The effect of immersion temperature using chlorophyll sensitizer (Amaranthus hybridus L.) on the performance of dye-sensitized solar cells

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Abstract. This article investigated the effect of immersion temperature on the TiO2 film using chlorophyll extract for dye-sensitized solar cells (DSSC). The chlorophyll was extracted from spinach leaves with ethanol solvent. The solution of spinach extract was used for the immersion process on the TiO2 film. The immersion temperatures were varied of 283 K, 303 K and 323 K. The optical properties of TiO2-dye films were analyzed by UV-Vis and Fourier Transform Infrared (FTIR) spectrometers. The DSSCs performance were characterized by I-V meter. The highest absorbance was revealed from the immersion temperature of 303 K. Characteristic of FTIR spectra resulted a maximum transmittance of 67.2% at the frequency peak of 3341 cm−1. Additionally, these results directly proportional with the maximum performance of DSSC at immersion temperature of 303 K. The best performance of DSSCs was obtained the Voc, Jsc, and conversion efficiency values of 0.43 V, 0.16 mA and 0.04%, respectively.

1. Introduction
A dye-sensitized solar cell (DSSC) is an energy device based on the sensitization that converts light into electrical energy [1]. One of the advantages of DSSC is simple and low cost fabrication, so it does not require the high and complicated technology [2,3].

The DSSC composed of a transparent conducting oxide (TCO) glass substrate, a semiconductor photoanode (usually TiO2 film which is coated on the TCO glass substrate), a dye sensitizer, a counter electrode and an electrolyte solution containing iodide/tri-iodide (I−/I3−) redox couple [4,5]. The dye sensitizer is one of the most important component that affects the performance of DSSC. The dye sensitizer has a major role in capturing the photons and converting it into electrical energy [6,7]. The number of dye molecules that can be adsorbed on the surface of TiO2 film affects the DSSC efficiency. The more dye molecules absorbed by the TiO2 film, the more effective the absorption of photons to excite the electrons.

The synthetic dyes are the most common dyes used in DSSC. These dyes provide great electrical output and high efficiency. However, these dyes are heavy metals and environmental threat, complex manufacturing procedure, hight cost, uneconomical for large scale production, etc [8,9]. These problems can be overcome by applying natural dyes. The advantages of natural dyes are low production cost, abundantly available and enviromental friendliness [10-12]. The natural dye utilized from plant sources, such as leaves, flowers, fruits, rind, etc [3]. The natural dye that is often applied as DSSC sensitizer is chlorophyll [13]. The chlorophyll absorbs the visible light spectrum from red, blue, and violet with maximum absorption at the wavelength of 670 nm. Chlorophyll is an attractive pigment as a sensitizer for DSSC application [14].
Many studies have been carried out on the chlorophyll as sensitizer of DSSC. Anita et al. (2013) reported the conversion efficiency of 0.002% using chlorophyll extract from long bean leaves [15]. The utilization of green cabbage and papaya leaves extract as DSSC sensitizers were resulted the conversion efficiency of 0.1% and 0.094%, respectively [13,16]. However, research on the adsorption properties of natural dye for DSSCs have been very limited. The temperature is one of the major parameter of adsorption process on the TiO\textsubscript{2} surface. In addition, the study of immersion temperature based on the stability aspects of chlorophyll which are easily degraded by condition such as light, heat, temperature, pH and oxygen [17]. This article presented the effect of immersion temperature on the performance of DSSC using chlorophyll extract from Amaranthus hybridus L. as a sensitizer. This work is our efforts to obtain the better TiO\textsubscript{2}/chlorophyll dye film in the fabrication of DSSC.

2. Experiments
Fluorine-doped Tin Oxide (FTO) conductive glass from Dyesol were used as the substrates with size of 2 cm x 2 cm. The TiO\textsubscript{2} paste was deposited on the FTO glass surface with effective cell area 0.75 cm\textsuperscript{2} by spin coating technique. The counter electrodes were coated using Pt catalyst by brush painting technique. The electrolyte solution was obtained from the mixture of the polyethylene glycol (PEG) 400, potassium iodide (KI) and iodine (I\textsubscript{2}). KI and I\textsubscript{2} were prepared by dissolving into the PEG 400 and stirred for 30 minutes. The chlorophyll dye was extracted from spinach leaves. The leaves were washed using distilled water then crushed using mortar and pestle. The crushed mass were dissolved into the ethanol solvent. The solution was stirred at room temperature. Then extract was filtrated and used as dye solution. The TiO\textsubscript{2} electrode was immersed into dye solution for 24 hours with immersion temperature of 283 K, 303 K and 323 K. Fabrication of DSSCs were arranged into the sandwich structure. The working and counter electrodes were assembled using scotch tape which has thickness of 76 \mu m [18]. The electrolyte solution was injected in the space between the two electrodes. Optical phenomena of dye adsorption on the TiO\textsubscript{2} electrodes were analyzed using UV-Vis Spectrophotometer (Lambda 25 UV-Vis Spectrophotometer, PE Electronics). While, functional groups for bonding between TiO\textsubscript{2} and dye molecules were characterized using fourier transform infrared spectroscopy (FTIR, Shimadzu Prestige 21). Efficiency of DSSCs were evaluated from current-voltage (I-V) curves measured using Keithley I-V meter 2602A.

3. Results and Discussion

3.1. Optical absorption spectrum of chlorophyll dye after adsorbed on the TiO\textsubscript{2} film
Fig.1 revealed the UV-Vis absorption spectra of TiO\textsubscript{2}/dye photoelectrodes. The absorbance peaks indicated the chlorophyll pigment that playing a role in the process of photon absorption. The highest absorbance can be exhibited at immersion temperature of 303 K. It showed that TiO\textsubscript{2}/dye photoelectrode at room temperature able to absorb the photon energy maximally, so that the more electrons are excited and produced the better electricity. A higher temperature involved the instability of chlorophyll dye. This condition inhibited the immersion process on the TiO\textsubscript{2} surface. Reported that the treatment of immersion temperature at high temperature will increase activity of chlorophyllase enzyme and formed the plheophytin [19]. It will replace magnesium ions that contained in the chlorophyll with hydrogen ions. As consequence, the number of chlorophyll will decrease.
3.2. FTIR spectral analysis

FTIR spectrum of TiO$_2$/dye photoelectrodes were recorded at wavenumber range of 4000 - 400 cm$^{-1}$ as shown in Fig.2. The curve from Fig.2 can be interpreted in Table 1. It revealed the characteristic of functional groups and absorption frequency.
transmittance of and its effect to electrons coupling. This is resulting more currents. The FTIR spectrum presented the vibration of chlorophyll $\nu_{3200}$, $\nu_{2850}$, and $\nu_{1630}$ cm$^{-1}$. The functional group of C=O carbonyl and O-H hydroxyl at immersion temperature of 303 K were higher than other temperatures. It indicated that the carboxyl group (-COOH) at immersion temperature of 303 K has a bond with hydroxyl of TiO$_2$. It enhanced the effect of electrons coupling from dye molecules to the conduction band of TiO$_2$ that allows fast electron transfer. A higher immersion temperature showed the degradation of C-H dan C=O groups. The degradation of these groups affected the weak contact between dye molecule with the TiO$_2$ surface, thus blocking electron transfer.

### 3.3. Performance of DSSCs

The current-voltage ($I$-$V$) response of DSSCs were measured by Keithley $I$-$V$ meter under light intensity of 100 mW/cm$^2$ from a xenon lamp. The $I$-$V$ plot of DSSCs with different immersion temperatures are shown in Fig. 3. A current-voltage characteristic was used to determine short-circuit current ($I_{sc}$), open-circuit voltage ($V_{oc}$), fill factor ($FF$), and efficiency ($\eta$). The photovoltaic parameters of the DSSCs are listed in Table 2. The fill factor $FF$ and efficiency $\eta$ were calculated using Eq. (1) and (2).

$$FF = \frac{V_{oc} \times I_{sc}}{I_{max}}$$

$$\eta = \frac{V_{oc} \times I_{sc} \times FF}{P_{in}} \times 100\%$$

where $P_{in}$ is the power of incident light. It calculated from multiplication between the light intensity and effective cell area. $I_{max}$ and $V_{max}$ are photocurrent and photovoltage for maximum power output $P_{out}$.

The highest performance of DSSC was showed at immersion temperature of 303 K. This result corresponded to the optical properties of TiO$_2$/dye photoelectrodes that revealing the highest absorbance and FTIR transmittance peaks at 303 K. When dye absorb more photon it will excite more electrons and resulting more currents. Also enhancement of C=O and O-H groups showed by FTIR transmittance will effect to electrons coupling. This is suggesting the more efficient of electron transfer, as reported by Chang and Lo [21]. Consequently, the resulting current and efficiency are higher with maximum FTIR transmittance of 67.2% as compared to other immersion temperatures.

#### Table 1. FTIR peak values and functional groups of TiO$_2$/dye photoelectrodes with different immersion temperatures

| Peak (cm$^{-1}$) | T (%) | Peak (cm$^{-1}$) | T (%) | Peak (cm$^{-1}$) | T (%) | Functional group |
|------------------|-------|------------------|-------|------------------|-------|------------------|
| 421              | 27.5  | 421              | 23    | Ti-O-Ti          |       |                  |
| 458              | 23.3  | 448              | 30.9  |                  |       |                  |
|                  |       | 440              | 18.6  |                  |       |                  |
| 1402             | 87.9  | 1403             | 96.6  | 1403             | 88.9  | C-H              |
| 1624             | 83.2  | 1622             | 90.8  | 1621             | 81    | C=C              |
| 1640             | 82.9  |                  |       |                  |       |                  |
|                  |       | 1724             | 93.7  |                  |       |                  |
| 2321             | 79.6  |                  |       |                  |       |                  |
| 2853             | 70.3  | 2854             | 75.7  | 2854             | 66.9  | C-H              |
| 2923             | 67.9  | 2924             | 73.61 | 2959             | 65.5  |                  |
| 3395             | 62.5  | 3411             | 67.2  | 3389             | 56.9  | O-H              |

The FTIR spectrum presented the O-H stretching vibration of ethanol (C$_2$H$_5$OH) at wavenumber range of 3200-3400 cm$^{-1}$. The spectra peak in the range of 2800-3000 cm$^{-1}$ corresponds to the C-H stretching vibration of chlorophyll [20]. The carbonyl bond (C=O) appeared at 1630-1725 cm$^{-1}$. The functional group of C=O carbonyl and O-H hydroxyl at immersion temperature of 303 K were higher than other temperatures. It indicated that the carboxyl group (-COOH) at immersion temperature of 303 K has a bond with hydroxyl of TiO$_2$. It enhanced the effect of electrons coupling from dye molecules to the conduction band of TiO$_2$ that allows fast electron transfer. A higher immersion temperature showed the degradation of C-H dan C=O groups. The degradation of these groups affected the weak contact between dye molecule with the TiO$_2$ surface, thus blocking electron transfer.
The immersion temperature of 323 K resulted in degradation of dye that showing the low performance of DSSC. This is caused by the reduced number of molecules dye on the TiO₂ surface, thus the number of electrons is also low. This analysis also can be absorbed from the FTIR results that degradation of the -COOH group occurred at the immersion temperature of 323 K. It prevented the electron injection and finally the output current decreased.

4. Conclusion
The immersion temperature of chlorophyll sensitizer affected the optical and electrical properties of DSSC. The characteristic of absorption spectra showed the maximum photon, while the FTIR spectrum exhibited the highest peak percent transmittance at the immersion temperature of 303 K (ambient temperature), respectively. Hence, the chlorophyll sensitizer successfully maintain its stability, which the rate of electron injection in the TiO₂ conduction band was faster and more efficient. This condition was also supported by the highest efficiency of DSSC at the immersion temperature of 303 K, with the efficiency value was 0.04%. Eventually, the ambient temperature as the best condition to optimize the DSSC efficiency.

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