitized solar cell using a TiO2 electrode with high haze Appl. Phys. Lett. 88 (2006) 223505.

[7] S.H. Kim and C.W. Park 2013 Novel application of platinum ink for counter electrode preparation in dye sensitized solar cells Bull. Korean Chem. Soc. 34(3) (2013) 831-836.

[8] C.P. Lee, C.A. Lin, T.C. Wei, M.L. Tsai, Y. Meng, C.T. Li, K.C. Ho, C.I. Wu, S.P. Lau and J.H. He 2015 Economical low-light photovoltaics by using the Pt-free dye-sensitized solar cell with graphene dot/PEDOT:PSS counter electrodes nano energy. 18 (2015) 109-117.

[9] Y.Y. Li, C.T. Li, M.H. Yeh, K.C. Huang, P.W. Chen and R. Vittal, K.C. Ho 2015 Ordered mesoporous carbon/graphene nano-sheets composites as counter electrodes in dye-sensitized solar cells Electrochimica Acta. 179 (2015) 211-219.

[10] S. Lowpa, S. Pimanpang, W. Maiaugree, S. Saekow, P. Uppachai, S. Mitravong and V. Amornkitbamrung 2015 Nanoporous carbon microspheres from carrot juice used as a counter electrode for a dye-sensitized solar cell Mater. Lett. 158 (2015) 115–118.

[11] D.J. Kwak, B.H. Moon, D.K. Lee, C.S. Park and Y.M. Sung 2011 Comparison of transparent conductive indium tin oxide, titanium-doped indium oxide, and fluorine-doped tin oxide films for dye-sensitized solar cell application J. Elec. Eng. Technol. 6(5) (2011) 684-687.

[12] L. Wei, Y. Yang, R. Fan, Y. Na, P. Wang and Y Dong 2015 Effects of rubrene co-sensitized TiO2 photoanode on the performance of ruthenium dye N719 sensitized solar cells Thin Solid Films 592 (2015) 14–23.

[13] J.H. Yang, C.W. Bark, K.H. Kim and H.W. Choi 2014 Characteristics of the Dye-Sensitized Solar Cells Using TiO2 Nanotubes Treated with TiCl4 Materials 2014 7 3522-3532.

[14] Y.M. Sung, H.J. Kim 2007 Sputter deposition and surface treatment of TiO2 films for dye-sensitized solar cells using reactive RF plasma Thin Solid Films. 515 (2007) 4996-4999.