Zinc-porphyrin-imide type sensitized TiO₂ nanotube arrays as photoactive electrode in a dyes sensitized solar cell

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Abstract. In this work, TiO₂ nanotube was prepared by rapid breakdown electrooxidation of Ti foil in electrolyte containing 0.15 M HClO₄. The obtained TiO₂ nanotube bundling powder was calcinated at 450°C for 3 hours, then characterized by SEM, XRD, UV-Vis DRS, and BET. Zinc-porphyrin-imide dyes was deposited into TiO₂ nanotube by immersion of TiO₂ nanotube in zinc-porphyrin-imide solution for 24 hours. Free zinc-porphyrin-imide dyes shows characteristics of absorption spectra in visible region at 439 nm and 620 nm. Meanwhile, when it was immobilized to TiO₂-nanotube, the absorption peak shifted to 421 nm and 640 nm. The zinc-porphyrin-imide/TiO₂ electrode showed an excellent response toward the visible light with the typical photocurrent density of 1.1 mA/cm². When the fabricated photoelectrode was assembled in a typical Dyes Sentsitize Solar Cell (DSSC), the I-V curve showed photoconversion efficiency of the assembled zinc-porphyrin-imide/TiO₂ DSSC was 1.914% (front side illumination) and 1.147% (backside illumination), respectively.

Keywords: Zinc-porphyrin-imide, TiO₂ nanotube, TiO₂/Zinc-porphyrin-imide

1. Introduction

Titanium dioxide (TiO₂) is great interest for a number of technological areas, including photocatalysis, photovoltaic solar cells, and waste remediation, because of its electronic, optoelectronic, catalytic, and biocompatibility properties. TiO₂ is a wide band gap semiconductor, which has great ability to produce oxidants (holes in the valence band) and reductants (electrons in the conduction band) upon photons absorption [1-3]. Because of this feature and its mechanical strength, TiO₂ has been widely studied for applications in photoelectrochemical systems, such as TiO₂ photoanodes for dye-sensitized photovoltaic solar cells.

Dyes sensitized Solar Cells (DSSC) is one of the photoelectrochemical systems that can convert light energy into electrical energy. Typically, DSSC system so far has achieved energy conversion efficiency of 13% under AM 1.5 lights 1000 Watt [4]. The sensitizer is one important factor in DSSC. Gratzel et al. [5] has developed a DSSC with promising energy conversion, using ruthenium complexes compounds. Typical sensitizer that can be used generally is a complex compound that has a cluster of anchoring as a bridge binder and an electron donor of the sensitizer to the semiconductor. The anchoring group used is hydroxyl and carboxyl, which attached to a chromophore groups that can absorb visible light efficiently. The Chromophore group must have a LUMO orbital located above the conduction band of TiO₂, in order to thermodynamically facilitate the injection electrons from the LUMO level of sensitizer into the conduction band of TiO₂. Cluster-based porphyrin complex compounds can be used as an alternative to the ruthenium-polypyrindine, wherein porphyrin acts as ligands in conjunction with
cobalt-based redox mediators [6-9]. Porphyrin group which has π donor-acceptor with a large molar absorptivity can be applied as a sensitizer in a thin layer of TiO$_2$ [2]. It also provides a highly flexible platform for the development of panchromatic sensitizers [8, 10]. The porphyrin chromophore has intrinsically strong light absorption in the visible region (400-600 nm) [6-9]. Recently, Zn$^{II}$ (5-(2-(4'-dimethylaminophenyl)-ethynyl)-10,20diphenylporphyrinate has been synthesized by Handayani, et al as a two-terminal wired single molecular diodes, not typical sensitizer in DSSC and it has porphyrin as a chromophore and imide as a linker. When the complexes are exposed to light, electron will be transferred from HOMO porphyrin to LUMO imide with the strong character charge transfer [11]. Zinc-porphyrin-imide has characteristicwhen in a polar solvent low-energy absorption bands of the Zn-complex will shift to longer wavelengths [11], therefore it is likely suitable as sensitizer in a DSSC system.

In this study, we constructed a DSSC system which was assembled using TiO$_2$ nanotubes sensitized by typical zinc-porphyrin-imide as the working photoelectrode. The TiO$_2$ nanotube bundle was prepared by a Rapid Breakdown Anodization (RBA) method. The developed visible responsive photoanode was characterized and assembled in a typical DSSC system, and the results will be discussed hereafter.

2. Materials and methods

2.1. Preparation of TiO$_2$ nanotubes powder
Titanium sheet (5 cm × 5 cm; Baoji Jinsheng Metal Material Co., 99.6% purity, 0.3 mm thickness China) was cleaned properly before used. Typically, the Ti sheet was abraded by sand paper, wiped by a clean soft paper, then rinsed subsequently by organic solvent, water, and organic solvent. Then, the clean Ti sheet was clamped onto a copper clip, positioned as anode and immersed directly in electrolytes containing 0.15 M. A titanium foil as a working electrode and a platinum foil as a counter electrode were used for anodization process under a constant potential of 15 V at a temperature of approximately 25°C.

2.2. Coating of TiO$_2$ to FTO
0.1 gram TiO$_2$ NT was dispersed in 10 mL of acetic acid 10%, then sonicated for 1 h to form a colloid with the aid of Triton X surfactant. The freshly prepared TiO$_2$ colloid was then used to coat the fluoride doped tin oxide (FTO) by the doctor blade method, performed on a hot plate set at 60°C. The TiO$_2$ coated with FTO was then annealed at 350°C for 1 h. The FTO was self- fabricated as reported by Supriyono et al. [12].

2.3. Immobilization of Zinc-Porphyrin-Imide on FTO/TiO$_2$
Approximately 11 mg of zinc porphyrinwas dissolved in 25 mL mixture of acetonitrile and tert-butanol 1:1. The solution is considered as the stock solution (440 ppm) and then diluted to a working solution at concentration of 110 ppm. The clean FTO/TiO$_2$ was then annealed at 350°C for 1 h. The FTO was self- fabricated as reported by Supriyono et al. [12].

2.4. Electrochemical characterization of photoanode working electrode
The FTO/TiO$_2$ or FTO/TiO$_2$/Dyes was placed as working electrode in three electrochemical cells, with Ag/AgCl as reference electrode, and platinum foil as counter electrode. The working electrode was illuminated by proper light source. The amperometric measurement was performed at a potential of 500 mV for 100 seconds, with a scan rate of 25 mV/s. The typical photocurrent was measured and evaluated.

2.5. Assembly of DSSC
The FTO/TiO$_2$/Dyes was arranged in a DSSC system, which the electrolyte (I$_3$/I$_2$ in a proper solvent) was sandwiched between working electrode (FTO/TiO$_2$/Dyes) and counter electrode (FTO/Pt). The parafilm was used as spacer to avoid short contact of the electrodes.
3. Results and discussion

3.1. Synthesis of TiO$_2$ nanotube powder
In figure 1, it shows in section I the significant current decrease of 0.158 Å to 0.0019 Å for 80 seconds. It is because on the Ti plate surface oxide layer was formed, when the oxide layer formed it become less conductive than the Ti plate, causing delays of the electron flow which characterized by the decrease in flow during the synthesis process. In section II the flow increased significantly from 0.0019 A to 0.4 A. This is because the oxide layer formed on the Ti plate to form small holes in the oxide layer of TiO$_2$, and a process of etching by chloride ions, so that the electrolyte can access Ti plate surface to form a new oxide layer. Ti transformation into TiO$_2$ and TiO$_2$ etching will continue until the flow is marked by the currents to reach the steady state. The section III shows the currents tend to stabilize at 0.4 A for 27 min. This is because TiO$_2$ that has been formed, dissolved to form a stable complex compounds with Cl ions of ClO$_4^-$ to be [TiCl$_6$]$_{2-}$.

3.2. Characterization of TiO$_2$ nanotube powder
Matrix of TiO$_2$ absorbs light having an equal or greater energy than its energy gap. Light that is not absorbed will be reflected and captured by the detector in the UV-Vis DRS instrument. UV-Vis spectra profile of prepared TiO$_2$ compared with Degussa P25 TiO$_2$ can be seen in figure 2. Energy band gap values is determined by changing the value of % R into the value of F using Kubelka-Munk equation, then the value of F is plotted against photon energy in a particular range. The F value of the photon energy in the equivalent area to wavelengths between 250-450 nm will produce linear region in a narrow energy range, and by using the Tauc equation the energy gap value can be determined.

Figure 3 shows the measurement results of prepared TiO$_2$ nanotubes. The results of XRD measurements indicate the presence of 6 diffractogram peaks corresponding to anatase TiO$_2$ diffractogram patterns. Measurement was done by comparing the data with the synthesis data.
Table 1. Comparison of BET and band gap value of TiO$_2$ nanotube and P25 Degussa.

| Material              | Surface area (m$^2$/g) | Band gap (eV) |
|-----------------------|------------------------|---------------|
| TiO$_2$ nanotube      | 120,971                | 3.21          |
| TiO$_2$ P25 Degussa   | 59                     | 3.31          |

Figure 3. Spectra UV-Vis of zinc-porphyrin-imide.

3.3. Characteristic of dyes zinc-porphyrin-imide

Figure 4 is a UV-Vis spectrum of Zn-porphyrin dyes. There is a specific absorption in the visible light region (visible) at the maximum wavelength of 439 nm, and 627 nm, as seen in the picture. Absorption occurs at a wavelength of 439 nm, which is characteristic for porphyrin components. Excitation occurs $\pi \rightarrow \pi^*$ intramolecular charge transfer character, which is the transition of an electron from porphyrin group to imide unit. Excitation occurs in the Zn-porphyrin is involving one electron at HOMO to LUMO character charge transfer [1]. A wavelength of 627 nm and 547 nm are the characteristic of low energy absorption of Zn$^{2+}$. It can be concluded that the Zn-porphyrin dyes can absorb photons in the visible light region. Free zinc-porphyrin-imide dyes shows characteristic of absorption spectra in the visible region, namely 439 nm and 620 nm. Meanwhile, when it was immobilized to TiO$_2$-nanotube, the absorption peak shifted to 421 nm and 640 nm.

3.4. Photoelectrochemical of working electrode (FTO-TiO$_2$ Dyes)

From the graph in figure 4(a), it can be seen that an increase in the current flow was observed when TiO$_2$-Zn porphyrin irradiated by visible light then reached the steady state at a current of about 1.1 mA/cm$^2$. While when the TiO$_2$-Zn porphyrin was illuminated by UV lamp the generated currents reach the steady state at 0.6 mA/cm$^2$. This phenomenon may indicate the contribution of Zn-porphyrin-imide, to give the absorption region of TiO$_2$-Zn shifted toward visible light.
The shifting uptake occurs because the TiO$_2$-Zn porphyrin has a cluster of chromophore as an absorber of visible light, in this case porphyrin, confirmed by the spectrum peak of UV-Vis Zn-porphyrin at 439nm region of visible light. The TiO$_2$-Zn porphyrin irradiated visible light electrons at HOMO porphyrin moved to the LUMO imide, and going to hole (h +) in the HOMO porphyrin. Hole in the HOMO porphyrin will be filled by an electron from the Zn metal as a donor (metal-ligand charge transfer) to prevent recombination of electrons and holes, due to orbital LUMO on imide is higher compared with ribbon conduction in TiO$_2$. Then the electrons in the LUMO imide will move into the conduction band of TiO$_2$ through anchoring group, namely hydroxyl groups and will create a chelating effect on TiO$_2$-Zn porphyrin. The produced Chelate can be monodentate or bidentate. This chelate will become a bridge that connected the dye with TiO$_2$.

3.4. DSSC performance

The present study measures the difference of current flow when exposed by backside and front side light illumination. The backside illumination condition mean that the rays do not directly exposed to the TiO$_2$ layer section but have to passes the Pt film first. At the time of irradiation at the front side position, the generated current is higher than the backside position, the maximum current that occurs at the front side was 1.434 mA, while at the backside flow only reached 0.824 mA. This is caused by the indirect radiation of dyes, since it was absorbed first on CE (Counter Electrode), so the energy of photons reached the dyes must be less. From the measurement results using a potentiostat, DSSC efficiency obtained different results between the front side and the backside illumination. In this study, the efficiency ($\eta$) DSSC by irradiating backside illumination was obtained at $\eta = 1.147\%$, while the value of efficiency ($\eta$) DSSC at front side illumination was $\eta = 1.914\%$.

4. Conclusions

Photoanode of FTO/TiO$_2$ zinc-porphyrin-imide dyes has been succesfully prepared and characterized, which showed an excellent response toward the visible light. The FTO/TiO$_2$ zinc-porphyrin-imide dyes photoanode was successfully assembled to a DSSC device, which gave a % light to current conversion of 1.914% and 1.147% upon front side and back side illumination, respectively.

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