Synthesis and application of TiO$_2$ nanorods as photo-anode in dye-sensitized solar cells

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Abstract. Titanium dioxide or TiO$_2$ with nanorods structure as photo-anode component in dye sensitized solar cell (DSSC) has attracted attention in many research because this morphology has the ability to transfer electron fastly, thereby reducing the risks of electron recombination. In this research, TiO$_2$ nanorods were synthesized using various ratios of titanium isopropoxide (TTIP) i.e. 1, 2, and 4, and mixed with hydrochloric acid (HCl) and deionized (DI) water with a ratio of 60:60. The growing process was done via hydrothermal method at 200 ºC for 3 hours. The morphology of TiO$_2$ nanorods photo-anode was characterized using scanning electron microscope (SEM). Meanwhile, the performance of DSSC cell was characterized using incident photon-to-current efficiency and current-voltage (I-V) measurement under solar simulator with an intensity of 500 W/m$^2$. The TiO$_2$ nanorods that were grown using 2 ratio of TTIP generated cell with the best efficiency, that is 0.08%. The highest efficiency was obtained using this ratio presumably because the produced TiO$_2$ nanorods had the optimized morphology for an optimum dye adsorption, good and fast electron transport, and thus was able to reduce the electron recombination within the photo-anode.

1. Introduction

Dye-sensitized solar cell (DSSC) is a solar cell technology that uses dye as light absorbing medium or sensitizer. The advantage of this technology are low production cost, easier fabrication process, and less by product (waste) that could be harmful into enviroment comparing to those produced by conventional one based on silicon [1]. Some of the important components in DSSC consist of transparent conductive substrate, photo-anode, dye, electrolyte, and counter electrode [1].

Photo-anode is an important element that can significantly influence the performance and efficiency of DSSC. Photo-anode serves to collect and transfer the electrons that have been excited from dye to external circuit [2]. One of the commonly applied material as photo-anode is titanium dioxide (TiO$_2$). This semiconductor material has a good conductivity for electron transport and stability [3].

Various studies on TiO$_2$ film morphology have been carried out to improve the DSSC performance. One of the study was done by modifying the TiO$_2$ morphology into nanoparticle scale, wherein the particle size typically around 10 – 40 nm [1, 4]. Therefore, modification into nanoparticle scale could increase the TiO$_2$ surface area so that more dye molecules could be adsorbed into the photo-anode.
More dye adsorption leads to more generated electrons that eventually could be converted into electricity. However, if the particle size is too small, the transfer of the excited electron to the external circuit could be inhibited and causes electrons recombinations that can degrade the DSSC performance. Many research has therefore developed TiO$_2$ with nanorods structure, which can provide good and fast path for electron transfer to reduce the risk of electron recombination and improve the DSSC performance [5].

There are various types TiO$_2$ precursor that can be used to grow TiO$_2$ nanorods, such as titanium isopropoxide (TTIP) and titanium (IV) butoxide (TBT). The difference between those two materials can be seen from their chemical bonds. The chemical formula of TTIP is C$_{12}$H$_{28}$O$_5$Ti, whereas TBT is C$_{16}$H$_{30}$O$_4$Ti. Less carbon ties on TTIP causes this material to react perfectly with the catalyst compound, therefore it can deposit nanorods quickly, and resulting in less side products [6].

There are several research that have be done to fabricate TiO$_2$ nanorods as DSSC photo-anode. Liu et al. [7], deposited TiO$_2$ nanorods using hydrothermal method by mixing TBT into HCl and DI water with volume ratio of 1:60:60. After that, the TBT ratio was increased to 1.5, 1.7, and 2. The highest efficiency obtained was 3% by using 2 ratio of TBT.

Based on research that have been done previously by [7], this paper reports the synthesis of TiO$_2$ nanorods using alternative precursor that is more commonly available, i.e. TTIP. The ratio of TTIP used were varied volume as 1, 2, and 4, which were mixed into 60:60 ratio of HCl and DI water. The reason for using relatively high volume of TiO$_2$ solution ratios compared the previous research was to indentify any further effects on the TiO$_2$ nanorods morphology and their impact on the DSSC performance.

2. Experimental Methods

2.1. TiO$_2$ nanorods photoanode preparation

Fluorine-doped tin oxide (FTO) coated glass TEC$^\text{™}$ 15 (15 Ω/sq, Dyesol) with a size of 1.5 x 1 cm$^2$ were uses as substrate. The FTO glasses were cleaned in teepol, DI water, and isopropyl alcohol (IPA) respectively each for 10 min by ultrasonic cleaning. The cleaned FTO glasses were then treated on 40 mmol L$^{-1}$ TiCl$_4$ solution at 70 ºC for 30 min followed by sintering process at 450 ºC for 15 min.

The pre-treated photo-anode substrates were then placed into teflon-liner hydrothermal chamber with the FTO film facing down. After that, mixture solution of TTIP (97 wt%), HCl (37 wt%), and DI water with volume ratio 1:60:60 was slowly poured into the chamber and followed by hydrothermal process at 200 ºC for 3 hours. After the hydrothermal process, the TiO$_2$ nanorods photo-anode was rinsed with DI water. After that, the TiO$_2$ nanorods was deposited using higher ratios of TTIP, i.e. 2 and 4.

2.2. DSSC fabrication

The TiO$_2$ nanorods photo-anode were immersed into dye solution of Z-907 (cis-Bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-di-nonyl-2'-bipyridyl) ruthenium(II), Dyesol) in ethanol, and kept for 24 hours at room temperature and under dark condition. The films were further rinsed with ethanol and dried in the air. Platina was used as counter electrode material and deposited by screen printing on top of separate FTO substrate. The photo-anode and counter electrode were assembled like sandwich structure using Surlyn thermoplastic (50 μm thickness, Dyesol). Then, electrolyte (Dyesol, EL-HPE) was injected into the DSSC cell through a gap between the two electrodes.

2.3. Characterization

The thickness of TiO$_2$ nanorods film was measured by digital thickness measurer Mitutoyo, Model ID-C112B. The TiO$_2$ nanorods film morphology, structure, and nanorods dimension were characterized using scanning electron microscope (SEM) type JSM-IT 300 with 15 kV of power beam. The quantum efficiency of DSSC cell was characterized used incident photon to current efficiency (IPCE) measurement system (Newport, Model: Configureable). The photocurrent-voltage (I-V) characteristics
were measured with National instrument I-V measurement system under simulated AM 1.5 illumination with constant light intensity of 500 W/m² provided by a solar light simulator (Oriel, Model: 91192). The active area of the DSSC cell was 0.25 cm².

3. Results and Discussion

3.1. Morphology analysis of TiO₂ film

The thickness of TiO₂ nanorods film that resulted from the variation of TTIP ratio were 0.4 µm for 1 TTIP, 2.6 µm for 2 TTIP, and 4.4 µm for 4 TTIP. These thickness increased proportionally with the addition of the TTIP ratios. The addition of the TTIP ratio causes the hydrolysis reaction that forms the TiO₂ nanorods occurs faster, so that the amount of TiO₂ nanorods deposited on the FTO substrate increased [7].

The variation of TTIP volume also affected the surface morphology of the TiO₂ nanorods produced. The effect is shown on SEM characterization results in figure 1. For ratio 1 of TTIP, it can be seen that TiO₂ nanorods has not been fully formed so that the surface morphology resembles small spheres and dimensions of the resulting nanorods were relatively small. Meanwhile for ratio 2 and 4 of TTIP, the TiO₂ nanorods were perfectly formed on FTO substrate. The TiO₂ nanorods that were deposited using a ratio 4 of TTIP have a more blunt nanorods edges than those of the 2 TTIP. This occured because the 4 TTIP ratio had been rapidly reacted into TiO₂ nanorods, leaving the solution of DI water and HCl, wherein the acidity of HCl was suspected to erode the surface of TiO₂ nanorods [8].

The morpholgy of TiO₂ such as dimensions, pores, and film thickness of TiO₂ nanorods affected the extent of dye adsorption into the photo-anode. Comparison of the dye adsorption ability can be visually observed in figure 2. It can be seen that dye adsorption on sample with 2 TTIP ratio was more pronounced than ratio 1 and 4. The amount of dye adsorption is indicated by the dye concentration on surface of TiO₂ nanorods film. The highest amount of dye adsorption was obtain on ratio 2 TTIP because the TiO₂ nanorods were not too large so that it had more surface area, and thus increased the amount of dye adsorption [9]. In addition, the thickness of TiO₂ nanorods film also affected the quality of dye absorption. Eventhough the dimension of TiO₂ nanorods in 1 TTIP ratio was smaller than 2 TTIP, but the thickness was too thin so that there was not enough medium for dye adsorption.

![Figure 1](image-url)

**Figure 1.** Top view (upper) and tilted cross sectional view (bottom) of TiO₂ nanorods for (a) dan (b) 1 TTIP, (c) dan (d) 2 TTIP, dan (e) dan (f) 4 TTIP.
3.2. Performance analysis of DSSC

The thickness and amount of dye adsorbed within the TiO$_2$ nanorods photo-anode layer affected the DSSC quantum efficiency as shown in figure 3.

In ultraviolet (UV) range of 300 – 380 nm, quantum efficiency enhancement was 2% for 1 TTIP, 8% for 2 TTIP, and 12% for 4 TTIP. The enhancement occurred due to the increase in the TiO$_2$ nanorods film thickness, suggesting more electrons that can be converted into electricity [10]. Meanwhile, the amount of dye absorbed could be indicated by the quantum efficiency peak at visible light wavelength range (i.e. 380 – 750 nm). The increase in the quantum efficiency at visible light wavelength range typically corresponds to more amount of dye molecules being adsorbed [11]. It can be seen that ratio of 2 TTIP has a highest quantum efficiency, thus it has the best dye adsorption capability.

The thickness, morphology, and amount dye absorption also affected the current – voltage characteristics as shown in figure 3. The DSSC performance can also be analyzed from the electrical parameters (Table 1) such as the value of short circuit current rating ($J_{sc}$) open circuits ($V_{oc}$), maximum power ($P_{max}$), fill factor (FF), and efficiency.

The thickness of TiO$_2$ film typically affected the value of $J_{sc}$. The thicker the TiO$_2$, the more excited electrons can be generated within the materials so that the value of $J_{sc}$ increases [10]. Therefore, the $J_{sc}$ value of 4 TTIP that is $4.23 \times 10^{-2}$ mA/cm$^2$ was the highest among other ratios because the TiO$_2$ film was the thickest.

![Figure 2. Photographs of TiO$_2$ photo-anodes prepared with (a) 1 TTIP, (b) 2 TTIP, dan (c) 4 TTIP.](image)

![Figure 3. Quantum efficiency of cells prepared with various TTIP ratio.](image)
Figure 4. J-V curves of the DSSC with TiO₂ nanorods photoanodes prepared using different TTIP ratios

Table 1. Photovoltaic characteristics of the DSSC with different photo-anode.

| Sample | P<sub>max</sub> (mW) | J<sub>sc</sub> (mA/cm²) | V<sub>oc</sub> (volt) | R<sub>s</sub> (kΩ) | R<sub>shunt</sub> (kΩ) | FF | eff (%) |
|--------|---------------------|------------------------|---------------------|-----------------|------------------|----|--------|
| 1 TTIP | 2.44 x 10⁻⁴         | 3.05 x 10⁻³            | 0.24                | n.a.            | n.a.             | 0.33| 0.002  |
| 2 TTIP | 9.88 x 10⁻³         | 3.33 x 10⁻²            | 0.57                | 4.56            | 65.74            | 0.51| 0.08   |
| 4 TTIP | 8.68 x 10⁻³         | 4.23 x 10⁻²            | 0.43                | 3.31            | 20.75            | 0.48| 0.07   |

The highest efficiency was obtained by 2 TTIP, that is 0.08%. The highest value of efficiency was determined by the highest value of V<sub>oc</sub>, which was 0.57 V. The high V<sub>oc</sub> value was achieved because this ratio provide the optimum nanorods length for electron transfer, inwhich the nanorods length was not too long so that it could causes high recombination resistance value [12]. Moreover, the high of V<sub>oc</sub> value was due to the high value of R<sub>shunt</sub> produced, in which R<sub>shunt</sub> also has important role to prevent the recombination electron in the DSSC cell [13]. The value of V<sub>oc</sub> also gave impact on the high value of P<sub>max</sub> and FF, which were 9.88 x 10⁻³ mW and 0.51, respectively, so that the overall resulting efficiency value was the highest.

4. Conclusions
TTIP with ratio variations of 1, 2, and 4 were mixed into HCl and DI water with a ratio 60:60 for TiO₂ nanorods deposition. The variation affected the morphology of the photo-anode and performance of DSSC cells. The length and width of TiO₂ nanorods increases along with the increase in TTIP ratio. TTIP:HCl:DI water with ratio of 2:60:60 produced the highest efficiency with a value 0.08%, which was higher than ratio of 1 and 4 with efficiency value of 0.002% and 0.07%, repectively. The highest efficiency of 2 TTIP ratio was mainly caused by the resulting morphology that led to optimum dye adsorbion and reduced the recombination electrons in the photo-anode.

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