Mg doped anthocyanin from *Hylocereus costaricensis* peel for improved conversion efficiency of DSSC

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Mg doped anthocyanin from \textit{Hylocereus costaricensis} peel for improved conversion efficiency of DSSC

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Abstract. The performance of dye sensitized solar cell (DSSC) is mainly based on the dye as sensitizer. Natural dyes become one of the most commonly used because of its low cost and abundance in supply of raw materials. However, the efficiency of DSSC with natural dyes is low because of low conductivity. In this research, modification of natural dye has been studied by doping Magnesium (Mg) to anthocyanin from \textit{Hylocereus costaricensis} peel extracted with methanol, aquades, and acetic acid. Mg metal was obtained from MgSO$_4$.7H$_2$O salt at various concentration. This research resulted that the conversion efficiency of DSSC was increase and the optimum efficiency was obtained at 0.0924\% when using Mg doped dye with MgSO$_4$.7H$_2$O salt concentration of 0.01 M. Fourier Transform Infra Red Spectrophotometer analysis showed that anthocyanin dye with 0.01 M doping has lowest transmittance. This suggested that 0.01 M doping has greatest dipole moment change, so it become the most polar molecule and has good conducting electrical current.

1. Introduction
Solar cells are one of alternative developed to overcome the scarcity of energy that utilized solar energy to be converted into electrical energy. Solar cells become a very potential alternative because the solar energy reaching the earth's surface is very large, that is 700 megawatts in every minute [1]. Research on solar cells was developed for the purpose of obtaining high efficiency and low cost fabrication. In 1991, solar cell using dyes as photosensitizers was discovered and developed by Michael Gratzel, known as dye sensitized solar cell (DSSC). DSSC becomes a potential solar cell generation because of its low cost and abundance in supply of raw materials [2].

There are 2 types of dye used as a sensitizer, synthetic and natural dye. Synthetic dye uses ruthenium-based materials, and natural dye is obtained by extracting plant parts, such as leaves, fruits, or flowers to obtain chlorophyll, carotene, or anthocyanin. Efficiency of DSSC with syntetic dye is higher than natural dyes, however it is high cost in production. Natural dyes are low cost and various colour [3]. So, research of DSSC with natural dye still developed to increase efficiency by modifying parts of DSSC.

Modifications are performed on each part of the DSSC: working electrode, counter electrode, electrolyte, or dye. Research of modification natural dye with metal doped had been studied by Prasada in 2016 which Fe doped anthocyanin dye from \textit{Oriza sativa glutinosa} and resulted increasing efficiency of DSSC up to 900\% [4]. Based on this reference, in this research, modification of dye has been studied by doping metal to natural dye to increase efficiency of DSSC. This research used anthocyanin dye from waste of \textit{Hylocereus costaricensis} peel with Mg doped from MgSO$_4$.7H$_2$O salt.
2. Experimental Methods

2.1 Dye Extraction and Doping Metal
This research used anthocyanin from *Hylocereus costaricensis* peel extract and doped Magnesium from Magnesium Sulphate Heptahydrate (MgSO₄·7H₂O) salt at various concentration. 25 grams of *Hylocereus costaricensis* peel was crushed using a blender and extracted by methanol, acetic acid and distilled water with the ratio of 50 ml:8 ml:42 ml. The mixture stirred at 300 rpm in an hour, then it was filtered and concentrated by Rotary Evaporator. Dye then added by MgSO₄·7H₂O at various concentration, 0.005, 0.01, 0.05, and 0.1 M.

2.2 Preparation of Working Electrode
TiO₂ paste made by mixing 0.5 grams of TiO₂ nanopowder with 10 ml of ethanol then stirred by 300 rpm in an hour. Then it deposited on size 0.5 cm x 1 cm of FTO substrate by spin coating method. Working electrode then annealed on Furnace Carboloyte at 400°C in 10 minutes then cooled at room temperature. Working electrode tested by FTIR Spectrophotometer to identify the chemical bond.

2.3 Preparation of Counter Electrode
Counter electrode made by deposited Platina solution on FTO glass. Platina solution made by mixing 1 ml of Platina Hexachloroplatinic (IV) acid solution and 100 ml of isopropanol and stirred at 300 rpm in 30 minutes. The solution then deposited on FTO glass by brush painting method.

2.4 Preparation of Electrolyte
Electrolyte made by mixing 0.8 grams of potassium iodide (KI) and 10 ml of polyethylenglikol (PEG) 400 as the first solution, and mixing 0.127 grams of iodine (I₂) dengan 10 ml polyethylenglikol (PEG) 400 as the second solution. Each solution stirred at 300 rpm in 30 minutes. Solutions then mixed and stirred at 300 rpm in 30 minutes.

2.5 Assembly of DSSC
Working electrode and counter electrode assembled by sandwich structure. Electrolyte injected between two electrodes. DSSC then characterized current and voltage (I-V) by Keithley I-V meter with Xenon lamp intensity of 1000 watt/m² as solar simulator to identified capability of DSSC on converting light energy.

3. Result and Discussion

3.1 IR Spectra of Working Electrodes
Infrared spectra of working electrodes after soaked on dyes in various concentration of doping Magnesium showed in Figure 1, and identification of functional groups showed in Table 1. It showed that was anthocyanin on dyes by identified chemical bonds characteristic of anthocyanin. O-H groups identified at frequency of 1900 cm⁻¹, C=C groups at 1600 cm⁻¹, dan C-O groups at 1300 cm⁻¹. O-H compound on TiO₂ nanopowder obtained from ethanol used as solvent in preparation of TiO₂ paste [4]. The addition of MgSO₄·7H₂O in anthocyanin dye can also be identified, by the presence of S=O bond at frequency of 1100 cm⁻¹ [5] and Mg-O bond at range of 400-450 cm⁻¹[6].

Figure 1 showed that various concentrations of dye have similar curve of infrared spectra, however different in the value of transmittance. doping interfered molecular structure of dye, caused a change in dipole moment and resulted in different transmittance values [7]. Working electrode with doping 0.01 M had lowest transmittance value. It indicated highest absorbance, and greatest dipole moment change. So, it became most polar molecule, and polar molecule bonds are better in conducting electric current.
DSSC with Magnesium doped Mg of 0.01 M had lowest transmittance, resulted in the highest absorbance. The absorbtion efficiency, 0.2. DSSC with anthocyanin dye doped Mg 0.01 M was the optimum modification of Doped with concentration of 0.01 M has the largest area with a Voc value of 5.30 x 10⁻² volts and Isc of -1.8 x 10⁻⁴ Ampere. This indicated greatest efficiency. Efficiency of each variation showed in Table 2.

DSSC with anthocyanin dye doped Mg 0.01 M was the optimum modification and yield highest efficiency, 0.924%. This result supported by FTIR analysis showed that working electrode with dye doped Mg of 0.01 M had lowest transmittance, resulted in the highest absorbance. The absorption of

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**Figure 1. Infrared Spectra of Working Electrode by FTIR Analysis**

**Table 1. Identification of functional groups in IR spectra**

| TiO₂ | A | A + Mg 0.005 M | A + Mg 0.01 M | A + Mg 0.05 M | A + Mg 0.1 M | Group   |
|------|---|---------------|---------------|---------------|---------------|---------|
|      | cm⁻¹ | %T | cm⁻¹ | %T | cm⁻¹ | %T | cm⁻¹ | %T | cm⁻¹ | %T |cm⁻¹| %T |
| 3443.1 | 78.6 | 3404.5 | 44.8 | 3376.6 | 31.2 | 3397.8 | 21.1 | 3383.3 | 31.6 | 3373.6 | 24.1 | O-H    |
| 2383.2 | 91.0 | 2384.1 | 89.3 | 2304.1 | 94.3 | 2303.1 | 91.4 | 2386.1 | 84.8 | C-H    |
| 2348.4 | 90.7 | 2303.1 | 88.9 | 2302.1 | 83.8 |            |      |        |      |        |      |
| 2298.3 | 90.9 | 1912.5 | 84.5 | 1911.5 | 91.6 | 1912.5 | 90.8 | 1913.5 | 86.7 | C=C    |
| 1661.8 | 64.9 | 1662.7 | 38.3 | 1663.7 | 22.1 | 1663.7 | 41.9 | 1662.7 | 38.4 |        |      |
| 1635.7 | 63.9 | 1636.7 | 40.9 | 1637.6 | 22.2 | 1637.6 | 42.2 | 1636.7 | 40.6 |        |      |
| 1639.0 | 95.4 |        |      |        |      |        |      |        |      |        |      |
| 1383.0 | 86.6 | 1372.4 | 66.6 | 1372.4 | 61.7 | 1372.4 | 72.6 | 1372.4 | 68.8 | C-O    |
| 1325.2 | 80.7 | 1324.2 | 52.9 | 1325.2 | 39.4 | 1324.2 | 58.1 | 1323.2 | 53.7 | S=O    |
| 587.4  | 71.6 | 567.1  | 13.7 | 580.6  | 19.7 | 568.1  | 19.8 | 591.2  | 18.2 | Ti-O-Ti|
| 596.0  | 14.5 | 593.1  | 20.3 | 592.2  | 20.9 | 597.0  | 19.0 | 411.8  | 25.1 | Mg-O   |
|        |      | 412.4  | 25.0 | 431.1  | 26.3 | 433.0  | 17.6 | 416.6  | 17.7 |        |
|        |      | 447.5  | 13.8 |        |      | 427.3  | 16.9 |        |      |        |
|        |      |        |      |        |      | 436.9  | 16.5 |        |      |        |
photon energy increased, so excited electrons increased too. Increasing absorption also associated with greater molecular dipole moment change, so molecule became more polar and increased ability to conducting electrical current. Increasing absorption is also associated with greater molecular dipole moment change, so that the molecule becomes more polar and the ability to conduct electrical current is greater. This resulted in highest efficiency of DSSC.

**Table 2.** Photovoltaic parameters of DSSC with various concentration of doping Mg

| Characteristics | A + 0 M | A + 0.005 M | A + 0.01 M | A + 0.05 M | A + 0.1 M |
|-----------------|--------|------------|-----------|-----------|---------|
| Voc (Volt)      | 3.63 x 10^{-1} | 5.46 x 10^{-1} | 5.30 x 10^{-1} | 5.15 x 10^{-1} | 5.01 x 10^{-1} |
| Isc (Ampere)    | -1.63 x 10^{-4} | -7.29 x 10^{-5} | -1.8 x 10^{-4} | -2.16 x 10^{-4} | -1.2 x 10^{-4} |
| Vmax (Volt)     | 1.97 x 10^{-1}  | 3.49 x 10^{-1}  | 3.33 x 10^{-1}  | 3.33 x 10^{-1}  | 3.03 x 10^{-1}  |
| Imax (Ampere)   | -1.04 x 10^{-4} | -1.11 x 10^{-4} | -1.4 x 10^{-4}  | -1.37 x 10^{-4} | -8.40 x 10^{-5} |
| FF              | 3.46 x 10^{-1}  | 9.74 x 10^{-1}  | 4.78 x 10^{-1}  | 4.11 x 10^{-1}  | 4.20 x 10^{-1}  |
| η (%)           | 4.11 x 10^{-2}  | 7.75 x 10^{-2}  | 9.24 x 10^{-2}  | 9.14 x 10^{-2}  | 5.09 x 10^{-2}  |

4. Conclusion

In conclusion, increasing efficiency of DSSC by modifying anthocyanin dye from *Hylocereus costaricensis* peel doped Magnesium metal in various concentration successfully done. The optimum efficiency was obtained at 0.0924% when using Mg doped dye with MgSO₄·7H₂O salt concentration of 0.01 M. FTIR analysis showed that anthocyanin dye with 0.01 M doping has lowest transmittance. This suggested that 0.01 M doping has greatest dipole moment change, so it become the most polar molecule and has good conducting electrical current, so this resulted in highest efficiency of DSSC.

5. References

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