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by Setia Budi Sasongko

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# Characterization of Dye-Sensitized Solar Cell (DSSC) With Acid Treatment by HNO<sub>3</sub> in Mangosteen Peel Dye

Agung Kurnia Yahya<sup>1, a)</sup> and Setia Budi Sasongko<sup>1,b)</sup>

<sup>1</sup>Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Jl. Prof Sudarto, Tembalang - Semarang, 50275, Indonesia

> <sup>a)</sup>Corresponding author : agungkurniayahya@gmail.com <sup>b)</sup>another author : sbudisas@gmail.com

**Abstract.** The influences of acid treatment of dye sensitizer using HNO<sub>3</sub> on the characteristics of DSSC were investigated. The acid treatment using HNO<sub>3</sub> improved morphology of TiO<sub>2</sub>, increased the amount of adsorbed dye molecules on TiO<sub>2</sub>, and diffusion of redox electrolyte became easier. The values of Isc and Voc of DSSC increased with the addition of HNO<sub>3</sub> on dye sensitizers. They were caused by the charge collected by adsorption of anions on the surface of TiO<sub>2</sub>. Without the addition of HNO<sub>3</sub> the efficiency produced is 0.141%. and with the addition of HNO<sub>3</sub> into the dye solution increased the efficiency by 0.201%

# INTRODUCTION

The availability of fossil energy sources, especially petroleum, which is the main component of energy producers in Indonesia is decreasing along with increasing of industry development. One of the alternative energy that environment friendly and its abundant presence is solar energy, which will never run out of availability. The energy released by sunlight is actually only received by the earth's surface by 69% of the total radiant energy of the sun. The energy supply from sunlight received by the earth's surface was enormous, reaching 3 x 1024 joules per year, this energy is equivalent to 2 x 1017 Watts. The amount of energy is equivalent to 10,000 times the energy consumption in the world [1].

Dye-sensitized solar cells (DSSC) were third-generation solar cells developed in 1991 by Gratzel. DSSC was able to convert light energy into electricity using the principle of photoelectrochemistry [2]. The advantages of DSSC compared to other types were environment-friendly, low production costs, the amount of dye availability extensive, easy extraction, biodegradability, and no further purification process needed [3,4].

DSSC is composed of a transparent conducting substrate, mesoporous oxide semiconductor layers, dye sensitizers, electrolytes, and counter electrode [5]. The principle of DSSC operation starts with the absorption of photons by photosensitizer (S) which results in the excitation of photosensitizer (S\*) and transfer electrons to the semiconductor conduction band by injection process. Photosensitizers that lose electrons are in the oxidized state (S<sup>+</sup>). On the other side, oxidized dye is returned to the ground state by the mediator and electrolyte oxidation reaction occurs. Then the injected electrons flow through the semiconductor to the counter electrode and are received by the redox electrolyte mediator.

$$\begin{split} & S + \overline{hv} \rightarrow S^{*} & (1) \\ & S^{*} \rightarrow S^{+} + e^{-} & (2) \\ & S^{+} + e^{-} \rightarrow S & (3) \\ & S^{+} + 3/2 \ \Gamma^{-} \rightarrow S^{+} \frac{1}{2} \ I^{3-} & (4) \\ & \frac{1}{2} \ I^{3-} + e^{-} \rightarrow \frac{1}{2} \ \Gamma^{-} & (5) \end{split}$$

Equation description:

(1) Excitation of dye during radiation

(2) Dye oxidation causes electron injection to TiO2

(3) Dye is returned to the basic state by the mediator electrolyte

(4) Electrolyte oxidation reaction

(5) Electrolyte reduction reaction in the opponent's electrode

Some reactions that are not expected can cause a loss of DSSC efficiency. Among are caused by injected electron recombination on  $TiO_2$  with photosensitizers oxidized or with oxidized redox pairs on the  $TiO_2$  surface [6].

$$\begin{array}{ll} S++e^{-} \rightarrow S & (6) \\ I^{3-}+2e \rightarrow 3I^{-} & (7) \end{array}$$

Sensitizers are an important component in DSSC. In the application of DSSC, sensitizers are divided into three categories: natural organic dye, synthesis organic dye, and metal complex dye. In a previous study using metal dye complexes, the efficiency value was 15%, while organic dye and natural dye produced 9.5% and 0.70% efficiency respectively [7,8,9]. Some efforts were needed to improve the performance of DSSC including increasing dye stability with a long immersion method, dye purification [10], increasing the acidity of solvents [11], increasing extraction and use of various solvents [9], addition of acetic acid loading [12] and optimization of dye structures [3].

# EXPERIMENTAL METHOD

#### Fabrication of Substrate Glass

20 gr SnCl<sub>2</sub>.2H<sub>2</sub>O and 5 gr NH<sub>4</sub>F were dissolved in 100 ml ethanol. Furnace was preheated to 200°C then the glass was put into furnace for 10 minutes. Then it was sprayed by a conductive solution. Repeated the steps for 4 times. After it, the temperature was raised to 400°C and the heating time was 60 minutes.

## Coating of TiO2 on Substrate Glass

 $TiO_2$  paste made from 3.5 gr of  $TiO_2$  powder was put into a glass beaker. Added 15 ml ethanol then stirred it for 10 minutes until homogeneous.  $TiO_2$  paste was applied to the substrate glass. Then the substrate glass was inserted into the furnace for the sintering process. This process was carried out at 400°C for approximately 30 minutes.

#### Preparation of Dye

Mangosteen peel was smoothed using a blender to form a fine powder. The powder 25 gr was extracted using 100 ml of ethanol for 24 hours and stored in a dark place. The material is then filtered using filter paper.

#### Making Electrolytes

0.8 gr KI was dissolved in 10 ml of acetonitrile. Then 0.127 gr  $I_2$  was added to the solution. The complete electrolyte solution is then stored in a bottle.

#### Dye Sensitization on TiO<sub>2</sub> Electrodes

The dye solution was placed in a vessel. Then HNO<sub>3</sub> was added to dye solution according to the variables (0%, 2%, and 5%). The glass oxide layer that had been sintered was dipped into the dye solution. The substrate glass was placed with the oxide layer facing up. Let soaked it in time according to 120 minutes. Then it was rinsed with distilled water, then was heated in an oven at  $^{60oC}$  for 30 minutes to dry.

#### **Characterization of Dye Sensitizer**

UV-Vis spectrophotometry measurements were carried out to see the ability of light absorbance and peak absorption values of UV-Vis waves.

## Characterization of DSSC

A DSSC prototype consists of two substrate glass. Namely a substrate glass that has been sensitized to dyes and substrate glass for the electrode counter. The DSSC assembly stages were as follows: Arranged the glass substrate to

form a sandwich structure, gave an offset at the end of each electrode for electrical contact, pinched the edges of the DSSC cells that were not offset by clips so that the prototype is correctly attached, Added 2-3 drops of triiodide electrolyte solution from both ends of the DSSC prototype offset. Pinned the two edges of the DSSC cell that were not offset by clips so that the prototype was correctly attached.



#### FIGURE 1. DSSC Structure

The DSSC layer formed is characterized by its current and voltage using a voltmeter (V) and an amperemeter (mA). The light source was directed perpendicular to the cell surface. Tests were carried out with halogen light sources.

# RESULT AND DISCUSSION

### **Characterization of Dye Sensitizer of Mangosteen Peel**

The study of dye absorption of mangosteen peel extract was carried out using UV-Vis spectrophotometry to see the ability of light absorbance and peak absorption values of UV-Vis waves.





From figure 2, it can be seen that mangosteen peel extract has absorption peaks at a wavelength of 550 nm and has a wide enough absorption range. The absorption is quite extensive in the visible light region of mangosteen peel extract because it is possible in the extract not only to contain one type of dye but rather consist of several different dyes, so that the electronic absorption produced is the addition of various dyes [13].

Mangosteen peel extract is very potential as an effective sensator in solar cell systems because it has a wide range of electronic absorption so that the solar cells produced will have a spectral response with a wide enough range in the visible area.



(a)
 (b)
 FIGURE 3. Morphology of TiO<sub>2</sub> After Immersion In Dye Solution. a) Soaked without the addition of HNO<sub>3</sub>.
 b) Soaked with the addition of HNO<sub>3</sub>.

#### Characteristics of TiO<sub>2</sub> Film

Analysis using scanning electron microscopy (SEM) was carried out to determine the morphology of TiO2 layers on glass substrates. TiO<sub>2</sub> films modified by HNO<sub>3</sub> showed larger pore size and higher porosity while TiO<sub>2</sub> films that were not treated showed greater particle aggregation [14]. That caused the amount of dye absorbed also increased and the redox electrolytes diffusion became easier. When compared between TiO<sub>2</sub> thin layers soaked in dyes solution with the addition of HNO<sub>3</sub> and without HNO<sub>3</sub> addition, the surface morphology of TiO<sub>2</sub> soaked with dyes by acid treatment showed a structure that formed a quite wide cavity resulting from the presence of HNO<sub>3</sub> absorbed in TiO<sub>2</sub>.

From the figure 3, it can also be seen that the surface morphology of  $TiO_2$  thin layer with acid treatment had a better cavity compared to the untreated  $TiO_2$  thin layer so that the  $TiO_2$  thin layer with acid treatment was more effective in adsorbing dyes, which later the dye could be reached by solution electrolytes so that the interaction between dye and electrolyte solutions became more effective. The existence of effective interactions between dyes and electrolytes could accelerate the process of regenerating dyes through the process of electron donation resulting from the oxidation of iodide to dyes that were positively charged because they had carried out electron injection.

### Effect of HNO3 Addition in Dye Sensitizer to Adsorption of Dye in TiO2 Layer

In solar cell systems electricity will not be produced if there is no dye because there will be no electron flow in the conduction band, where the dye on the surface of the thin layer  $TiO_2$  acts as an electron injector in the conduction band [15].



FIGURE 4. Results of Addition of HNO<sub>3</sub> to Adsorbed Concentration of Dye on TiO<sub>2</sub>

In Figure 4, it can be seen that the addition of HNO<sub>3</sub> in the dye solution will cause the concentration of the adsorbed dye to increase. The addition of HNO<sub>3</sub> will cause the pH of the dyes solution to become more acidic. The addition of acids that had polar character resulted in a redshift in the peak of spectral absorption due to the interaction of the extreme groups of dye molecules with solvents and increased intensity of wave absorption [16].

The pH conditions greatly affect absorbance, in acidic conditions, anthocyanins are in the form of flavylium, which is able to coordinate more effectively with the  $Ti^{4+}$  site [17]. The adsorption power of a sensitizer is strongly influenced by surface charge. The surface charge of  $TiO_2$  changes positively when it is acidic and is able to bind strongly to the negative molecule sensitizer, the surface charge of TiO2 changes to negative under alkaline conditions and attracts positive sensitizer molecules [18]

The dye-immersed TiO<sub>2</sub> particles added HNO<sub>3</sub> cause the surface of TiO<sub>2</sub> to be positively charged, thus increasing particle dispersion due to electrostatic forces. TiO<sub>2</sub> films which were immersed with dyes plus HNO<sub>3</sub> showed higher porosity and larger pore size whereas TiO<sub>2</sub> films without HNO<sub>3</sub> showed more significant particle aggregation, so the number of absorbed dyes increased and diffusion of redox electrolyte became easier [14].

#### Effect of HNO3 Addition in Dye Sensitizer to Efficiency of Dye in TiO2 Layer

From table 4.3 it can be seen that the increasing number of HNO<sub>3</sub> addition affects the performance of DSSC. Without the addition of HNO<sub>3</sub> the efficiency produced is 0.141%. After acid addition, using HNO<sub>3</sub> with the addition of 2% and 5% of HNO3 into the dye solution increased the efficiency by 0.146% and 0.201%. In addition to increasing efficiency, adding acid in the dye solution used as a DSSC sensitizer will increase the value of Isc and Voc.

Table 1. Performance of DSSC with variations in the HNO3 Addition			
HNO <sub>3</sub> addition	0%	2%	5%
Isc (mA)	1,29	1,67	1,97
Voc (V)	0,23	0,29	0,3
Imax (mA)	0,87	1,18	1,51
Vmax (V)	0,18	0,13	0,14
% FF	49,7	31,6	35,7
% Efficiency	0,141	0,146	0,201

In solution, anthocyanins have 5 molecular types in chemical equilibrium; color pseudo carbinol, red flavylium cations, purple quinoidal bases, yellow chalcone, and blue quinoidal anions [19], their stability and color are affected by pH of the dye solution. The more addition of HNO<sub>3</sub> resulted the dye solution was more acidic. According to Tedesse, et al, the flavylium cation was the dominant form at acid pH and it had a strong absorption. When the pH increased, the flavylium cation gradually changes to the quinoidal base by losing the proton [16].

The increase of Isc in the treatment of HNO<sub>3</sub> was caused by the charge collected by surface protonation of TiO<sub>2</sub>. which was TiO<sub>2</sub> surface was more positively charged and attracted a negative charged of dye. It was also caused by electron transfer by adsorption of anions (NO<sup>3-</sup>) on the surface of TiO<sub>2</sub>. In the energy band theory, Voc is the maximum voltage generated by the difference between the quasi-fermi level of the TiO<sub>2</sub> and the redox electrolyte potential. The H<sup>+</sup> ions adsorption on the surface of TiO<sub>2</sub> caused the TiO<sub>2</sub> flat band potential may have shifted in a positive direction in the HNO3 treatment of dye sensitizer [14].

# CONCLUSIONS

The conclusion of this study was that the addition of HNO<sub>3</sub> would improve the morphology of TiO<sub>2</sub>. TiO<sub>2</sub> films which were immersed with dyes added HNO<sub>3</sub> showed higher porosity and larger pore size while TiO<sub>2</sub> films without HNO<sub>3</sub> showed more significant particle aggregation, so the amount of absorbed dye increased and diffusion of redox electrolyte became easier. The addition of HNO3 in a dye solution used as a DSSC sensitizer will increase the value of Isc, Voc, and efficiency of DSSC.

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