International Journal of Nanoelectronics and Materials
Volume 15 (Special Issue) December 2022 [293-300]

The Effect of *Spinacia oleracea* Dye Absorption Time on ZnO-based Dye-Sensitized Solar Cells' Electrical Performance

Kaiswariah Magiswaran[1,2], Ili Salwani Mohamad[1,2,*b], Norsuria Mahmed[1,3], Mohd Natashah Norizan[1,2,*a], Siti Norhafizah Idris[1,2], and Zuraida Abal Abas[4]

[1]Geopolymer & Green Technology, Centre of Excellence (CEGeoGtech), Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia
[2]Faculty of Electronic Engineering & Technology, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia
[3]Faculty of Chemical Engineering & Technology, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia
[4]Fakulti Teknologi Maklumat dan Komunikasi, Universiti Teknikal Malaysia Melaka (UTeM), Melaka, Malaysia

ABSTRACT

Dye-sensitized solar cells (DSSC) have attracted much attention over the past 20 years due to their significance in energy conversion. However, the dye soaking time may significantly impact the efficacy of the photoanode semiconductor to carry the electronic charge to which the dye molecules adhere. An optimized dye soaking time may prevent the recombination of photo-excited electrons that are injected into the semiconductor of the DSSC. This study scrutinized the dependence of the zinc oxide (ZnO) photoanode soaking time of Spinacia oleracea (spinach) dye on the photocurrent-voltage characteristics. The ZnO film layer (photoanode) was prepared with commercial ZnO nanopowder and applied onto a fluorine-doped tin oxide (FTO) glass substrate using the doctor blade method. The prepared DSSCs' were subjected to a variety of characterizations, including current density-voltage (J-V) characterization, UV-visible characterization, scanning electron microscope (SEM), and X-ray diffraction (XRD). Comparing four variations of dye soaking time, ZnO-based DSSC photoanode soaked in the dye for an hour achieved an optimum efficiency of 0.03 %. This study proved that the efficiency of a DSSC can be improved by optimizing the dye soaking time.

Keywords: dye-sensitized solar cells (DSSC), natural dye, renewable energy, solar cells, spinach dye, ZnO

1. INTRODUCTION

Dye-sensitized solar cells (DSSC) use the photovoltaic effect to capture solar energy and transform it into electricity [1]. A photoanode (working electrodes), a counter electrode, an electrolyte, and a dye make up the DSSC [2, 3]. A DSSC's primary components, configuration, and straightforward operation are depicted in Figure 1. As the photoanode and counter electrode substrates, TCOs, the transparent conductive glasses, are used [4]. In addition, indium-doped tin oxide (ITO) and fluorine-doped tin oxide (FTO) has been extensively studied as metal oxides that can be used as photoanodes because of their transparent and conductive nature [5].

The DSSC's efficiency is affected by several factors, including the counter electrode material, dye materials, photoanode morphology, structure, and the type of electrolyte [6]. The photoanode controls the collection and transportation of photoexcited electrons from the dye molecules to the external circuit, rendering the material of the photoanode and the type of dye utilized in the cell the two most essential elements [7, 8]. Although titanium dioxide (TiO_2) has been utilized in DSSC photoanode commercially [9], zinc oxide (ZnO), on the other hand, has the potential to replace TiO_2 with the advantages of cost-effective, environmentally friendly, optically and

[*] [a] mohdnatashah@unimap.edu.my, [b] ilisalwani@unimap.edu.my

chemically stable, and recyclable [10]. The energy gap of the ZnO material (3.37 eV) [11] is very similar to TiO_2 (3.2 eV) [12], and the conduction band edge's energy level is at the same level as TiO_2's with similar electronic structures. ZnO with high exciton binding affinity (60 meV) [13], higher electron mobility (100 times larger than TiO_2), and a higher electron lifetime has been reported to efficiently absorb and transport photoexcited electrons from dye molecules to an external circuit.

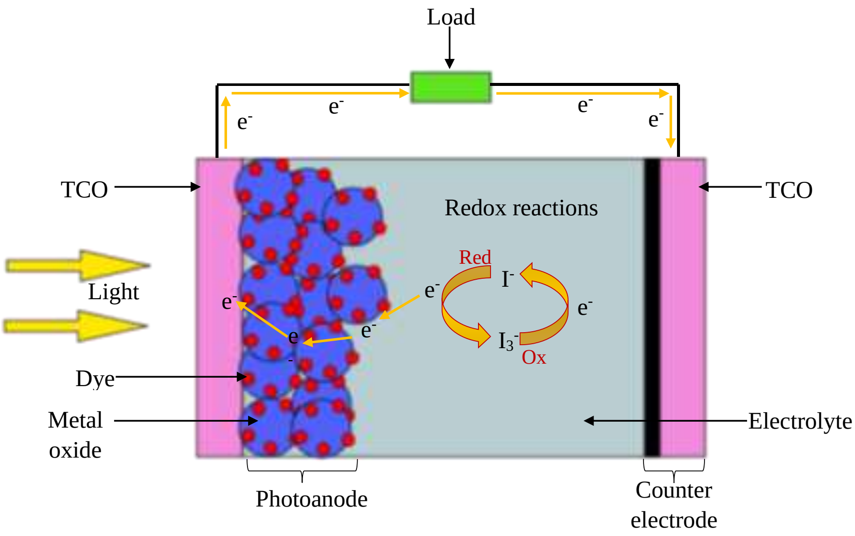

Figure 1. DSSC structure and the working principle [8].

The dye works as a molecular pump [14] in a DSSC and absorbs a range of visible light wavelengths [15]. Ruthenium (Ru) complexes, N719, and N3 dyes [16], used as a baseline for the DSSC, are the most reliable dye. However, Ru complexes have several drawbacks, including a high cost [14], heavy metals, and polluting the environment [13]. Therefore, researchers have been working on natural dyes derived from the colors of flowers, roots, fruits, and leaves [15]. Natural dyes are easily synthesized [13] and have a meager processing cost [15]. These dyes are abundant and biodegradable [11, 12, 14], making them environment friendlier than the Ru complexes, which consist of noble metals [17]. The low binding energy of natural dyes with semiconductor oxide [18] causes them to have a low photovoltaic response in DSSC; because of their high absorption coefficient, natural dyes are still considered an alternative for Ru complexed dyes [19].

In this paper, extracts of *Spinacia oleracea* were to be used as the natural dye onto the prepared ZnO photoanodes. *Spinacia oleracea* is commonly found in central and western Asia and is widely known as spinach. With the aid of an X-ray diffraction (XRD), UV-visible spectrometer (UV-Vis), scanning electron microscope (SEM), and photocurrent density-voltage (J-V) measurement, the optical and electrical characteristics of the constructed cells were investigated.

2. EXPERIMENTAL METHODS

2.1 Materials

In this study, fluorine-doped tin oxide (FTO) coated glass 7Ω/sq, zinc oxide nanopowder (Nanoshel, 99.5%), Triton X-100, N719 dye (Sigma Aldrich), ethanol, deionized water, and *Spinacia oleracea* (spinach) was used.

2.2 Preparation of Spinacia oleracea Natural Dye

10 g of fresh *Spinacia oleracea* leaves were cut and placed in a beaker with 0.1 L of deionized water and 0.1 L of ethanol, as illustrated in Figure 2(a). 5 g of sodium bicarbonate powder was added, and the solution was heated for an hour on a hotplate. The solid dregs were removed using a filter to obtain a pure and natural dye solution. As shown in Figure 2(b), the dye solution was kept in a sealed bottle at room temperature.

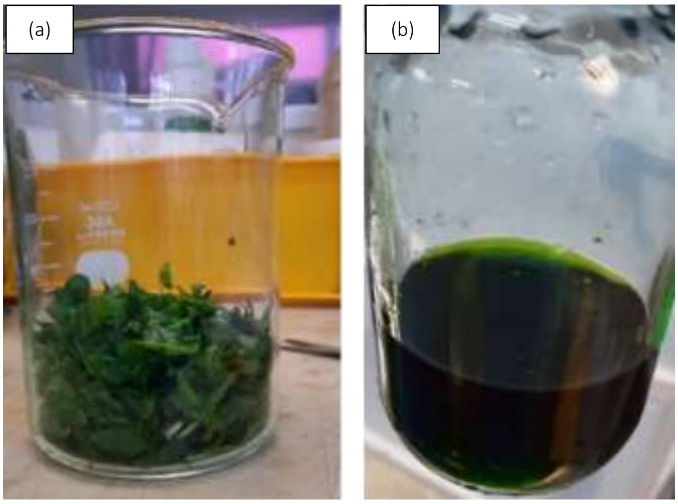

Figure 2. (a) *Spinacia oleracea* (b) Dye of *Spinacia Oleracea.*

2.3 Preparation of ZnO Photoanode

1 g of ZnO powder, 2 ml of deionized water, and 1 ml of ethanol were added and stirred until a paste was formed. Next, two drops of Triton X-100 were added. In a precleaned FTO glass (25 mm x 25 mm), boundaries were made using scotch tape, and the active area of the DSSC was 225 mm^2. The prepared ZnO paste was spread onto the conductive side of the FTO glass. Doctor blade method was used to apply the paste. The film was then annealed for one hour at 450 °C in the furnace after being soft-baked for 10 minutes at 150 °C. The film was then placed in the prepared *Spinacia Oleracea* dye for 30 minutes, one hour, two hours, and 24 hours.

2.4 The Assembly of DSSC

Three drops of iodine solution were added to the carbon counter electrode prepared (cleaned FTO glass was coated with the soot from a burning candle). Next, the dye-soaked photoanode and the carbon counter electrode were combined and sealed using parafilm. The excessive iodine solution was wiped off from the edges.

2.5 Characterization of the DSSC

The fabricated samples were analyzed using different characterization methods. X-ray diffraction (XRD) and scanning electron microscope (SEM) were used to examine the ZnO photoanode's crystallographic structure and surface morphology. The UV-Visible spectroscopy (Lambda 950) was utilized to examine the *Spinacia oleracea* dye's absorption spectra. Solar Simulator was used to investigate the electrical properties of the developed DSSC. Xenon lamp power supply (XPS-1600, Solar Light) provided a 1000 W/m^2 (A.M. 1.5G) light that imitated solar energy for the DSSC.

3. RESULTS AND DISCUSSION

3.1 Surface Morphology

Figure 3 shows the ZnO photoanode's surface morphology. Mesoporous ZnO photoanode composed of commercial ZnO nanoparticles was prepared by the doctor blade method onto the FTO glass substrate. Figures 3(a) and 3(b) show the ZnO photoanode's surface morphology and cross-section. 23.98 μm ZnO film thickness of ZnO was observed through this measurement.

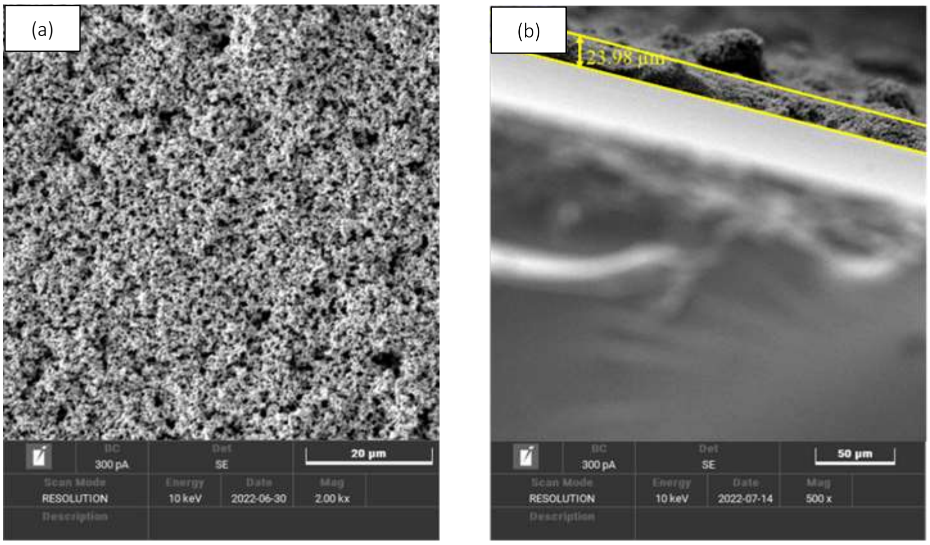

Figure 3. (a) Surface morphology of ZnO nanoparticles, (b) cross-section of ZnO photoanode.

XRD patterns of the ZnO photoanode and FTO glass substrate are shown in Figure 4. The Brag diffractions were observed at 26.82°, 34.04°, 38.05°, 54.94°, and 61.83° correlate to (110), (011), (020), (220), and (130) tin oxide, respectively with a crystal structure of FTO according to the JSCPDS card no. (98-006-3707) [17]. The peaks shifted slightly to the right when the FTO glass was coated with the ZnO layer.

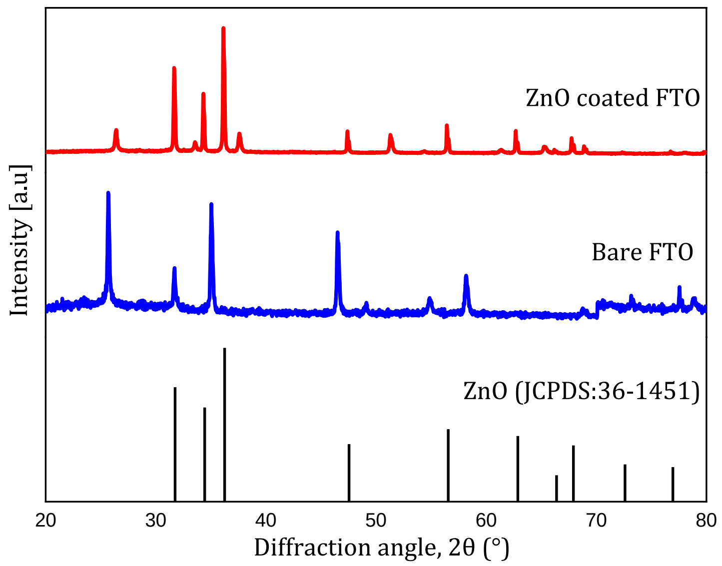

Figure 4. XRD analysis of ZnO photoanode and FTO glass.

The diffraction peaks other than those related to the FTO substrate were observed at 35.08°, 40.43°, 53.77°, 64.54°, 72.15°, and 78.23° are indexable to the hexagonal wurtzite ZnO (JCPDS 36-1451) [18]. This peak corresponds to (002), (101), (103), (004), and (202), and no additional diffraction peaks were detected, demonstrating the purity of the wurtzite phase in the fabricated ZnO films[19] and that the heat treatment does not cause any phase transformations [20].

3.2 Optical Properties

According to the UV-Vis absorption spectra in Figure 5, spinach dye absorbs light at wavelengths between 300 and 400 nm and 650 and 670 nm. In addition, the spinach dye contains chlorophyll pigments that give off green color. Chlorophyll 'a' and 'b' are the two primary forms of chlorophyll in spinach dye. The wavelength of light that chlorophyll 'a' can absorb is 372 and 642 nm, while chlorophyll 'b' absorbs light at 392 and 626 nm [21, 22]. Hence, the spinach dye could absorb light at a wide range of wavelengths, making it a suitable dye as a sensitizer in DSSC. Furthermore, the absorption spectra of the ZnO film soaked in the spinach dye show a wide absorption coverage overlapping at the same wavelengths as the spinach dye. Hence, the ZnO film soaked in the spinach dye could absorb the light at a visible range, and the spinach dye was proven suitable to use as a sensitizer in DSSC.

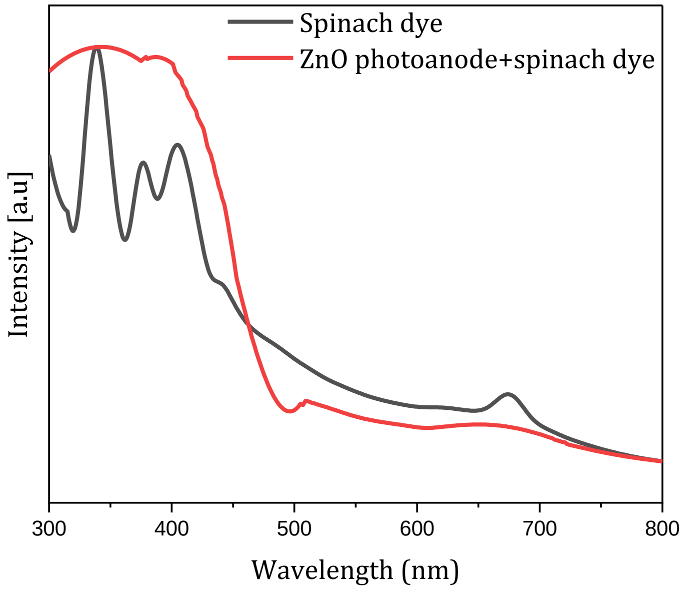

Figure 5. UV-vis absorption spectra of spinach dye and ZnO photoanode soaked in spinach dye

3.3 Electrical Properties

In order to study the effectiveness of the developed DSSC, one solar AM 1.5 G simulated light was used. The photovoltaic characteristics of the fabricated DSSC soaked in dye at various times are displayed in Table 1.

Table 1 Electrical characteristics of the ZnO photoanodes soaked in spinach dye

Photoanode	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η(%)
ZnO soaked in spinach for 30 minutes	0.10	0.43	0.27	0.01
ZnO soaked in spinach for 1 hour	0.13	0.40	0.50	0.03
ZnO soaked in spinach for 2 hours	0.12	0.40	0.33	0.02
ZnO soaked in spinach for 24 hours	0.07	0.38	0.33	0.01

Figure 6 shows the current density-voltage characteristics for the ZnO-based DSSC soaked in the spinach dye at a different soaking time. The photoanode soaked in spinach dye for 30 minutes and 24 hours showed the lowest efficiency, 0.01 %, with a short circuit current of 0.10 mA/cm^2 and 0.07 mA/cm^2, respectively. The short time for the photoanode to soak in the dye was insufficient, resulting in the lower short circuit current, whereas the longer time, 24 hours, leads to the deterioration of the ZnO layer. As the dye soaking time increases, the open circuit voltage, V_{oc}, keeps declining. When the ZnO photoanode was submerged in the dye for one hour, the fill factor, FF, reached its maximum, 0.50. The highest efficiency in this study was reached when the ZnO photoanode was soaked in the spinach dye for an hour, 0.03 %.

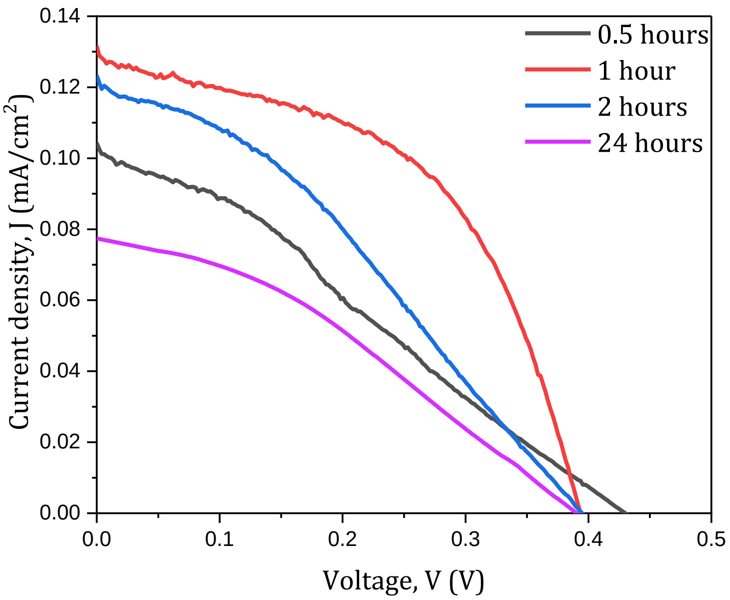

Figure 6. The J-V curve of ZnO photoanodes soaked in spinach dye at different soaking times.

4. CONCLUSION

The extraction, processing, and photovoltaic characteristics of DSSC developed using spinach dye were examined. Simple techniques can quickly and safely extract natural dyes, such as spinach dye, for DSSC preparation. The spinach dye's UV-visible absorption measurement shows that the developed cell absorbed photons in the visible region. The ZnO photoanodes' responses to four variations of soaking time were investigated, and an hour of dye soaking period produced the optimized DSSC with the highest efficiency of 0.03 % with a fill factor of 0.50. This study established that using natural dye, an environmentally friendly dye, can increase the energy conversion efficiency of ZnO-based DSSC. ZnO and spinach dye shows the potential of photoanode and natural dye to be developed as suitable candidate for research and development of the DSSC technology.

ACKNOWLEDGEMENTS

The Ministry of Higher Education of Malaysia and Universiti Malaysia Perlis provided financial assistance to the author under the Fundamental Research Grant Scheme (FRGS) under grant number FRGS/1/2020/TK0/UNIMAP/02/35. Special thanks to the Centre of Excellence for Renewable Energy (CERE), Centre of Excellence Frontier Materials Research (CFMR), and Universiti Malaysia Perlis for providing the characterization equipment.

REFERENCES

[1] J. Gong, K. Sumathy, Q. Qiao, and Z. Zhou, Review on dye-sensitized solar cells (DSSCs): Advanced techniques and research trends, Renew. Sustain. Energy Rev-Feb. 2017.
[2] S.N. Karthick and H.J. Kim, Dye-sensitized solar cells: History, components, configuration, and working principle, Interfacial Eng. Funct. Mater. Dye. Sol. Cells, 2019, pp. 1–16.
[3] N. Jamalullail, I. Smohamad, M. Norizan, and N. Mahmed, Enhancement of Energy Conversion Efficiency for Dye Sensitized Solar Cell Using Zinc Oxide Photoanode, IOP Conf. Ser. Mater. Sci. Eng., 2018.
[4] N.T.R.N. Kumara, A. Lim, C.M. Lim, M.I. Petra, and P. Ekanayake, Renew. Sustain. Energy Rev., vol. 78, (2017) pp. 301–317.
[5] E. Kouhestanian, M. Ranjbar, S.A. Mozaffari, and H. Salaramoli, Investigating the Effects of Thickness on the Performance of ZnO-Based DSSC, Prog. Color. Color. Coatings, pp. 101–112, 2021.
[6] S. Ghosh, R. Sartape, and J. Chakraborty, Role of dye-induced corrosion in determining the efficiency of ZnO-based DSSC: the case of ZnO nanoforest in N719, J. Mater. Sci. Mater. Electron., 2020, pp. 2202–2220.
[7] A. Hezam et al., Electronically semitransparent ZnO nanorods with superior electron transport ability for DSSCs and solar photocatalysis, Ceram. Int. , 2018, pp. 7202–7208.
[8] K. Magiswaran, M.N. Norizan, I.S. Mohamad, N. Mahmed, S.N. Idris, and S.A. Sobri, Charge Recombination in Zinc Oxide-Based Dye-Sensitized Solar Cell: A Mini Review, Int. J. Nanoelectron. Mater. 2021.
[9] N.A. Norhisamudin et al 2021 J. Phys.: Conf. Ser. 1755 012024.
[10] H. Aliah et al., Dye Sensitized Solar Cells (DSSC) Performance Reviewed from the Composition of Titanium Dioxide (TiO2)/Zinc Oxide (ZnO), IOP Conf. Ser. Mater. Sci. Eng., 2018.
[11] AIP Conference Proceedings 1660, 070049 (2015); doi: 10.1063/1.4915767.
[12] D. Sinha, D. De, D. Goswami, A. Mondal, and A. Ayaz, ZnO and TiO2 Nanostructured Dye sensitized Solar Photovoltaic Cell, Mater. Today Proc., vol. 11, pp. 782–788, Jan. 2019, doi: 10.1016/J.MATPR.2019.03.043.
[13] A. Chauhan et al., Photocatalytic dye degradation and antimicrobial activities of Pure and Ag-doped ZnO using Cannabis sativa leaf extract, Sci. Rep., 2020, pp. 1–16.
[14] N. Jamalullail, I.S. Mohamad, M.N. Norizan, N.A. Baharum, and N. Mahmed, Short review: Natural pigments photosensitizer for dye-sensitized solar cell (DSSC), IEEE Student Conf. Res. Dev. Inspiring Technol. Humanit. SCOReD 2017 - Proc., 2018, pp. 344–349.
[15] N. Rosli et al 2021 J. Phys.: Conf. Ser. 1755 012025.
[16] H. Chang, H.M. Wu, T.L. Chen, K.D. Huang, C.S. Jwo, and Y.J. Lo, Dye-sensitized solar cell using natural dyes extracted from spinach and ipomoea, J. Alloys Compd. Apr. 2010, pp. 606–610.
[17] M.A.M. Al-Alwani, N.A. Ludin, A.B. Mohamad, A.A.H. Kadhum, and A. Mukhlus, Application of dyes extracted from Alternanthera dentata leaves and Musa acuminata bracts as natural sensitizers for dye-sensitized solar cells, Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., 2018, pp. 487–498.
[18] S. Shalini, R. Balasundara Prabhu, S. Prasanna, T. K. Mallick, and S. Senthilarasu, "Review on natural dye sensitized solar cells: Operation, materials and methods," Renew. Sustain. Energy Rev. , Nov. 2015, pp. 1306–1325.
[19] P. Ravikumar, K. Ravichandran, and B. Sakthivel, Effect of Thickness of SnO2:F over Layer on Certain Physical Properties of ZnO:Al Thin Films for Opto-electronic Applications, J. Mater. Sci. Technol., 2012, pp. 999–1003.
[20] H. Widiyandari, S. Wijayanti, A. Prasetio, and A. Purwanto, ZnO hollow sphere prepared by flame spray pyrolysis serves as an anti-reflection layer that improves the performance of dye-sensitized solar cells, Opt. Mater. (Amst), 2020, p. 110077.

[21] R. Syafinar, N. Gomesh, M. Irwanto, M. Fareq, and Y.M. Irwan, Chlorophyll Pigments as Nature Based Dye for Dye-Sensitized Solar Cell (DSSC), Energy Procedia, Nov. 2015, pp. 896–902.
[22] F. Kabir, M.M.H. Bhuiyan, M.S. Manir, M.S. Rahaman, M.A. Khan, and T. Ikegami, Development of dye-sensitized solar cell based on combination of natural dyes extracted from Malabar spinach and red spinach, Results Phys., Sep. 2019, p. 102474.