Performance of Natural Dye and Counter Electrode from Robusta Coffee Beans Peel Waste for Fabrication of Dye-Sensitized Solar Cell (DSSC)

T Setiawan, W Y Subekti, S S Nur’Adya, K Ilmiah, *S M Ulfa
Chemistry Department, Faculty of Science, Brawijaya University, Jl. Veteran Malang, East Java, 65145-Indonesia

Abstract. The DSSC prototype using activated carbon (AC) and natural dye from Robusta coffee bean peels have been investigated. The natural dye obtained from the extraction of Robusta coffee bean peels is identified as anthocyanin by UV-Vis spectrophotometer at maximum wavelength 219.5 nm and 720.0 nm in methanol. From the FT-IR analysis, the vibration of O–H observed at 3385 cm⁻¹, C=O at 1618 cm⁻¹, and C–O–C at 1065 cm⁻¹. The counter electrode prepared by calcined the peels at 300°C. Surface analyser of AC showed the larger surface area compared prior activation. The DSSC prototype was prepared using FTO glass (2x2 cm) coated with carbon paste in various thickness. The working electrode is coated with the TiO₂ paste. The optimum voltage measured was 395mV (300 μL of CA), 334 mV (200 μL AC), and 254 mV (100 μL AC). From this result, we understand that the thickness of counter electrode influent the voltage of the DSSC.

1. Introduction
Solar cell is a device which capable to convert solar light energy into electrical energy as photovoltaic system. Solar energy is one of the energy sources for solar cells. The study of solar cells was developed as the diminishing source of fossil energy. The type of solar cells is divided into inorganic-based and organic-based materials. The development of inorganic-based solar cells, such as by the used of silicon, GaAs, InP, CdTe, and other semiconductor materials were popular. Currently, conventional silicon-based solar cells have been able to achieve up to 30% efficiency. However, silicon solar cells have a very high fabrication cost cause the silicon must have in high purity. In addition, silicon is a very mine-stacked material [1,2].

Dye-Sensitized Solar Cell (DSSC) is one of the most promising strategy as an alternative energy since solar energy is unlimited. Although the efficiency is lower than conventional solar cells, DSSC have several advantages among others, such as, lower production costs and simple manufacturing process. The use of natural dye source is also the interesting factor since Indonesia has many natural products resources [3].

Anthocyanin and β-carotene were reported as prospective natural dye for DSSC. Anthocyanin found in extracts of strawberries, mangos teen skin, red spinach leaves, Rosella flowers, super red dragon fruit, purple sweet potatoes and black sticky rice [3,4]. Another potential biomass as a source of anthocyanin is red coffee skin waste. Coffee skin waste also contains natural antioxidants such as β-carotene, polyphenols and vitamin C [5]. Since the coffee production in Indonesia reached 675,882 tons and consist of 35% of coffee skin waste, it became a potential source for natural dye.
The most important factor for fabrication of DSSC is counter electrode which coated with platinum metal (Pt) as a catalyst. The comparative electrode is the electron capture electrode from the electrolyte so that the DSSC cell can produce an electric current. The use of Pt is considered less economical because the price is expensive, cannot be reuse and not environmentally friendly. Activated carbon is cheaper material that can be used to substitute Pt with almost equal effectiveness. Raw carbon from carbonization of biomass is reported to produce active carbon with a large surface area size and can be applied as a comparative electrode equivalent to Pt metal [6,7].

The mechanism of transfer electron on DSSC system using dye and TiO$_2$ is depicted in Fig. 1. Anthocyanin bind with TiO$_2$ to form complexes junction involved the carbonyl (C=O) and hydroxyl (O–H) groups causing excited electrons to be injected into TiO$_2$ band gap [3]. Here, we reported the used of Robusta coffee bean peels for the sensitizer source that is anthocyanin and activated carbon as counter electrode become DSSC based on natural resources. By varied the thickness of counter electrode from 100-300 µL/cm$^2$ gave 254-395 mV under the UV sunlight equivalent.

Figure 1. Structure of anthocyanin (a); complex binding anthocyanin–TiO$_2$ [3].

2. Experimental

2.1. Isolation of Anthocyanin

Coffee beans peel was dried under sunlight for four days and ground into a powder. Extraction of anthocyanin were carried out using methanol:citric acid:water in the ratio of 50:8:42 (v/v) for 24 hours. Residue and filtrate were separated using vacuum filtration. The excess of solvent was evaporated in vacuum. The crude anthocyanin extract was obtained in 12.23 mL/80 g.

2.2. Characterization of Anthocyanin Extract

Characterization of the extract was conducted using UV–Vis Spectrophotometry in methanol. Functional group of extract was identified using Fourier Transform Infrared Spectroscopy (FTIR) using NaCl window. The Liquid Chromatography Mass Spectroscopy (LCMS) was used for the identification of anthocyanin types based on mass analysis.

2.3. Fabrication of DSSC

2.3.1. Preparation of Carbon Active as Counter Electrode

After the extraction process, the solid waste from coffee beans peel is carbonated by drying and calcining at 300°C for two hours. The carbon was activated by stirring in HCl solution 0.1 M for three hours, followed by filtration. Drying the activated carbon in oven for three hours. Counter electrode was prepared from 0.3 g activated carbon and added with 5 mL ethanol. Activated carbon (AC) was characterized using Scanning Electron Microscope (SEM) to identify morphology and size distribution of compared with carbon. To prepare counter electrode, an activated carbon paste was deposited on the conductive substrate glass in various thickness (300 µL, 200 µL, 100 µL) and dried at 100°C for 15 min.
2.3.2. Preparation of conductive glass FTO coated with TiO$_2$

A fluorine-doped tin oxide (FTO) glass was used as conductive glass. FTO was first cleaned and coated with TiO$_2$ paste. The paste was prepared by diluted 2.8 g TiO$_2$ in 12 mL ethanol, stirred until homogeneous, then coated the paste on to FTO by slip casting method. Dried the layer at 350°C for 15 min. The conductive glass was then immersed into anthocyanin extract during 24 h. The working electrode and counter electrode were assembled into a cell. A drop of electrolyte solution containing triiodide injected in the cell and the hole of counter electrode was sealed using sealing spacer.

2.3.3. Characterization and measurement of voltage and current

The efficiency of DSSC was measured by multi-meter under halogen lamp (150 watt) as solar source model with radius 60 cm from the lamp. The test was conducted for various thickness counter electrode in FTO glass in 300 µL, 200 µL, 100 µL of the carbon solution.

3. Results and Discussion

3.1. Dye Characterization

The absorption spectrum of coffee beans peel extracts was measured using spectrometer UV–Vis 1601 Shimadzu on 200–800 nm. The result showed that the maximum wavelength at $\lambda_{\text{max}} = 219.5$ and 720 nm in the presence of methanol. This result showed the crude extract of coffee bean peels consist of anthocyanin properties [4]. From the analysis of UV-Vis spectrum showed that the extract can absorb not only ultraviolet but also visible region. It indicated that natural dye fulfil the characteristics to become potential dye sensitizers because it has absorption ability in the visible region under the illumination of the halogen lamp and also can convert light energy to electrical energy. The minimum energy needed by the electrons to the excitation states is around 720 nm then anthocyanin is suitable precursor for DSSC sensitizer.

![Figure 2. FTIR spectrum of natural dye](image)

Functional groups of natural dye from coffee beans peel extracts were identified by Spectrophotometer FTIR Shimadzu 8400S. Fig 2 showed that there are three specific functional groups were detected, that is, O–H group at 3380 cm$^{-1}$, C=O group at 1618 cm$^{-1}$ and C–O–C group at 1065 cm$^{-1}$. Analysis from FTIR confirmed the structure of anthocyanin which consist of benzene skeleton, conjugated double bond, carbonyl group, C–H bond, and O–H bond [8].
Structure identification was also carried out by LC-MS to identify the anthocyanin type based on its aglycon moiety. Fig. 3 showed that anthocyanin type is cyanidin with m/z 286.50. The aglycon type is identified as cyanidin-3-glucoside (m/z = 449), cyanidin-3-rutinoside (m/z=581), and cyanidin-3-sambubioside (m/z=595) as reported by Trikas, et al (2016) [9]. Cyanidin was more stable than another type of anthocyanin, especially cyanidin-3-glucoside.

![LC-MS spectrum of natural dye type](image)

**Figure 3.** LC-MS spectrum of natural dye type

3.2. Activated Carbon Characterization

Activated carbon (AC) was characterized using Scanning Electron Microscope (SEM) to identify surface morphology of the carbon, before activated (Fig. 4a) and after activated (Fig. 4b). The activated carbon has a uniform shape and small size distribution, while non-activated carbon has an irregular shape. The activated carbon has larger surface area and absorbs sensitizer effectively to reduce triiodide electrolyte solution to iodide, then the electron transport cycle is faster [6].

![SEM micrograph of (a) activated carbon and (b) non-activated carbon](image)

**Figure 4.** SEM micrograph of (a) activated carbon and (b) non-activated carbon
3.3. Voltage and Current Measurement

The measurement of voltage and current of DSSC prototype was done using digital multimeter and halogen lamp 150 watt. Halogen lamp can absorb visible area so that it is said to be analog with solar light. Table 1 showed the photovoltaic result from DSSC prototype using antocyanin and activated carbon in different thickness of counter electrode. Antocyanin gave high intensity and can absorb light due to cyanidin moiety is the most stable anthocyanin type [4].

On the other hand, the thickness of counter electrode influences the voltage of DSSC. The thicker the layer of the activated carbon provide the homogenous distribution of the pores. It would make triiodide as an electrolyte solution easily reduce to iodide, and then the cyclic of electron transport proceed faster than the thinner one in DSSC system. Anthocyanin as sensitized dye in DSSC system can also easily adsorb light from the solar energy. Therefore, the combination of anthocyanin and activated carbon from coffee beans peel is prospective material for DSSC system.

Table 1. Photovoltaic parameters for different samples

| No | Thickness variation of counter electrode | Volt (mV) | Resistance (mΩ) | Current (mA) |
|----|----------------------------------------|----------|-----------------|-------------|
| 1  | 300 µL                                  | 395      | 158             | 2.50        |
| 2  | 200 µL                                  | 334      | 199             | 1.67        |
| 3  | 100 µL                                  | 254      | 271             | 0.93        |

4. Conclusion

Coffee beans peel can be used for natural dye and counter electrode in DSSC system. The best result was obtained from 300 µL/cm² counter electrode with voltage 395 mV and 2.50 mA. The used of anthocyanin and activated carbon from coffee beans peel supposed to be the prospective material for improvement of DSSC system.

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