

Extraction, Preparation and Application of Anthocyanin Pigments from Mulberry using Polar Solvent in Various pH as Photosensitizer for Dye-Sensitized Solar Cells

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ABSTRACT

The purpose of this study is to evaluate the effect of polar solvent acetone and ethanol towards Morus nigra L. (Mulberry) anthocyanin dye extraction and suitable solvent sensitization of the same extracted dye on mesoporous titanium dioxide (TiO₂) for dye-sensitized solar cells (DSSCs) applications. Polar extraction solvent, namely acetone, ethanol and combination of polar protic and polar aprotic solvent of acetone and ethanol which containing of 0.5% and 1% hydrochloric acid (HCl) were employed to extract anthocyanin natural dye from Mulberry. The dye extraction effectiveness and dye active component was analysed using-ultraviolet-visible spectroscopy and fourier transform infrared. Then, the extracted dye sensitization over TiO₂ was monitored with current-voltage characteristic to obtain the cell power conversion efficiency. The DSSCs equipped with Mulberry extraction achieved the conversion efficiency in ranged of 0.0003% to 0.30%. Open circuit voltage and current densities obtained ranged from 0.024 to 0.574 V and 0.0023 to 0.352 mAcm⁻². The performance of the fabricated cells was investigated at various pH values in presence of acidic environment in Mulberry dye extractions. This work provide an insight into the importance of choosing a right medium for photosensitizer as well as the favourable solvent for mulberry anthocyanin dye adsorption on TiO₂ photoanode.

Keywords: Anthocyanin, Dye-sensitized solar cells, natural dyes, polar solvent

1. INTRODUCTION

Breakthrough of using dye sensitization occurred in 1991 at Laboratory of Photonic and Interfaces in Lusanne, Switzerland by Gratzel and his co-workers which was successful developed a solar cell that have a combination of nano-structured electrodes with efficient charge injection dyes [1], called as dye-sensitized solar cells (DSSCs). In DSSCs, a wide band gap semiconductor oxide materials acts as photoanode which accepts electrons from the dye sensitizer. The dye molecule regenerated by redox mediator system which regenerated electron at the counter electrode by the electron passing thorough the load [2]. Each component in DSSCs structure contributes towards the power conversion efficiency of the solar cell and the reliable design of DSSCs is always the optimization and compensation between of different components [3].

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The use of green energy materials (natural dyes) in the fabrication of DSSCs has proved to be an alternative source of energy production as it does not contain rare, harmful and inorganic material of metal [4]. Extensive study focusing using natural dyes as a dye sensitizer instead of using common dyes such as ruthenium (Ru) based complexes and synthetic dye. Natural dyes exhibit unique advantages, such as easy to prepare, low cost, no pollution to environment and have various colors of dyes which can appeared as multi-colored that responsible to be as semi-transparent solar cells [5] that reflecting to visible region [6].

Anthocyanin is one type of natural plant pigment that used as a photosensitizer in application of DSSCs. The structure of natural dyes or pigments used as sensitizer determines its attachment strength to the semiconductor surface. Previous study reported that the dyes or pigments contain of hydroxyl and carbonyl functional groups strongly bind on the surface of semiconductor oxide material such as titanium dioxide [7]. Solid-liquid extraction using polar solvents like methanol, ethanol and acetone under acidic conditions has been popular methods due to the recovery anthocyanins and phenolic compounds from the plant materials [8]. The most commonly solvent used for natural plant extraction are hydro-alcoholic solutions containing methanol, ethanol or acetone at composition of 70-80% in water [9].

Mulberry (*Morus nigra L.*) is one of the most important species of the genus *Morus* and *Moraceae* that was domesticated thousands of years ago and widely distributed worldwide. Study of chemical composition of Mulberry come into consideration due to the use of Mulberry in large extent for variety of purposes [9–11]. Mulberry fruits are rich in phytochemicals such as ascorbic acid, phenolic compounds, anthocyanins and other flavanoid compound [10] that ascertained by most of researchers. Previous study reported that Mulberry achieved power conversion efficiency 0.21% which shows that Mulberry have a potential as dye sensitizer in application of DSSCs [13].

The aim of this work to evaluate the effect of polar solvent ethanol and acetone on Mulberry dye extraction and optimization the function of dye extraction as a potential dye sensitizer in application of DSSCs. Mulberry is chosen due to availability in tropical areas as in native Malaysia climate. Two solvents base on polar protic and polar aprotic solvent index namely acetone, ethanol and combination of acetone and ethanol containing 0.5% and 1% hydrochloric acid were employed to extract Mulberry anthocyanin natural dye. The adjustment pH by adding HCl to the dye extract caused pigment absorption spectrum spreading [14] and could enhance the efficiency of DSSCs [15]. The performance of extraction and functional group of anthocyanin exists on Mulberry was analysed using UV-Vis spectroscopy and FTIR, respectively. The photovoltaic properties of the DSSCs were carried out under an incident irradiation of 100 mW/cm² light bulb. Photoelectrochemical analysis parameters including open-circuit voltage, short circuit current density, fill factor and conversion efficiency were determined to evaluate overall cell performance

2. EXPERIMENTAL METHODS

2.1 Preparation of anthocyanin dye extraction

The dye used in this work has been extracted from Mulberry (*Morus nigra L.*) (Figure 1(a)) that available from plants growing in the moderate Malaysia climate is selected. Mulberry fruit changes the colour from green to black purple through red with maturity [16]. Two major components of anthocyanins structure (Figure 1(b)) can be identified in Mulberry, namely, cyanidin-3-O-glucoside and cyanidin-3-O-rutinoside as the major components [17].

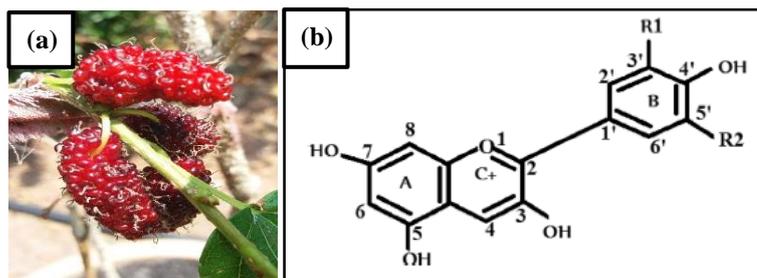


Figure 1. Images of (a) Mulberry (*Morus nigra L.*) and (b) general structure of anthocyanin pigment [18].

In order to determine the Mulberry anthocyanins extraction protocol, different solvent solution which are acetone and ethanol (v/v 1:2) and acetone were tested. 1g of fresh weight (f.w) Mulberry were grinded and homogenized in 30 mL of solvent. Then, the extracts was filtered using Whatman 125 mm filter paper, sonicated in an ultrasonic water bath for 10 minutes and the pH values of extracts were measured. To investigate the pH control (Table 1) on the DSSCs performance, the extraction of Mulberry was prepared by adding 0.5% and 1% HCl to the solvent during extraction process. All dye solutions were stored at 4°C in darkness condition until were used in order to avoid the degradation [19].

Table 1 Extraction solvent composition utilized in Mulberry extraction.

| Non-acidified extraction (%) | | Acidified extraction (%) | |
|------------------------------|--------|--------------------------------------|--------|
| Acetone (100, v/v) | pH 5.2 | Acetone: HCl (99.5:0.5, v/v) | pH 1.5 |
| | | Acetone: HCl (99:1, v/v) | pH 0.7 |
| Ethanol (100, v/v) | pH 5.7 | Ethanol HCl (99.5:0.5, v/v) | pH 1.6 |
| | | Ethanol: HCl (99:1, v/v) | pH 1.2 |
| Acetone-ethanol (100, v/v) | pH 5.5 | Acetone-ethanol: HCl (99.5:0.5, v/v) | pH 1.4 |
| | | Acetone-ethanol: HCl (99:1, v/v) | pH 1.0 |

2.2 Preparation of DSSCs device

Glass treated with Indium Tin Oxide (ITO) conductive glass sheet (2 × 2 cm) as photoanode, was first cleaned with acetone and ethanol for 30 minutes in each step using ultrasonic bath and rinse with DI water. Prepared slurry colloidal titanium paste (Evonik Degussa P25) was deposited onto ITO glass surface by doctor blade deposition technique employing glass rod and the prepared film was annealed on a hot-plate at 450°C. Thickness of the deposited films were in range of 12 to 15 μm. Counter electrode was prepared by holding conductive side of the ITO glass electrode with tweezers at the tip of a candle flame for 30 seconds. The black-carbon soot counter electrode was allowed to cool before used. Photoanode TiO₂ was sensitized by dipping in the dyes extraction for 20 minutes. Coated glass TiO₂/dye was rinse with water to get rid the any unattached dye molecules on the surface of the film and withdrawn from any solution under a stream of a dry air. Only the cells that have uniform colour of the TiO₂ surface were assembled as a DSSCs device. Cells were fabricated by placing the counter electrode above the dye-sensitized TiO₂ electrode in a sandwich technique and the gap between two electrodes were filled with the iodide/triiodide electrolyte. Overall assembling process of DSSCs was shown in Figure 2.

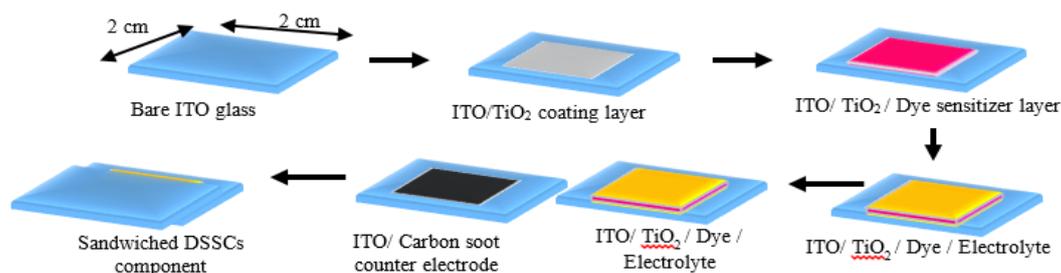


Figure 2. Graphical abstract of dye-sensitized solar cells fabrication.

2.3 Optical and photoelectrochemical characterization and measurement

Ultraviolet-visible spectroscopy (UV-Vis) absorption characteristic of Mulberry extracted were measured using PerkinElmer Lambda 950 UV-Vis-NIR. Absorbance of Mulberry anthocyanin extraction were recorded at wavelength 400 nm to 800 nm. All of measurements were made directly after the sample preparation. Absorbance reading were made against acetone, ethanol and mixture of acetone and ethanol, respectively. For each extraction, calibration curve was conducted before the sample were measured. Fourier transform infrared (FTIR) was used to probe the structure of dye molecules. FTIR spectra of dye extraction were measured between 4000 cm^{-1} and 400 cm^{-1} with a scan of 200 cm^{-1} at interval on a PerkinElmer FTIR spectrometer at room temperature.

For measuring performance of the dye as dye sensitizer in DSSCs, I-V characteristics were done using Keithley Semiconductor Parametric Analyzer (Keithley 2400) instrument under light bulb illumination of 100 mW/cm^2 and calibrated by using silicon reference photodiode. The conversion efficiencies of the DSSCs are calculated from the short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (ff) and the intensity of the incident light (P_{in}) according to equations (1) and (2), respectively.

$$ff = \frac{V_{max} \cdot J_{max}}{V_{oc} \cdot J_{sc}} \quad (1)$$

$$\eta (\%) = \frac{V_{oc} \cdot J_{sc} \cdot ff}{P_{in}} \times 100 \quad (2)$$

3. RESULTS AND DISCUSSION

3.1 Absorption spectrum of mulberry anthocyanin dye

All of the absorption peaks of mulberry extraction are closely related to the absorption peaks of anthocyanin which indicates anthocyanin is the major components of the observed pigments as reported earlier [19]. The UV-Vis absorption spectra of the mulberry extraction in polar aprotic solvent of acetone are shown in Figure 3. As can be seen from the Figure 3(a), mulberry extraction in acetone (MEA) solvent shows the presence of the two broader peaks at wavelength of 518 nm to 544 nm and 656 nm to 670 nm. There was a shifted peak and strong absorption peak at wavelength 508 nm in MEA with presence of 0.5% and 1.0% HCl. The absorption spectra shifted usually interpreted in terms of the different solvation interactions between the polar groups of the dye molecule and the solvent, and mainly depend on solvent polarity and hydrogen-bond [20].

Figure 3(b) display the adsorption spectrum MEA onto TiO_2 film. Absorption spectra of TiO_2 -MEA in 0.5% acid appear as higher peak which significant with absorption spectra of MEA (0.5% HCl).

Figure 4(a) and shows the absorption spectrum of Mulberry extraction in ethanol (MEE). MEE with 0.5% HCl shows the relatively higher absorbance peak than MEE with 1% HCl due to the optimum pH value of acidification of anthocyanin extraction which leads to a suitable protonation reaction and the equilibrium shifts from the quinonoidal to the flavylium form [21] and strong acid media may promote the hydrolysis of glycoside bonds [22]. MEE with 0.5% HCl resulted high intensity and strong peak at wavelength 537 nm, while MEE and with 1% HCl obtained the broader peak at 538 nm and 513 nm. When the MEE sensitized onto TiO_2 surface (Figure 4(b)), the results show significant spectra with the absorption of extraction which the MME (0.5% HCl) on TiO_2 shows the highest intensity results. The results of MEE shows different performance with MEA due to the effectiveness of polar aprotic for dye diffusion compare to polar protic solvent as the intensity of absorption decreases from acetone to ethanol [23].

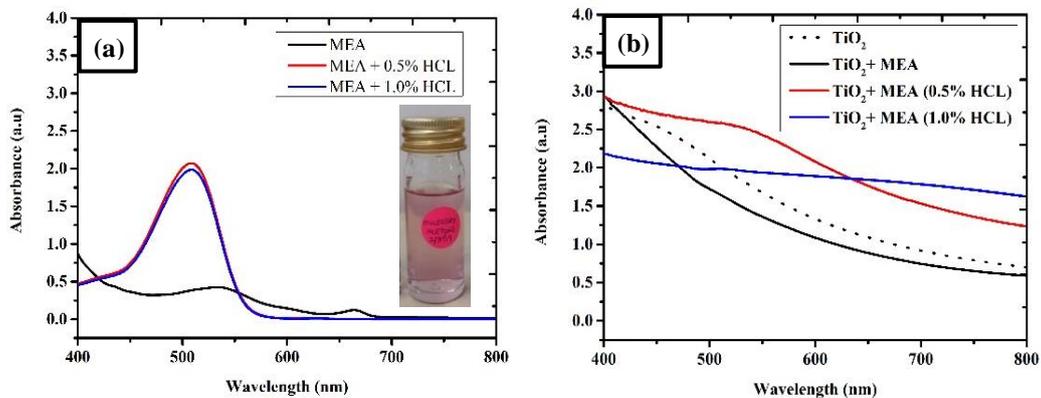


Figure 3. UV-Vis absorption spectrum of (a) Mulberry extraction in acetone (MEA) and (b) TiO_2 photoanode sensitized by mulberry extraction in acetone (MEA) in different acidity solvent.

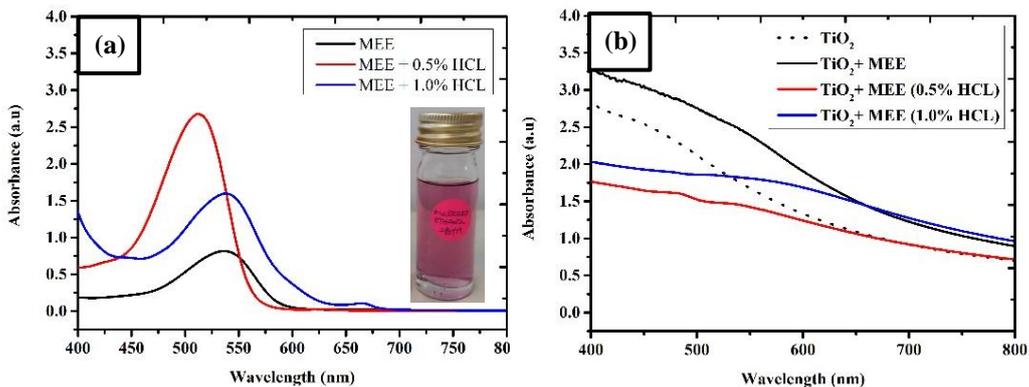


Figure 4. UV-Vis absorption spectrum of (a) Mulberry extraction in ethanol (MEE) and (b) TiO_2 photoanode sensitized by mulberry extraction in ethanol (MEE) in different acidity solvent.

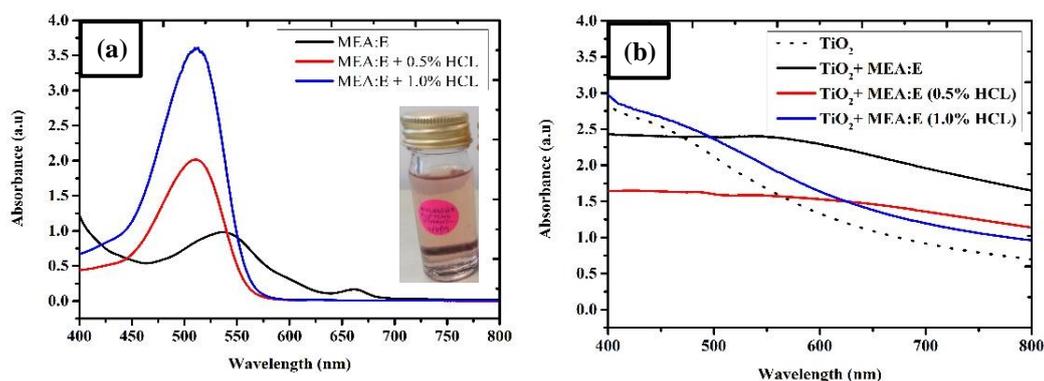


Figure 5. UV-Vis absorption spectrum of (a) Mulberry extraction in mixture of acetone and ethanol (MEA:E) and (b) TiO₂ photoanode sensitized by mulberry extraction in mixture of acetone and ethanol (MEA:E) in different acidity solvent.

Mulberry extraction in acetone-ethanol (MEA:E) solvent shows the presence of the two broader peaks at wavelength of 537 nm and 662 nm (Figure 5(a)). In presence of acid, MEA:E with 0.5% and 1% HCl shows a strong peak at wavelength 510 nm and MEA:E with 1% HCl shows the highest intensity that proved acidified extraction can enhance the performance of the dye as acidified solvents due to the sensitivity of pH anthocyanin of the extracted solvent and intense to improve the solubility of the anthocyanins extraction [9]. Figure 5(b) display the MEA:E onto TiO₂ photoanode. The mixture solvent in 1% HCl boost the performance of extraction when sensitized on TiO₂ surface. This stipulates that mulberry anthocyanin dissolves better in mixture of polar solvents acetone and ethanol. The UV-Vis spectra indicated that the stability of anthocyanins from mulberry pigment was strongly influenced by pH-value. However, increasing of pH resulted the anthocyanin occurs as a mixture of various equilibrium forms in proportions with unknown for practically all anthocyanins [16]. Combination factors will determined the optimal condition of the extraction in order to obtain suitable yield of anthocyanins [24] and also to achieve high effectiveness in extraction process [25]. Thus, the different of the absorption spectra in each solvent and pH indicated the stability of anthocyanins from mulberry. The addition of acid increase the colors intensity as acid can improve the stability of anthocyanin [26] as well as the identical component in the chemical structure [27].

3.2 FTIR spectra studies of mulberry anthocyanin dye

The plotted FTIR spectra of extracted mulberry in acetone (MEA) solvent is showed in Figure 6(a). In the FTIR spectrum of MEA, a strong and broad band at 3418 cm⁻¹ due to the bonded -OH groups. The peak between 2920 to 2933 cm⁻¹ is corresponds to the -CH stretching vibration. Without presence of acid in acetone solvent, the strong vibration was occurred at 1704 cm⁻¹ that assigned to the vibration of carbonyl (C=O) in anthocyanin. In presence of HCl acid, the peak was existed at 1600 cm⁻¹ which correspond to the C=C stretching vibration. However, the spectra shows the different of vibration peak in MEA with 1% HCl at nearly 1000 cm⁻¹, which cannot be explained.

As seen in Figure 6 (b), MEE with presence of acid environment resulted the same spectra pattern as without presence of acid. MEE shows the strong broad adsorbtion spectrum at 3311 cm⁻¹ that indicate the -OH streching. A small shoulder at 2974 cm⁻¹ peaks corresponds to the symmetric and antisymmetric -CH streching vibration modes of methyl and methylene groups [28], repsectively, was observed. Medium peak at 1414 cm⁻¹ attributed to the O-H bending, while a

strong peak at 1087 cm^{-1} is attributed to the C-O stretching vibrational modes of acid and carbohydrate groups. An examination of MEA:E (Figure 6(c)) reveals that the spectra exhibit broad absorption in the range of 3000 cm^{-1} to 3500 cm^{-1} with wide and strong band at 3391 cm^{-1} (without HCl), 3338 cm^{-1} (0.5% HCl) and 3348 cm^{-1} (1% HCl), respectively, which attributed to the -OH stretching and due to the wide variety of hydrogen bonding between OH groups. In presence of acid in MEA:E, the peak was existed at 2885 cm^{-1} that assigned to -CH stretching and a sharp peak at around 1650 cm^{-1} , corresponds to the C=C stretching vibration that can be correlated with the stretching of aromatic C=C in anthocyanin. In this spectrum also, a small shoulder in range of 1420 cm^{-1} which assigned to the -OH bending that occurred due to the presence of alcohol.

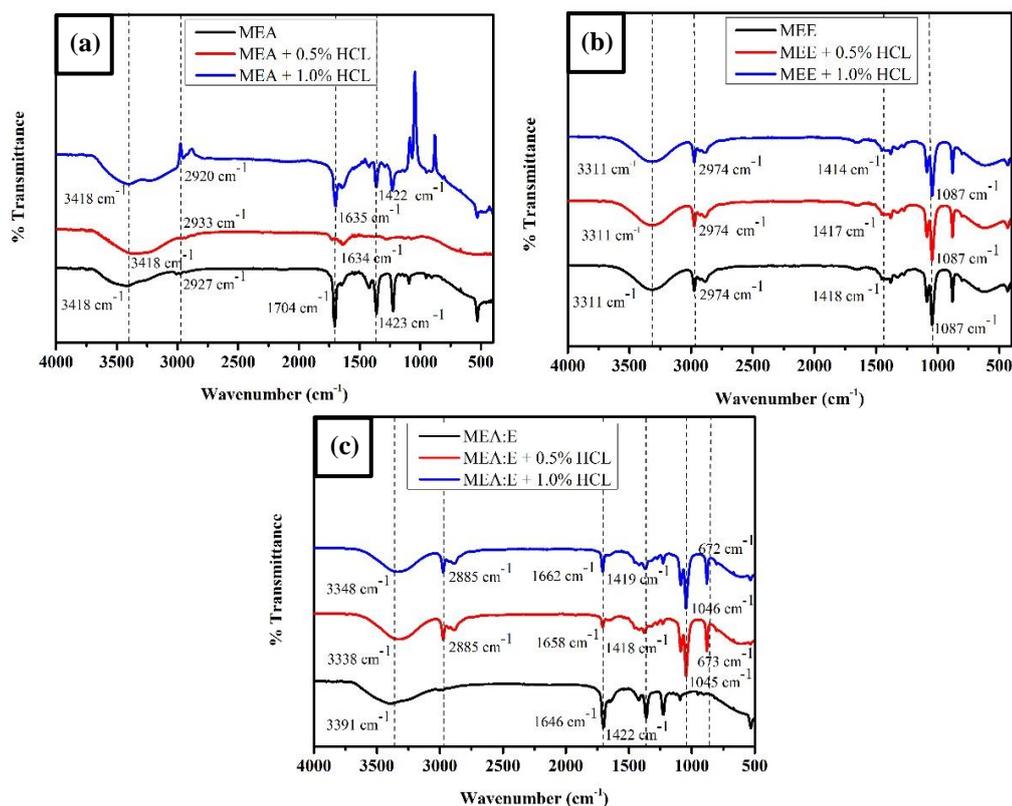


Figure 6. FTIR spectra of extraction in different solvent and pH; (a) Mulberry extraction in acetone (MEA), (b) Mulberry extraction in ethanol (MEE) and Mulberry extraction in mixture of acetone and ethanol (MEA:E)

As seen in Figure 6 (b), MEE with presence of acid environment resulted the same spectra pattern as without presence of acid. MEE shows the strong broad adsorbtion spectrum at 3311 cm^{-1} that indicate the -OH stretching. A small shoulder at 2974 cm^{-1} peaks corresponds to the symmetric and antisymmetric -CH stretching vibration modes of methyl and methylene groups [28], respectively, was observed. Medium peak at 1414 cm^{-1} attributed to the O-H bending, while a strong peak at 1087 cm^{-1} is attributed to the C-O stretching vibrational modes of acid and carbohydrate groups. An examination of MEA:E (Figure 6(c)) reveals that the spectra exhibit broad absorption in the range of 3000 cm^{-1} to 3500 cm^{-1} with wide and strong band at 3391 cm^{-1} (without HCl), 3338 cm^{-1} (0.5% HCl) and 3348 cm^{-1} (1% HCl), respectively, which attributed to the -OH stretching and due to the wide variety of hydrogen bonding between OH groups. In presence of acid in MEA:E, the peak was existed at 2885 cm^{-1} that assigned to -CH stretching and a sharp peak at around 1650 cm^{-1} , corresponds to the C=C stretching vibration that can be

correlated with the stretching of aromatic C=C in anthocyanin. In this spectrum also, a small shoulder in range of 1420 cm^{-1} which assigned to the -OH bending that occurred due to the presence of alcohol.

3.3 Photoelectrochemical properties

The most significant parameter to determine the performance of the sandwich-type solar cells using Mulberry dye extraction in different type of solvent (TiO₂-dye/electrolyte/carbon counter electrode) are the current density, J_{sc} , and open circuit voltages, v_{oc} were determined by obtaining the current-voltage potential curves displayed in Figure 7(a), Figure 7(b) and Figure 7(c). The short circuit current, density, open circuit voltages, fill factors and efficiencies extracted from these J-V curves are summarized in Table 2.

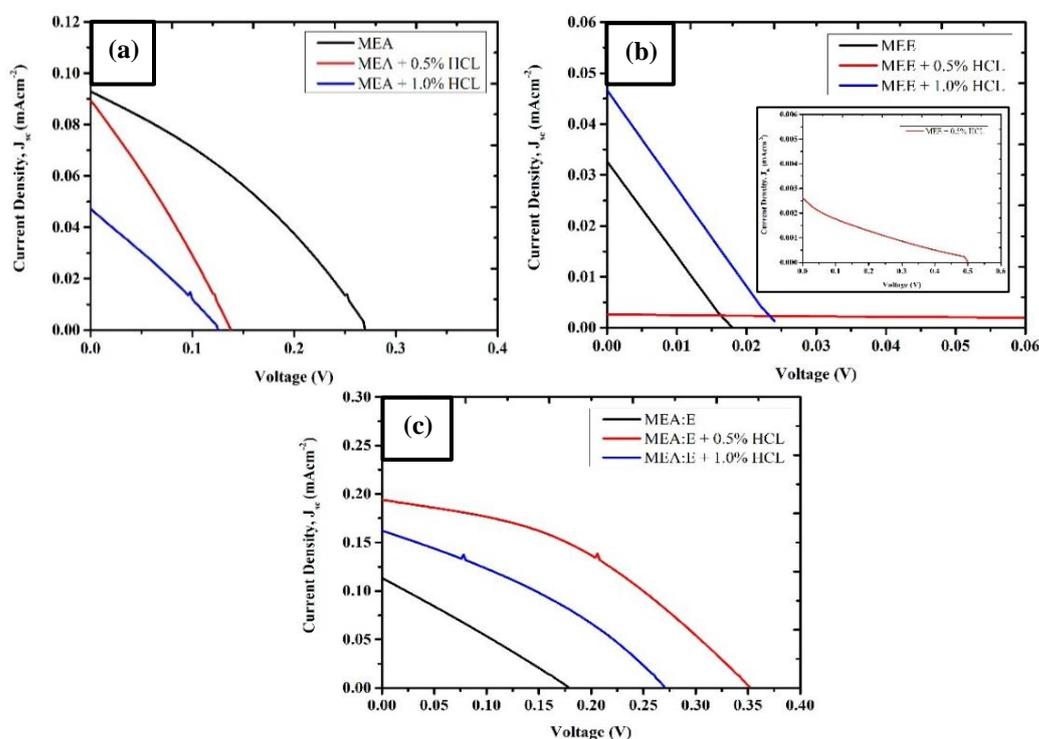


Figure 7. Photocurrent-voltage characteristics of DSSC fabricated with (a) Mulberry extraction in acetone (MEA), (b) Mulberry extraction in ethanol (MEE) and Mulberry extraction in mixture of acetone and ethanol (MEA:E)

Table 2 Effect of extracting solvent and pH in Mulberry extraction dye towards the DSSCs performance.

| Solvent | V_{oc} (V) | J_{sc} (mA cm ⁻²) | FF | η (%) |
|--------------|--------------|---------------------------------|---------|------------|
| MEA | 0.272 | 0.093 | 5.051 | 0.13 |
| MEA (0.5%) | 0.138 | 0.089 | 24.008 | 0.30 |
| MEA (1.0%) | 0.128 | 0.047 | 5.477 | 0.03 |
| MEE | 0.180 | 0.033 | 268.052 | 0.16 |
| MEE (0.5%) | 0.574 | 0.0023 | 0.176 | 0.0003 |
| MEE (1.0%) | 0.024 | 0.0467 | 139.841 | 0.16 |
| MEA:E | 0.180 | 0.114 | 1.399 | 0.03 |
| MEA:E (0.5%) | 0.194 | 0.352 | 1.832 | 0.12 |
| MEA:E (1.0%) | 0.272 | 0.162 | 1.887 | 0.08 |

As shown in Table 2, the efficiencies observed in this study significantly low compare to other type of dyes. The short circuit current obtained for the DSSCs sensitized with MEA, MEE and MEA:E without presence of acidic environment were, 0.093, 0.033 and 0.114 mAcm⁻², while the open circuit voltage ranged from 0.272, 0.180 and 0.180 V, respectively. The low performance of current densities of the cells may be attributed to the how fast the charge is injected into the conduction band of TiO₂ [29]. The conversion efficiency for the devices cell in acetone, ethanol and mixture of acetone-ethanol obtained the percentage power conversion of 0.13%, 0.16% and 0.03%, respectively. Previous research [13], [30], [31] also shows that DSSCs sensitized by natural dyes resulted low performance on conversion efficiency that might be due to the lack of available bond in between dye molecules with TiO₂ surface. As observed, in presence of acid, the device responded the different performance in all types of solvent. Obviously, the results shows the a significant impact of the pH on the device performance. As observed on Table 2, photovoltaic properties of the DSSCs sensitized with Mulberry in presence of acid on dye extracted shows the efficiencies in ranged of 0.0003% and 0.30%. It is obvious that there is significant impact of the pH on the cell performance. However, based on overall results obtained, the value of fill factor are higher than one which is not applicable for photovolatic device. Previous research also reported the highest one FF value which using red cabbage as a dye sensitizer [32]. The reason for this behaviour unclear and requires further investigation.

4. CONCLUSION

The implementation using muberry dyes shows the potential and the strong candidate of nature-based dyes to be apply in DSSCs application. Importantly, the results showed the optimal performance and condition of the dye extraction compared to other natural dyes employed so far by other groups. The absorption spectrum indicate the maximum peak in ranged of 450 nm to 550 nm in all types of polar solvent extraction. The FTIR ananlysis shows the presence of carbonyl (C=O) and hydroxyl group (-OH) functional active group in Mulberry dye which ascribed in anthocyanin pigment. The conversion efficiency achieved in this work ranged of 0.0003% to 0.30% which MEA (0.5% HCl) achieved as highest efficiency at pH 1.5. Based from the obtained results, proved that ethanol was not suitable solvent for mulberry extraction dye. Thus, it shows that extraction pH and solvent has a crucial impact on the fabricated cell. Low conversion efficiency might be due to the short time duration of dye adsorption which governs the amount of dye to be absorbed which influencing the overall cell performance. However, the scientific reason behind this kind of behaviour interaction between anthocyanin dye from mulberry and polar solvent medium still in questioned and the results demand some additional studies on mulberry dyes as photosensitizer.

REFERENCES

- [1] M. A. M. Al-Alwani, N. A. Ludin, A. B. Mohamad, A. A. H. Kadhum, and K. Sopian, "Extraction, preparation and application of pigments from Cordyline fruticosa and Hylocereus polyrhizus as sensitizers for dye-sensitized solar cells.," *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.*, vol. **179**, (2017) pp. 23–31, May.
- [2] R. Ramanarayanan, N. P., N. C.V., and S. S., "Natural dyes from red amaranth leaves as light-harvesting pigments for dye-sensitized solar cells," *Mater. Res. Bull.*, vol. **90**, (2017) pp. 156–161.
- [3] M. Shakeel Ahmad, A. K. Pandey, and N. Abd Rahim, "Advancements in the development of TiO₂ photoanodes and its fabrication methods for dye sensitized solar cell (DSSC)

- applications. A review," *Renew. Sustain. Energy Rev.*, vol. **77**, (2017) pp. 89–108.
- [4] L. K. Singh and B. P. Koiry, "Natural Dyes and their Effect on Efficiency of TiO₂ based DSSCs: a Comparative Study," *Mater. Today Proc.*, vol. **5**, no. 1, Part 2, (2018) pp. 2112–2122.
- [5] P. Gu, D. Yang, X. Zhu, H. Sun, and J. Li, "Fabrication and characterization of dye-sensitized solar cells based on natural plants," *Chem. Phys. Lett.*, vol. **693**, (2018) pp. 16–22.
- [6] M. A. M. Al-Alwani, A. B. Mohamad, A. A. H. Kadhum, and N. A. Ludin, "Effect of solvents on the extraction of natural pigments and adsorption onto TiO₂ for dye-sensitized solar cell applications," *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, vol. **138**, (2015) pp. 130–137.
- [7] M. A. M. Al-Alwani, N. A. Ludin, A. B. Mohamad, A. A. H. Kadhum, M. M. Baabbad, and K. Sopian, "Optimization of dye extraction from *Cordyline fruticosa* via response surface methodology to produce a natural sensitizer for dye-sensitized solar cells," *Results Phys.*, vol. **6**, (2016) pp. 520–529.
- [8] A. Zuleta-Correa, M. Chinn, M. Alfaro Córdoba, V. D. Truong, C. Yencho, and J. Bruno-Barcena, "Use of Unconventional Mixed Acetone-Butanol-Ethanol Solvents for Anthocyanin Extraction from Purple-Fleshed Sweetpotatoes," *Food Chem.*, vol. **314**, Dec. (2019) pp. 125959.
- [9] I. Salamon, R. Mariychuk, and D. Grulova, "Optimal Extraction of Pure Anthocyanins from Fruits of *Sambucus nigra*," *Acta Hort.*, (2015) pp. 73–78.
- [10] T. Bao et al., "Systematic study on phytochemicals and antioxidant activity of some new and common mulberry cultivars in China," *J. Funct. Foods*, vol. **25**, (2016) pp. 537–547.
- [11] M. Tomas, G. Toydemir, D. Boyacioglu, R. Hall, J. Beekwilder, and E. Capanoglu, "The effects of juice processing on black mulberry antioxidants," *Food Chem.*, vol. **186**, (2015) pp. 277–284.
- [12] Q. Jin, J. Yang, L. Ma, D. Wen, F. Chen, and J. Li, "Identification of polyphenols in mulberry (genus *Morus*) cultivars by liquid chromatography with time-of-flight mass spectrometer," *J. Food Compos. Anal.*, vol. **63**, (2017) pp. 55–64.
- [13] S. Suhaimi and M. M. Shahimin, "Effect of varied extracting solvent on stability and reliability of DSSCs using natural dyes as photosensitizer," *IEEE Student Conference on Research and Development*, (2014) pp. 1–6.
- [14] D. Sutikno S, Yulianti I, Saputra S, "An Investigation of pH Effects on the Properties of the Fabricated Banana Flower Extracts-based Organic Solar Cell," *Orient J Chem*, vol. **33**, no. 1, (2017).
- [15] I. J. Junger Sarah Vanessa, Meissner, Hubert, Grethe, Thomas, Pfeiffer, Anne Schwarz, Fiedler, Johannes, Herrmann, Andreas, Blachowicz, Tomasz, Ehrmann, Andrea, "Influence of the pH value of anthocyanins on the electrical properties of dye-sensitized solar cells," *AIMS Energy*, vol. **5**, no. 2, (2017) pp. 258–267.
- [16] C. Qin et al., "Analysis and Characterisation of Anthocyanins in Mulberry Fruit," *Czech J Food Sci*, vol. 28, Nov. (2009).
- [17] E. Espada-Bellido, M. Ferreiro-González, C. Carrera, M. Palma, C. G. Barroso, and G. F. Barbero, "Optimization of the ultrasound-assisted extraction of anthocyanins and total phenolic compounds in mulberry (*Morus nigra*) pulp," *Food Chem.*, vol. **219**, (2017) pp. 23–32.
- [18] N. Y. Amogne, D. W. Ayele, and Y. A. Tsigie, "Recent advances in anthocyanin dyes extracted from plants for dye sensitized solar cell," *Mater. Renew. Sustain. Energy*, vol. **9**, no. 4, (2020) pp. 23.

- [19] S. Suhaimi, N. M. Nasri, S. Wahab, N. S. Ismail, M. M. Shahimin, and Z. Sauli, "Ultraviolet-visible absorbance analysis on solvent dependent effect of tropical plant anthocyanin extraction for dye-sensitized solar cells," *AIP Conf. Proc.*, vol. **2203**, no. 1, Jan. (2020) pp. 20054.
- [20] S. Tadesse, "Natural dye-sensitized solar cells using pigments extracted from *Syzygium guineense*," *J. Photonics Energy*, vol. **2**, no. 1, (2012) pp. 027001.
- [21] W. A. Ayalew and D. W. Ayele, "Dye-sensitized solar cells using natural dye as light-harvesting materials extracted from *Acanthus sennii* chiovenda flower and *Euphorbia cotinifolia* leaf," *J. Sci. Adv. Mater. Devices*, vol. **1**, no. 4, (2016) pp. 488-494.
- [22] S. Silva, E. M. Costa, C. Calhau, R. M. Morais, and M. E. Pintado, "Anthocyanin extraction from plant tissues: A review," *Crit. Rev. Food Sci. Nutr.*, vol. **57**, no. 14, Sep. (2017) pp. 3072-3083.
- [23] C. O. Sreekala et al., "Influence of Solvents and Surface Treatment on Photovoltaic Response of DSSC Based on Natural Curcumin Dye," *IEEE J. Photovoltaics*, vol. **2**, no. 3, (2012) pp. 312-319.
- [24] K. A. Askar, Z. H. Alsawad, and M. N. Khalaf, "Evaluation of the pH and thermal stabilities of rosella anthocyanin extracts under solar light," *Beni-Suef Univ. J. Basic Appl. Sci.*, vol. **4**, no. 3, (2015) pp. 262-268.
- [25] N. T. R. N. Kumara, A. Lim, C. M. Lim, M. I. Petra, and P. Ekanayake, "Recent progress and utilization of natural pigments in dye sensitized solar cells: A review," *Renew. Sustain. Energy Rev.*, vol. **78**, (2017) pp. 301-317.
- [26] Z. M. Zin, N. Mohamad, C. K. A. H. Hui, N. I. Majid, and M. K. Zainol, "Effect of Acidified Ethanol on Antioxidant Properties of *Morinda citrifolia* Leaf Extract and Its Catechin Derivatives," *Curr Res Nutr Food Sci* 2021, vol. **09**, no. 1, (2021).
- [27] J. Ramirez-Perez, C. Maria, and C. P. Santacruz, "Impact of solvents on the extraction and purification of vegetable dyes onto the efficiency for dye-sensitized solar cells," *Renewables Wind. Water, Sol.*, vol. **6**, no. 1, (2019) pp. 1.
- [28] I. C. Maurya, P. Srivastava, and L. Bahadur, "Dye-sensitized solar cell using extract from petals of male flowers *Luffa cylindrica* L. as a natural sensitizer," *Opt. Mater. (Amst.)*, vol. **52**, (2016) pp. 150-156.
- [29] A. H. Ahliha, F. Nurosyid, A. Supriyanto, and T. Kusumaningsih, "Optical properties of anthocyanin dyes on TiO₂ as photosensitizers for application of dye-sensitized solar cell (DSSC)," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. **333**, (2018) pp. 12018.
- [30] N. Rosli et al., "Dyes extracted from *Hibiscus Sabdariffa* flower and *Pandanus amaryllifolius* leaf as natural dye sensitizer by using an alcohol-based solvent," *J. Phys. Conf. Ser.*, vol. **1755**, no. 1, (2021) pp. 12025.
- [31] N. A. Norhisamudin et al., "The Effect of Different Solvents in Natural Dyes from Roselle (*Hibiscus Sabdariffa*) and Green Tea Leaves (*Camellia Sinensis*) for Dye-Sensitized Solar Cell," *J. Phys. Conf. Ser.*, vol. **1755**, no. 1, (2021) pp. 12024.
- [32] R. Hemmatzadeh and A. Jamali, "Enhancing the optical absorption of anthocyanins for dye-sensitized solar cells," *J. Renew. Sustain. Energy*, vol. **7**, no. 1, Jan. (2015) pp. 13120.