High Efficiency Dye Sensitized Solar Cell from *Tectona Grandis* and red *Crysanthemum Morifolium* as a Sensitizer

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Abstract. *Tectona Grandis* leaves and red *Crysanthemum Morifolium* have been used as sensitizers for dye sensitized solar cell (DSSC) using organic solvents by ethanol, citric acid, and distilled water in respectively with the ratio of 5 : 1 : 4. TiO$_2$ paste was spin-coated on top Indium Tin Oxide (ITO) conductive glass and calcinated at temperature of 450°C for 10 min. The chemical properties were analysis by using Fourier transform infrared spectroscopy (FTIR) indicated the presence of anthocyanin from *Tectona Grandis* leaves and red *Crysanthemum Morifolium* petal. The physical properties were analysis by using UV-Vis spectrophotometer was performed to measure the absorbance of dye solution in the visible spectrum range and X-Ray Diffractometer (XRD) was used to determine the structure of TiO$_2$/ITO and Dye/TiO$_2$/ITO. Among the three dyes studied, the mixed dye solution from *Tectona Grandis* leaves and red *Crysanthemum Morifolium* was shows the best photosensitization effects with the conversion efficiency is 0.834 %.

1. Introduction
Research activities in the field of energy especially for green sources which are renewable, low-cost, and eco-friendly increase every year [1], due to the limitation of energy sources from fossil fuel which is non-renewable. Ref. [2] described in detail about the availability of amount of the fossil fuel in the form of coal, natural gas, and crude oil are 1.139 billion tonnes, 187 trillion cubic meters, 1.707 billion barrels, respectively [2]. The energy crisis occurring revealed that the total energy demand was much higher than that the supply energy available from fossil fuel. To overcome these problems, solar energy is regarded as the most alternative energy source. Because it is a promising alternative energy sources which are available in every country around the world. In addition, solar energy is the most powerful sources of energy providing a continuous stream with solar radiation with approximately of 3x10$^24$J per year [1, 3]. One example of solar energy technology is photovoltaic. Photovoltaic solar energy is being widely studied as one of the efficient technology due to its ability to convert sunlight directly into electricity [3].

DSSC is kind of photoelectrochemical solar cell which is the third generation and working on the principle of plant photosynthesis [1, 4]. DSSC appeared immediately as a promising low-cost and eco-friendly photovoltaic technology since 1991 [1, 5]. Unlike the conventional systems, based on DSSCs function principle in both: light absorption and charge transport performed separately [4, 6]. The dye absorbs the photon energy, the electrons in the dye become exited and then injected to the conduction band of semiconductor. As a result, the dye becomes oxidized and then the electrolyte donates electron to the initial state of dye. The electrons move through the semiconductor to a current collector and
electrolyte restores its initial state by accepting electrons from the external circuit and the process is cyclic [1, 4].

Several previous works have been published in DSSC by utilizing natural dyes as sources of natural sensitizer [5]. Natural dyes were used in DSSCs because of their availability and easy extraction, nontoxicity, complete biodegradability, and temperature compatibility [1, 5]. Several of natural dyes have been extensively investigated as a sensitizer for DSSC such as anthocyanin, tannin, carotene, betalain, and chlorophyll [5], but only anthocyanin is responsible for cyanic colors [1]. Many studies utilized anthocyanin as sensitizer for DSSC. Abdou et al. (2013) used anthocyanin from Hibiscus Sabdariffa L. and they reported that the conversion efficiency was 0.27 % ; Ayalew & Ayele (2016) also used anthocyanin from Acanthus sennii chiovenda flower as a sensitizer with the conversion efficiency of 0.150 % [7, 8].

Tectona Grandis leaves and red Chrysanthemum morifolium contain an anthocyanin that can be utilized as a sensitizer. Recently, the utilization of the Tectona Grandis leaves waste in everyday life is not maximized so that it would be wasted. The purpose of the present study is fabrication DSSCs were prepared with natural dyes extracted from Tectona Grandis leaves. Red Chrysanthemum morifolium petal is another natural dye that used in this study. Furthermore, Tectona Grandis leaves and red Chrysanthemum morifolium petal has been selected due to its widely available in Indonesia.

2. Experimental

2.1 Preparation of Dye Extraction

Tectona Grandis leaves and red Chrysanthemum morifolium petal were washed with distilled water and cut into small pieces about 2 cm. They were dried in the open air for three days then ovened them at 40°C for an hour and crushed into fine powder by using a blender. Infrared spectroscopy was carried out on IRPrestige-21 FT-IR spectrometer (Shimadzu Corp, Japan) equipped with a bright ceramic light source, a KBR beamsplitter, and deuterated triglycine sulfate doped with L-alanine (DLATGS) detector. The measurements of the sample were collected over the range of 4000-500 cm⁻¹ and 16 co-added scans. All spectra were in Transmittance units.

Organic solvents was made by ethanol, citric acid, and distilled water in the ratio 5 : 1 : 4. 10 gr dye powders were mixed with 35 ml organic solvents for Tectona Grandis and 20 ml for red Chrysanthemum Morifolium using a magnetic stirrer for 30 minutes. The solution was stored in the dark room and covered with aluminum foil for 24 hours then filtered. Each solution with the ratio of 50 : 50 were mixed using a magnetic stirrer for 30 minutes used as mixed dye. The absorbance of the dyes in this study was determined by UV-2600 Series (Shimadzu Corp, Japan).

2.2 Preparation of Working Electrode

1 gr TiO₂ powders were mixed with 8 ml ethanol in a beaker and stirred using a magnetic stirrer for 30 minutes to form TiO₂ paste.

The conductive side of ITO glass was determined by a multimeter. A size of 2.1x2.1 cm² area on the conductive glass was made by using scotch tape to cover the four-sided border. Applying a few drops of the TiO₂ paste until the conductive side of the ITO glass surface was covered evenly by spin coating method at 3000 rpm for 30 seconds, then processed was repeated in three times. Then sample was calcined in low oxygen environment at temperature of 450°C for 10 minutes to solidify TiO₂. The X-ray Diffraction (XRD) spectra was collected (Shimadzu 7000) with Cu Kα radiation (λ =1.5405 Å) over the anguler range 15° ≤ 2θ ≤ 80°, operating at 30 kV and 10 mA. It was performed to examine the crystallinity of the TiO₂/ITO.

The TiO₂/ITO was directly immersed in the each dye solution extracted for 24 hours in the dark environment at room temperature for good adsorption of the dye on the TiO₂ surface. The Dye/TiO₂/ITO was rinsed with distilled water to remove non-adsorbed dyes and excess water from porous TiO₂ and then dried for several minutes in the open air. The sample was characterized by XRD again to examine the crystallinity of Dye/TiO₂/ITO.

The electrolyte solution was prepared by mixing 0.8 gr Potassium Iodide (KI) and 10 ml Polyethylene Glycol (PEG) in a beaker and added by 0.127gr Iodine (I₂) then stored in a sealed bottle.
2.3 DSSC Assembly

Another ITO glass was coated with graphite on the conductive side. Apply electrolyte solution on the graphite/ITO side until surface of the sample covered. Then DSSC was assembled to form a sandwich by placing the working electrode face to face with the counter electrode. The two pieces of ITO glass were clamped on the opposite side. The DSSC were tested under natural sunlight and the intensity of sunlight was measured by LIGHTMETER CA813 AEMC.

3. Result And Discussion

3.1 XRD Characterization

Figure 1 shows the XRD pattern of TiO2 nanomaterial which has been coated on top of conductive side of ITO glass and calcined at 450°C for 10 minutes. This result indicates high intensity of the main peak due to the absorption of the anthocyanin dye on the TiO2 surface. While figure 1 (b), (c), and (d) represent the Tectona Grandis, red Chrysanthemum morifolium, and mixed dye were absorbed on the TiO2 nanomaterial surface. Table 1 shows intensity of the main peak after adsorption of dye on the TiO2 nanomaterial surface compared with peak of pure TiO2. For more clear the difference of pure TiO2 and TiO2 which has been immersed into dye as shown in the Table 1. All peaks of TiO2 are anatase structure as in Figure 1 (indicated by A). The intensity and the crystal orientation of the main peaks of TiO2 shows increased after absorption of dye solution compared with pure TiO2. This result is comparable with the previous research which is reported by Al-Alwani et al. (2017) [9].

Figure 1. XRD of (a) Pure TiO2, (b) TiO2 + Tectona Grandis, (c) TiO2 + Red Chrysanthemum morifolium, and (d) TiO2 + Mixed dye. We have added symbol A indicated the anatase structure and crystal orientations for pure TiO2.

3.2 FTIR Characterization

Figure 2 shows the FTIR spectrum was recorded in the range from 500 – 4500 cm⁻¹. Spectra of TiO2 confirms the –OH group stretching appears at wavenumber of 3419.79 cm⁻¹ with low signal. Thus C-H bonds of the aromatic ring at wavenumber of 2926.01 cm⁻¹ with moderate intensity. Then,
the C=C bonds of an alkene compound type seen at wavenumber 1645.28 cm\(^{-1}\), while at 1514.21 cm\(^{-1}\) – 1541.12 cm\(^{-1}\) indicate C=C bonds of the aromatic ring compound type. The existence of O-Ti-O bond which is shown by a broad wavenumber from 490 cm\(^{-1}\) to 800 cm\(^{-1}\).

Spectra of Tectona Grandis and red Chrysanthemum morifolium exhibit a wide and strong band at 3414 cm\(^{-1}\) which is related to the –OH stretching. At wavenumber 2920.23 cm\(^{-1}\) was shows the sharp peak and at 2852.72 cm\(^{-1}\) shows small shoulder which is related to the C-H bonds stretching vibration. C=O bonds stretching vibration at wavenumber of 1735.93 cm\(^{-1}\) and 1732.08 cm\(^{-1}\) while C=C bonds at 1647.21 cm\(^{-1}\) and 1668.43 cm\(^{-1}\), C-H bonds of an alkene compound type at 1361.74 cm\(^{-1}\) – 1452.40 cm\(^{-1}\) (bending vibration). At wavenumber from 1098 cm\(^{-1}\) to 1246 cm\(^{-1}\) were found the stretching vibration of C-O due to presence of some esters [10]. The band at 775.38 cm\(^{-1}\) and 763.81 cm\(^{-1}\) indicated the bending vibration of C-H. The IR spectra of extracts are shows existence of C=O, C-H, and C-O bands that contribute to coloring components in Tectona Grandis and red Chrysanthemum morifolium extracts which is indicated the existence of the anthocyanin [11].

Figure 2. FTIR spectra of (a) TiO\(_2\), (b) Tectona Grandis, and (c) Red Chrysanthemum morifolium. The anthocyanin structure exist in C=O, C-H, and C-O bond.

3.3 UV-Vis Characterization

Figure 3 compares the absorption spectra of natural dye solutions extracted from Tectona Grandis leaves, red Chrysanthemum morifolium, and mixed dye. The results exhibited the absorption at the visible region of light spectrum. To be more specific, broad absorption band of Tectona Grandis leaves in the range 400-480 nm with an absorption peak at 420 nm, broad absorption band of red Chrysanthemum morifolium in the range 400-490 nm with an absorption peak at 440 nm, and mixed dye showing a sharp absorption at 460 nm with the broad absorption band in the range 500-580 nm with an absorption peak at 532 nm. The differences in the absorption spectra of dyes may due to the different colors of the pigments present in them [10]. Common peak of anthocyanin pigments at 500–600 nm which is the main characteristics [8].
Figure 3. UV-Vis absorption spectra of dye solution (a) Tectona Grandis, (b) red Chrysanthemum morifolium, and (c) Mixed dye

3.4 Conversion Efficiencies

Table 2 shows the cell output and conversion efficiencies of DSSCs sensitized by three kinds of natural dyes. The power conversion efficiency (η) from the data in Table 2 was calculated by using the following expression.

\[
\eta = \frac{P_m \text{ (mW/cm}^2\text{)}}{\text{Light intensity (mW/cm}^2\text{)}} \times 100 \%
\]

From the table can be concluded that the extract from mixed dye performed slightly better than the two other dyes. Mixed dye was found to have the highest efficiency of 0.834 % while Tectona Grandis and Chrysanthemum morifolium is found to be 18.92 x 10^{-4} % and 37.99 x 10^{-4} % respectively. Mixed dye shows higher efficiency than previous research used Hibiscus sabdariffa L. (0.27 %) and Acanthus semnii chiovena flower (0.150 %) which are reported by Abdou et al. (2013) and Ayalew & Ayele (2016), respectively [7, 8].

4. Conclusion

In this research, fabrication and characterization DSSCs have been successfully prepared from TiO₂ nanomaterial and extract Tectona Grandis leaves and red Chrysanthemum morifolium as a dye. The extracted dyes contain anthocyanin as the major coloring. Among the three dyes studied, the extract obtained from mixed dye has shown the best photosensitization in this study with the highest efficiency of 0.834 %.

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