The chemical bonds effect of anthocyanin and chlorophyll dyes on TiO$_2$ for dye-sensitized solar cell (DSSC)

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Abstract. Anthocyanin and chlorophyll dyes have been blended as the photosensitizer of Dye-Sensitized Solar Cell (DSSC). The results study showed the effect of chemical bond dyes on TiO$_2$ and the efficiency of DSSC. Ratio blend of the anthocyanin and chlorophyll dyes are 1:1. The absorbance of dyes and TiO$_2$ were characterized using UV-Vis Spectrophotometer. The chemical bonds contained in TiO$_2$- dyes were characterized using FT-IR spectrophotometer. The efficiency of DSSC was calculated using I-V meter. The absorption spectra of chlorophyll: anthocyanin blend dye solutions and TiO$_2$ films can increase after the dye adsorption. Absorbance characterization of anthocyanin and chlorophyll dye blend solutions showed three peaks at the wavelength of 412 nm; 535.5 nm; and 656.5 nm. Absorbance characterization of spinach before being blend with anthocyanin dyes solutions showed two peaks at the wavelength of 431 nm and 665.5 nm. The absorption spectra of TiO$_2$ films can increase after the dyes adsorption at the wavelength of 400 nm. FT-IR spectra of TiO$_2$ founded the functional groups C-Br, C=C, and O-H. The functional groups founded in anthocyanin: chlorophyll dye blended on the surface of TiO$_2$ are C-Br, C-O, O-H, C-H, C=C, C=O, and O-H. The result showed that the greatest efficiency of 0.0544% at dye red cabbage-spinach. Adsorption blends of anthocyanin and chlorophyll dyes on the surface of TiO$_2$ can be used as the photosensitizer for DSSC.

1. Introduction

Dye-sensitized solar cell (DSSC) is third generation solar cells that can convert photon energy into electrical energy$^{[1 - 4]}$. In general of DSSC, these devices are based on a nanostructured metal oxide film, sensitized by an adsorbed dye molecule to harvest the visible light. These cells are composed of three basic components: a dye sensitizer, which absorb visible light to generate excitons and transfer electrons from the excited state into the metal oxide conduction band$^{[5,6]}$; an electrons-transporting layer such as a metal oxide material$^{[5,7]}$, in which the injected electrons travel throughout the electrode. The dye is regenerated by an electron donor in the electrolyte solution$^{[5,8]}$.

In DSSC, the dye as a sensitizer plays a key role in absorbing sunlight and transforming solar energy into electrical energy. In DSSC, the sensitizers used such as the ruthenium complexes and the natural dyes$^{[9]}$. The highest efficiency of DSSC sensitized by Ruthenium complexes absorbed on TiO$_2$ reached 11-12%. Dyes are not cheaper but have also been reported to reach an efficiency as high as 9.8%$^{[10]}$. The natural dyes found in flowers, leaves, and fruits can be extracted by simple procedures. Several natural dyes have been employed as sensitizers in DSSC, such as
anthocyanin\cite{11}, chlorophyll\cite{12}, and carotene\cite{13}. Many researches have been developed kinds of natural dyes. Pratiwi et al. employed anthocyanin dyes from dragon fruit and red cabbage as the sensitizer in DSSC and reported conversion efficiency of 0.024\% and 0.054\%\cite{14}. Sengupta et al. reported that a conversion efficiency of 0.148\% was obtained using spinach leaves dye as sensitizer\cite{15}.

In this study, natural dyes were extracted from pigments of anthocyanin and chlorophyll such as dragon fruit, black rice, red cabbage, and spinach. These extracted dyes were characterized by UV-Vis spectrophotometer. The chemical properties of the DSSC using these extracts as sensitzers were investigated. The anthocyanin and chlorophyll dyes blended as the photosensitizer of DSSC. The results study expected to find the effect of chemical bonds dyes on TiO\(_2\) and the efficiency of DSSC.

2. Experiments

2.1. Preparation of TiO\(_2\) Paste

TiO\(_2\) pastes were prepared using TiO\(_2\) powder in ethanol. The TiO\(_2\) solution was stirred at 300 rpm for 30 minutes. TiO\(_2\) pastes that have been formed are inserted into the bottle covered with aluminum foil and stored in an area free from direct sunlight.

2.2. Preparation of Working Electrode

TiO\(_2\) pastes were deposited on the FTO conductive glass with an active area of 1 cm x 1 cm by spin coating technique. TiO\(_2\) films were annealed in a furnace at 400\°C for 10 minutes.

2.3. Preparation of Natural Dye Sensitizers

The materials used are natural dyes from dragon fruit, red cabbage, black rice, and spinach leaves which were cut into small pieces and mash in a mortar. The anthocyanin dyes were dissolved in acetic acid: quads: methanol solvents. The chlorophyll was dissolved in acetone solvent. It was stirred for 60 minutes at room temperature using vortex stirrer with a rotational speed of 300 rpm. It was kept for 24 hours. It was stored in closed containers and protected from the sun. Extract of anthocyanin and chlorophyll dyes solutions were filtered using filter paper quality no. 42, respectively. The dye solutions are evaporated using a rotary evaporator to get the more concentrated solutions. The anthocyanin dye solution blended with chlorophyll dye solution, respectively. Ratio blends of anthocyanin and chlorophyll dye are 1:1. The absorption spectra of dye solutions were characterized by using UV-Vis spectrophotometer 1601 PC.

2.4. Preparation of Counter Electrode

The counter electrode was prepared from platinum (Hexachloroplatinic (IV) acid 10\%) catalyst on the FTO conductive glass. FTO glass is heated using a hot plate at a temperature 250\°C for 10 minutes and then apply a platinum solution on the surface of the FTO glass. The glass that has been spilled by the platinum is directly cooled to room temperature.

2.5. Preparation of Assembly Sandwich DSSC

The working electrode and counter electrode were assembled into a sandwich type arrangement. The electrolyte solution has filled the space between the two electrodes. The DSSC were characterized using FT-IR spectrophotometer Shimadzu Prestige 21 and I-V meter Keithley 2602A.

3. Results and Discussions

3.1 Characterization of Dye

Characterization of absorbance and functional groups of dye were examined by using UV-Vis and FT-IR spectrophotometer. The results of absorbance spectra are shown in Figure 1 and 2.
Figure 1 presents the absorption peaks of anthocyanin dye solutions from dragon fruit, black rice, and red cabbage at the wavelength of 533 nm; 526.5 nm; and 529.5 nm. Before blending, the dye of dragon fruit has higher absorption as compared to the black rice and red cabbage. The absorption peaks of spinach dye solution at the wavelength of 431 nm and 662.5 nm. The absorption peaks of anthocyanin and chlorophyll blended dye solution at the wavelength of 412 nm; 535.5 nm; and 665.5 nm. The wavelength of the blend indicates that the blend contains anthocyanin and chlorophyll pigments. The graph in Figure 1 showed that the dye solution of black rice and spinach blend resulted in widest and highest of absorbance. The dye of blend was resulted in the lowest of absorbance than the spinach dye before blended. The results of absorption wavelength showed that the dye solutions can be used as the photosensitizer for DSSC because they appeared the absorption of the visible region. The dye solutions contribute to the absorbance at the absorption peak each.

Figure 2 shows the absorption spectra of TiO₂ films can increase after the dye adsorption at the wavelength above 400 nm. The dye of red cabbage and spinach blended on the surface TiO₂ resulted in the highest of absorbance than the others of dyes was presented in Figure 2. The results of this study showed that the dye adsorption on the surface TiO₂ could be used as the photosensitizer for DSSC
which absorbed the light from visible region. Danladi et al. reported that the chemical adsorption of these dyes is accepted to occur because of the formation of bond with the surface of nanostructured TiO$_2$[17].

The chemical structure of anthocyanin dyes from red cabbage, black rice, and dragon fruit before blended are shown in Figure 3. The dye of dragon fruit anthocyanin resulted in the lowest of intensity than the other of anthocyanin dyes and spinach chlorophyll dyes. The O-H bond is polar group appearing in the wave number at 3600-3200 cm$^{-1}$ forming both intramolecular and intermolecular hydrogen bonded so that the absorption of widened and shifts in wave numbers.

The FT-IR spectra of extracted anthocyanin and chlorophyll dyes blended are shown in Figure 4. The broad absorption at wave number range 3600-3200 cm$^{-1}$ arises due to the O-H stretching vibration of anthocyanin and chlorophyll dyes blended. The bond is represented by the appearance of weak bonds at wave numbers 1420-1330 cm$^{-1}$ caused in the plane O-H bending. The dye of red cabbage and spinach blend resulted in the highest of intensity. The sharp peak at wave number range 2700-2900 cm$^{-1}$ corresponds to the O-H stretching in aldehydes, where the O-H group of each molecule forms a hydrogen bond with the carbonyl group C=O molecules with dimer form. The hydrogen bond between the O atoms of the C = O aldehyde group will give rise to different OH bonds of strength, caused by the environment in which the hydrogen bonds are rather different for different molecules. The result will be a variety of OH stretching vibration at different frequencies. This peak at wave number range
3000-2900 cm\(^{-1}\) corresponds to the C-H stretching vibration of chlorophyll. The bending vibration of C-H asymmetric with medium intensity appeared on the region at 1485-1445 cm\(^{-1}\).

Infrared absorption appears at wave number 1725-1705 cm\(^{-1}\) resulting in the C=O stretching vibration. The dye of dragon fruit and spinach resulted in the lowest of polarity. Stretching of carbonyl group showed changes of dipole moment large enough so that the high of the intensity. The dye of black rice and spinach blend at 94.714% of transmittance in the region of double bonds of the stretching vibration caused by located of C=C absorption at 1680-1620 cm\(^{-1}\). This area is used for identifying olefins. Olefins are unsaturated hydrocarbons with a double bond between the carbon atoms. This is because olefins have a much higher of acidity as compared with the alkanes.

The compound in the fingerprint region placed at 1260-1000 cm\(^{-1}\) wave number, which shows medium intensity into strong intensity. The dye of dragon fruit and spinach blended has the highest of transmittance of 93.219% than the other dye. This is due to the plane vibrations which include the C-O bonds the absorption of frequency has a variable value. The position of the tape in the region at 680-500 cm\(^{-1}\) indicates the absorption of alkyl halide caused by the stretching C-Br. The dye dragon fruit and spinach blended has the highest of transmittance of 64.555% when compared with other dye. In this area, absorption cannot be made a diagnosis because the thin layer and dye samples are mixed with KBr powder during FT-IR testing. Based on the result of a UV-Visible spectrum and FT-IR spectrum it is concluded that the extracted compound is a blended of anthocyanin and chlorophyll.

3.2 Performance of DSSC
Characterization of the current-voltage (I-V) is a method to determine how much ability DSSC can convert light into electrical energy. The samples were illuminated with Xe light source of I-V meter. The light intensity was kept constant at 1000 W/m\(^2\) and active area of the cell exposed to light was 1 cm\(^2\) (1 cm x 1 cm). Photovoltaic test of DSSCs using these natural dyes as sensitizers are summarized in Table 1.

| Dye solution | \(V_{oc} (V)\) | \(I_{sc} (mA)\) | \(FF\) | \(\eta (%)\) |
|--------------|---------------|----------------|-------|-----------|
| Spinach      | 0.639         | 0.33           | 0.337 | 0.0713    |
| Black rice   | 0.580         | 0.126          | 0.272 | 0.0198    |
| Dragon fruit | 0.166         | 0.490          | 0.267 | 0.0217    |
| Red cabbage  | 0.191         | 0.641          | 0.353 | 0.0432    |
| Spinach leaves : Dragon fruits | 0.460 | 0.19 | 0.0298 | 0.0258 |
| Spinach leaves : Red cabbage | 0.565 | 0.29 | 0.0328 | 0.0544 |
| Spinach leaves : Black rice | 0.565 | 0.19 | 0.0341 | 0.0358 |

The efficiency of the DSSC sensitized by the spinach was significantly higher than the DSSC sensitized by other natural dyes before blended. It gives a \(I_{sc}\) of 0.33 mA, \(V_{oc}\) of 0.639 V, \(FF\) of 0.337 and efficiency of 0.0713%. After blended, the DSSC sensitized by spinach leaves: red cabbage was higher than the DSSC sensitized by other natural dyes. It gives a \(I_{sc}\) of 0.29 mA, \(V_{oc}\) of 0.565 V, \(FF\) of 0.0328 and efficiency of 0.0544%. This is because there are available bonds between the dye and TiO\(_2\) molecules through which electrons transport from the excited dye molecules to the TiO\(_2\) film[18]. This result indicates that the interaction between the natural dye sensitizer and the TiO\(_2\) film is significant in enhancing the energy conversion efficiency of DSSCs.

The results of the I-V test are supported by FT-IR test results (Figure 3 and 4) and UV-Vis spectra (Figure 2) showing that the absorption between the blended of dragon fruit and spinach dye, and black rice and spinach dye is almost the same. This is influenced by the few of the raised exciton and the low amount of charge that reaches the electrode when the cell is irradiated by low of intensity light. The few of charge reaches the electrode, caused by the length of the charge diffusion path so that many charges are recombined before it reaches the electrode. The measured parameters are influenced
by each of the sample compiler's active layers. In DSSC made from organic, the stability of the voltage is still low and experiencing a rapid voltage drop when illuminated by light.

4. Conclusion

The absorption spectra of dye adsorption on the surface of TiO$_2$ which was resulted in the highest absorbance of red cabbage and spinach blended. Based on the results of a UV-Visible spectrum and FT-IR spectrum it is concluded that the extracted compound is a blended of anthocyanin and chlorophyll. The results were efficiency for DSSC that the solar cells using red cabbage and spinach blended as the sensitizer have highest values of efficiency. The few of the raised excitons and the low amount of charge that reaches the electrode when the cell is irradiated by low of intensity light. The few of charge reaches the electrode, caused by the length of the charge diffusion path so that many charges are recombinde before it reaches the electrode. The efficiency was higher as the higher adsorption of the dye to the surface of TiO$_2$.

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