The Effect of Mangosteen Varieties as Dyes and ZnO Nanostructures Mixture to DSSC - Dye-sensitized Solar Cell Characteristics

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Abstract. Dye-sensitized Solar Cell (DSSC) based on ZnO nanostructures has been fabricated using mangosteen peel extract as dyes using the Yonekawa method and the Grätzel method. This research synthesized ZnO nanostructures with nanoparticles, nanorods, nanoflower, and nanotree morphologies. Two different morphological structures of ZnO were mixed with the ratio of 25:75, 50:50, and 75:25, and the performance of the DSSC was investigated. The dye used in the DSSC was extracted from mangosteen peel of different varieties obtained from Blitar, Purwakarta, and Gede Bage. The highest anthocyanin levels were obtained from the Gede Bage sample with a value of 105.774 mg L^{-1}. The results of the I–V curve measurement showed that the most stable values of open-circuit voltage (V_{oc}) and short circuit current (I_{sc}) were obtained from the dye extracted from the Blitar sample with the value of 0.312 V and 3 μA respectively for the Yonekawa method (0.001 28 % efficiency) as well as 0.222 V and 5.5 μA respectively for the Grätzel method (0.00264 % efficiency). The best efficiency was obtained from the mixtures of nanoparticles (75) : nanotrees (25) with the value of 0.034 77 % (0.285 V V_{oc}, 27.5 μA I_{sc}, and FF 26.5 %) using the Yonekawa method.

Keywords: Anthocyanin, gratzel method, solar cell, zinc oxide, yonekawa method

1 Introduction

In Dye-sensitized Solar Cell (DSSC), light absorption is performed by dye molecules and electrical charge separation occurs in a separate process. The process of separating the electrical charge occurs in a semiconductor (inorganic) material which has a wide energy bandgap. Among various wide bandgap semiconductors used in DSSC are Zinc Oxide (ZnO) and Titanium dioxide (TiO_2). ZnO is usually chosen over TiO_2 due to its higher electron mobility. ZnO also has a wide variety of morphology of nanostructures that are easily synthesized through a variety of methods that can also be applicable in solar cell

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fabrication. Apart from being a photoanode, the morphology of the ZnO nanostructure plays a very important role in improving the ability of the dye to absorb light. The solar–to–electrical energy efficiency of nanoparticles and nanorods are 0.2 % and 0.15 % respectively with N_3 dye type [2]. While nanoflower and nanotree yields higher efficiency of 0.53 % [3] and 2.63 %, respectively. In this study, the researchers fabricated different morphological structures of ZnO, i.e., nanoparticles, nanoflower, nanorod, and nanotree to be used as photoanode [1], and investigated the performance of DSSC fabricated from different combinations of ZnO morphological structures.

Dyes as a sensitizer in DSSC also play an important role in the conversion of sunlight into electrical energy. So far, the dye with the highest efficiency was found in the Ruthenium complex (Ru) which can reach 11 % to 12 % [4]. However, this type of dye is expensive and very difficult to synthesize so many studies are focusing on finding new dyes that are more abundant in nature and cheaper in price. Most common natural dyes can be extracted from fruits, flowers, and other organic materials.

Anthocyanin is one of the natural dyes that can be found in fruits, flowers, and plants that have reddish or purplish colors [5]. The high content of anthocyanin can be extracted from mangosteen fruit peel. Indonesia is one of the largest producers countries of mangosteen fruit. This study, also investigated different varieties of mangosteen to be used as natural dyes. Different varieties of mangosteen were obtained from three different cities, *i.e.,* Blitar, East Java, Purwakarta, and Gede Bage, West Java, Indonesia.

The selection of mangosteen varieties was based on their anthocyanin content and their efficiency in absorbing solar energy. The analysis was carried out in an acidic atmosphere because in an acidic atmosphere anthocyanin is more stable than in an alkaline or neutral atmosphere [6]. Moreover, the acidic condition will help in increasing the polarity of ethanol so that it increases the performance of the soluble dyes in the filtrate because the mangosteen peel is more polar.

This research use the doctor blade technique based on the method developed by Grätzel [4] and Yonekawa [13] to fabricate DSSC using ZnO nanostructures and natural dye derived from mangosteen peel of various varieties. The authors investigated the effect of mangosteen varieties as dyes and mixing of various ZnO nanostructures on the characteristic of the fabricated DSSC.

2 Method

This research synthesized ZnO nanostructure with various morphology, *i.e.*, nanopartikel, nanorod, nanoflower, and nanotree. ZnO nanoparticles were synthesized by the same method done by Syukron *et al.* [7]. ZnO nanoflowers were synthesized by the coprecipitation method as done by Iqbal *et al.* [8]. The synthesis of ZnO nanorods was done by the hydrolysis method as done by Wahyuono [9] and Mahendra [10]. ZnO nanotrees were synthesized by the coprecipitation method as done by Mahendra *et al.* [11]. The synthesized ZnO nanostructures were characterized by ultraviolet-visible spectroscopy (UV–Vis), X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Fourier Transform Infrared spectroscopy (FT–IR).

The dye used in this study was extracted from mangosteen peel at pH 1. Amount 10 g of mangosteen peel powder were dissolved in 100 mL of 96 % ethanol and stirred at 200 °C for 5 h, then cooled for 20 min and filtered [12]. The anthocyanin levels from the mangosteen peel extract were measured by UV–Vis spectrophotometer at wavelengths of 300 nm to 700 nm.

DSSC fabrication begins with the preparation of the ZnO photoelectrode which is carried out by two methods, the Grätzel method [4] and the Yonekawa method [13]. Both methods use the doctor blade technique and annealing at 200 °C. Next, a carbon

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electrode was coated on the conductive side of a Transparent Conductive Oxide (TCO) glass and glued to the side that corresponds to the TCO area that has been coated with ZnO and the dye is then pressed onto it. Next, the electrolyte gel solution was sandwiched between two TCO glasses. The electrolyte was made by dissolving 0.8 g of potassium iodide (KI) 0.5 M with 10 mL of acetonitrile and addition of 0.127 g iodine (I_2) 0.05 M. After all the components were dissolved, 7 g of polyethylene glycol were, and 25 mL of chloroform were added to the solution. The electrolyte solution was then heated at 80 ° C for 60 min at medium speed. The performance of the fabricated DSSC was characterized by I–V measurement.

3 Results and discussions

3.1 ZnO nanostructures

Figure 1 shows the XRD test results of the ZnO nanostructures (nanoparticles, nanoflowers, nanorods, and nanotrees). The results were compared with the reference standard (JCPDS 36–1451) and the crystal structure was in good agreement with the hexagonal wurtzite.

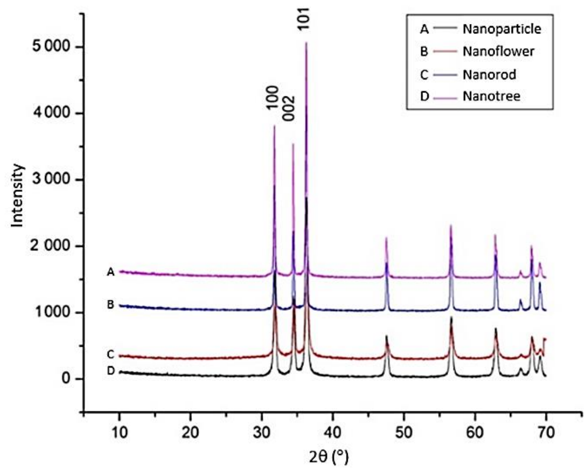

Fig. 1. XRD pattern of ZnO nanostructures

Figure 2(a) shows the SEM image of ZnO nanoflowers at a magnification of 35 000 times. The morphology of the nanoflowers was unexpected because the nanoflowers experienced agglomeration due to the addition of KOH which increases the pH by releasing OH-ions. This caused an increase in precipitation that affects the structure of ZnO nanoflowers [14]. The morphology of ZnO nanoparticles at a magnification of 50 000 times is shown in Figure 2(b). Figure 2(c) shows the ZnO nanotrees at a magnification of 20 000 times. The morphology of the nanotrees shows long branches and wide surface area so it can be expected that the dye is better absorbed and collect more light. Figure 2(d) shows the ZnO nanorods at 10 000 times magnification where the morphology shows elongated roots.

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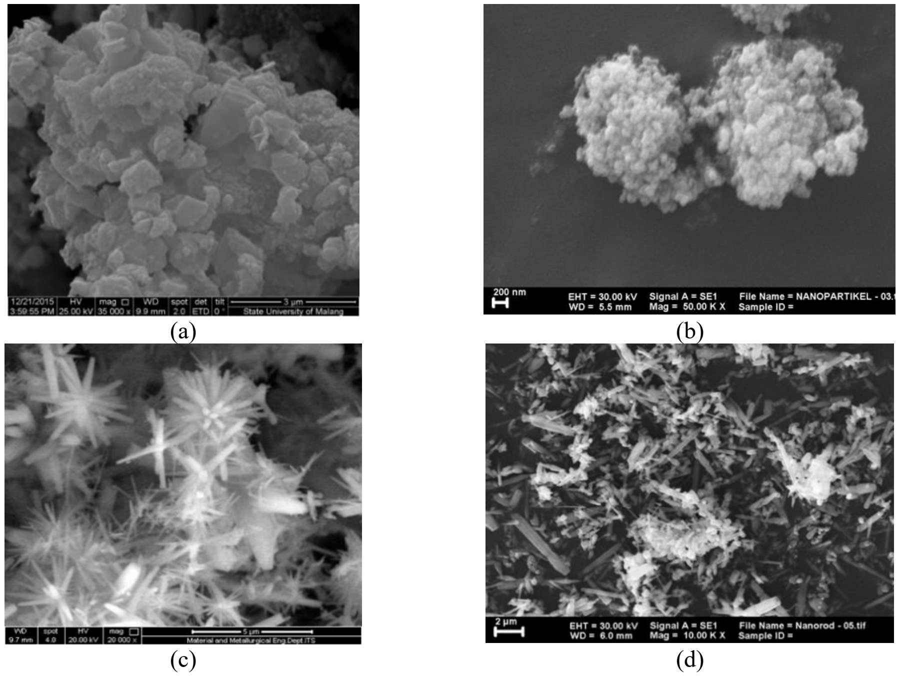


Fig. 2. SEM results of ZnO nanostructures synthesized (a) *nanoflower* ZnO, (b) nanopartikel ZnO (c) nanotree (d) nanorod

3.2 Characteristics of mangosteen peel and its effect on DSSC efficiency

UV–Vis test results (Figure 3) shows that the anthocyanin absorption spectrum of mangosteen peel extract from Blitar, East Java, Purwakarta and Gede Bage, West Java are at their highest on wavelengths (λ) between 407.5 nm to 420.5 nm, 428.5 nm to 460 nm, 418 nm to 449.5 nm respectively. This fairly wide anthocyanin absorption spectrum from the extracted mangosteen peel will increase the performance of the DSSC.

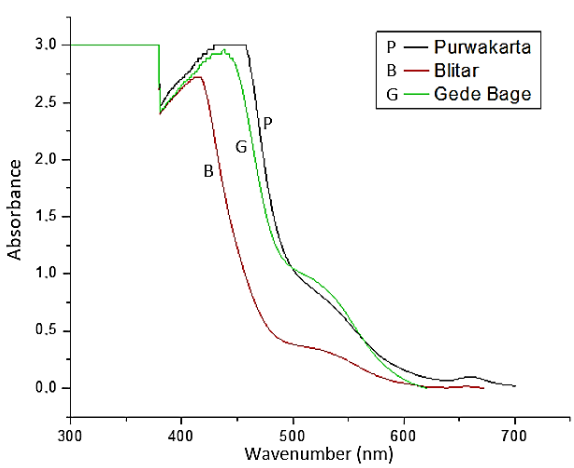
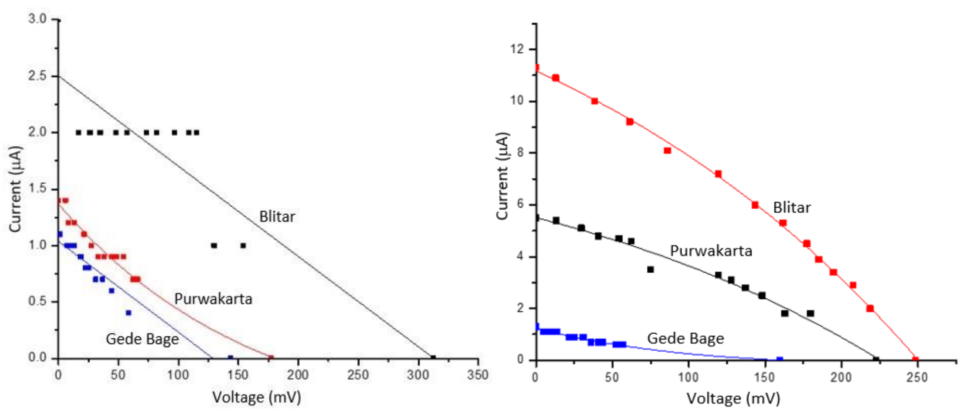


Fig. 3. UV–Vis results of mangosteen peel extract

Anthocyanins containing cyanidin have absorption peaks at wavelengths ranging from 400 nm to 500 nm. In addition to showing the ability of ZnO absorption, a large energy band from each dye was also observed. Based on the interpretation of the infrared spectrum shown in Figure 3, absorption bands appeared in the wavelength range of 1 019.12 cm^{-1} to 1 019.44 cm^{-1} indicating the presence of C-O stretching for the three samples of mangosteen peel extract. While the absorption band in the range of 1 112.23 cm^{-1} to 1 112.75 cm^{-1} indicates the presence of C-O-C stretching. The absorption band for C=O stretching appeared in the range of wave numbers 1 645.45 cm^{-1} to 1 648.28 cm^{-1}, while for stretching of O–H appeared in the range 3 308.83 cm^{-1} to 3 320.44 cm^{-1}.

3.3 The I-V curve

The I–V curves were obtained by measuring DSSC under direct solar contact at 10.00 to 14.00 Western Indonesian Time. Figure 4 shows the results of I–V measurements with different resistances.



(a) (b)

Fig. 4. I–V curves of ZnO nanorod–based using (a) Yonekawa method, (b) Grätzel method

The results of the measurement of the I–V show that the highest open-circuit voltage (V_{oc}) and short circuit current (I_{sc}) values for the Yonekawa method were produced by dye from Blitar, East Java with an efficiency of 0.001 28 %. Whereas the Grätzel method was produced by dye from Purwakarta, West Java with an efficiency of 0.005 73 %. The V_{oc} values for each doctor blade method vary from 0.143 V to 0.312 V and I_{sc} values ranging from 1.1 µA to 11.3 µA. Table 1 summarizes in detail the photoelectrochemical parameters based on the experimental results and calculations.

Table 1. Sensitized Photoelectrochemical Parameters of ZnO Nanorod Based Mangosteen Skin Dye Based on Experiment (P) and Exponential Calculation (TE)

Method	**Mangosteen Peel From**	**FF (%)**	**V_{oc} (mV)**	**I_{sc} (µA)**	**E_{ff} (%) (P)**	**E_{ff} (%) (TE)**
Yonekawa	Blitar	0.206	312.5	3.0	0.001 28	0.001 29
	Purwakarta	0.196	177.4	1.4	0.000 32	0.000 30
	Gede Bage	0.168	143.2	1.1	0.000 17	0.000 22
Grätzel	Blitar	0.323	222.6	5.5	0.002 64	0.002 38
	Purwakarta	0.306	248.3	11.3	0.005 73	0.005 78
	Gede Bage	0.164	159.5	1.3	0.000 22	0.000 21

Based on the results, the efficiency values obtained from the measurements and calculations did not differ greatly. DSSC performance with dyes originating from Blitar, East Java has a stable efficiency for both doctor blade methods. The anthocyanin absorption value possessed by the Blitar, East Java sample was no better than other dye samples, but the Blitar, East Java sample has wavelength absorption closer to UV wavelength absorption in visible light and the energy gap values were greater than the two dye samples as shown in Figure 4(a) and (b). Based on this, from the wavelength absorption in the three types of dye used, the Blitar, East Java dye has the absorbance that is closest to the UV wavelength of visible light at 400 nm (the wavelength of visible light is ranging from 400 nm to 800 nm). Therefore, the energy absorbed is sufficient to excite electrons from the Highest Occupied Molecular Orbital (HOMO) energy to the Lowest Unoccupied Molecular Orbital (LUMO) level to the ZnO conduction band.

3.4 Characteristics of ZnO morphological mixing

The authors characterized the DSSC fabricated with mixed ZnO morphologies and obtained some parameters related to the efficiency of the DSSC. Table 2 summarizes the best DSSC performance of each ZnO morphology mixing.

Table 2. Best Performance of ZnO Morphological Mixing based on Experiment (P) and Theory (T)

ZnO Variation	Method	V_{oc} (mV)	I_{sc} (μA)	E_{ff} (%) (P)	E_{ff} (%) (T)
F(25):R(75)	Grätzel	403.0	3.5	0.003 58	0.008 94
F(50):T(50)	Grätzel	319.1	2.8	0.001 64	0.007 43
P(75):F(25)	Grätzel	373.3	9.8	0.004 68	0.021 26
P(50):R(50)	Yonekawa	293.8	13.4	0.020 05	0.031 77
P(75):T(25)	Yonekawa	285.4	27.5	0.034 77	0.063 34
T(25):R(75)	Grätzel	256.6	22.2	0.036 08	0.044 59

The greatest efficiency was produced by the morphological mixture of nanoparticles/P (75): nanotree/T (25) using the Yonekawa method which is equal to 0.034 77 % (V_{oc} = 0.285V, I_{sc} = 27.5 μA). This is reasonable considering that nanotrees and nanoparticles have a very wide surface area so that the dye can be absorbed better to collect more light and reduce the recombination at the conduction band [2, 15]. The efficiency is better than the previous research using the same mix of nanoparticles and nanotrees which is equal to 0.015 7 % [10].

The smallest efficiency was produced by the mixture of nanoflowers/F (50): nanorods/R (50) using the Grätzel method (shown in Table 2) which is equal to 0.000 55 % (Voc = 0.232V, Isc = 2.2 μA). The efficiency of the mixed F:R morphology was smaller than the previous research by Mahendra *et al.* [11] where the efficiency obtained was 0.061 6 % using Tasikmalaya, West Java mangosteen pH 4.5 as a dye. This is because the agglomerated ZnO nanoflowers as shown in Figure 2a caused a decrease in the effectiveness of the DSSC in converting sunlight into electricity. The low value of the efficiency is also caused by the recombination between photo-excited carriers of the electrodes with I_3^- ions in the electrolyte [16, 17].

The efficiency values differ greatly from previous studies because the pH used in the dye is in an acidic atmosphere. In the acidic atmosphere, the oxygen level is increased in ZnO, causing a release of electrons on the surface of ZnO [18]. This causes instability in the injection of electrons [19]. The instability of electron injection affects the photovoltage and photocurrent since it depends on the ability to bind electrons to the surface of ZnO [20]. Karim *et al.* [21] investigated various ZnO morphologies and found that nanosheet/flake shows the maximum efficiency with a filling factor of around 0.5 due to better porosity and larger surface area. This helped in enhancing the capability of the nanosheet to trap and scatter light.

4 Conclusions

Based on the data and the discussion, it can be concluded that the mangosteen variant originating from Blitar, East Java gave the most optimum results as a dye for DSSC with the stable efficiency obtained from the IV curve measurements using two doctor blade techniques, namely 0.001 28 % for the Yonekawa method and 0.002 64 % for the Grätzel method. While for the absorption in the UV–Vis mangosteen variant of Gede Bage, West Java gave the greatest value of anthocyanin levels that is 105.774 mg L^{-1}. The best efficiency of the DSSC fabricated with mixed ZnO nanostructure morphology using dye from Blitar, East Java sample was produced by the mixture of nanoparticles (75) and nanotrees (25) with the value of 0.034 77 % (Voc 0.285 V; Isc 27.5 µA; and FF 26.5 %) obtained using the Yonekawa method. While the smallest efficiency is produced by the mixture of nanoflowers (50): Nanotrees (50) with the value of 0.000 55 % (Voc 0.232V; Isc 2.2µA; and FF 16.2 %) obtained using the Grätzel method.

References

1. Z. Liu, Y. Li, C. Liu, J. Ya, W. Zhao, L. E, et al. Solid State Sci. **13**,6:1354–1359(2011). https://doi.org/10.1016/j.solidstatesciences.2011.04.005.
2. T–H. Lee, H–J. Sue, X. Cheng. Nanoscale Res. Lett. **6**:517(2011). https://doi.org/10.1186/1556-276X-6-517.
3. C.Y. Jiang, X.W. Sun, G.Q. Lo, D.L. Kwong. Appl. Phys. Lett. **90**,26:263501(2007). https://doi.org/10.1063/1.2751588.
4. M. Grätzel. J. Photochem. Photobiol. C: Photochem. Rev. **4**,2:145–153(2003). https://doi.org/10.1016/S1389-5567(03)00026-1.
5. V. Pramananda, T.A.H. Fityay, E. Mirsan. IOP Conf. Ser.: Mater. Sci. Eng. **1122**:012104(2021). https://doi.org/10.1088/1757-899X/1122/1/012104.
6. B. Enaru, G. Dretcanu, T.D. Pop, A. Stanila, Z. Diaconeasa. Antioxidants. **10**,12:1967(2021). https://doi.org/10.3390/antiox10121967.
7. A. Syukron, R.A. Wahyuono, D. Sawitri, D.D. Risanti, Adv. Mat. Res. **896**:183–186(2014). https://doi.org/10.4028/www.scientific.net/AMR.896.183.
8. M. Iqbal, R. Mahendra, R.A. Wahyuono, D. Sawitri, D.D. Risanti, Adv. Mat. Res. **1123**:219–222(2015). https://doi.org/10.4028/www.scientific.net/AMR.1123.219.
9. R.A. Wahyuono. *Dye-sensitized Solar Cells (DSSC) fabrication with TiO2 and ZnO nanoparticle for high conversion efficiency*. [Thesis]. Engineering Physics, Institut Teknologi Sepuluh Nopember Surabaya (2013). https://www.researchgate.net/profile/Ruri_Wahyuono/publication/273955833_Dye-Sensitized_Solar_Cells_DSSC_Fabrication_with_TiO2_and_ZnO_Nanoparticle_for_High_Conversion_Efficiency/links/551162490cf29a3bb71da9ae/Dye-Sensitized-Solar-Cells-DSSC-Fabrication-with-TiO2-and-ZnO-Nanoparticle-for-High-Conversion-Efficiency.pdf.

10. R. Mahendra. Fabrikasi *Dye-Sensitized solar cells (DSSC) berbasis nanorod zno (oksida seng) dengan variasi metode preparasi pasta*. [Dye-Sensitized Solar Cells (DSSC) based on Nanorod ZnO (Zinc Oxide) based on variations of Pasta Preparation Method]. [Thesis]. Teknologi Industri, Institut Teknologi Sepuluh Nopember Surabaya (2014). [in Bahasa Indonesia]. https://scholar.google.com/scholar?hl=id&as_sdt=0%2C5&q=Dye-Sensitized+Solar+Cells+%28DSSC%29+berbasis+Nanorod+ZnO+%28Oksida+Seng%29+dengan+variasi+Metode+Preparasi+Pasta&btnG=.
11. R. Mahendra, R.A. Wahyuono, D. Sawitri, D.D. Risanti. *Dye-Sensitized solar cells (DSSC) based on ZnO non-and vertically aligned nanorod structures*. Applied Science for Technology Innovation (ASTECHNOVA): International Energy Conference (Yogyakarta, Indonesia 2014). https://scholar.google.com/scholar?hl=id&as_sdt=0%2C5&q=Dye-Sensitized+Solar+Cells+%28DSSC%29+Based+on+ZnO+Non-and+Vertically+Aligned+Nanorod+Structures&btnG=.
12. S. Agustini, R.A. Wahyuono, D. Sawitri, D.D. Risanti. AIP Conf. Proc. **1554**:66–69(2013). https://doi.org/10.1063/1.4820285.
13. H. Yonekawa. *Dye-Sensitized solar cells fabricated with ZnO nanoparticles for high conversion efficiency*. [Thesis] Kumamoto University, Chou Ward, Kumamoto, Japan (2012). https://scholar.google.com/scholar?cluster=528059274275303576.
14. A. Rayerfrancis, P.B. Bhargav, N. Ahmed, B. Chandra, S. Dhara. Phys. B: Condens. Matter. **457**:96–102(2015). https://doi.org/10.1016/j.physb.2014.09.044.
15. H. Aliah, B. Bernando, F. Puspitasari, A. Setiawan, P. Pitriana, B.W. Nuryadin, et al. IOP Conf. Ser.: Mater. Sci. Eng. **288**,1:012070(2018). http://dx.doi.org/10.1088/1757-899X/288/1/012070.
16. C.H. Ku, J–J. Wu. Appl. Phys. Lett. **91**,9:093117(2007). https://doi.org/10.1063/1.2778454.
17. J–J. Wu, G–R. Chen, H–H. Yang, C–H. Ku, J–Y. Lai. Appl. Phys. Lett. **90**,21**:**213109(2007). https://doi.org/10.1063/1.2742639.
18. Q. Zhang, C.S. Dandeneau, S. Candelaria, D. Liu, B.B. Garcia, X. Zhou, et al. Chem. Mater. **22**,8:2427–2433(2010). https://doi.org/10.1021/cm9009942.
19. A.P. Uthirakumar. *Fabrication of ZnO based dye sensitized solar cells, solar cells-dye-sensitized devices*, UK: InTech (2011). p. 19. https://books.google.co.id/books?hl=id&lr=&id=wayZDwAAQBAJ&oi=fnd&pg=PA435&dq=Fabrication+of+ZnO+Based+Dye+Sensitized+Solar+Cells,+Solar+Cells-Dye-Sensitized+Devices&ots=kW2C12AwEM&sig=l2uAUskgY6jqUSlIvFj_9pBpNL4&redir_esc=y#v=onepage&q=Fabrication%20of%20ZnO%20Based%20Dye%20Sensitized%20Solar%20Cells%2C%20Solar%20Cells-Dye-Sensitized%20Devices&f=false.
20. V. Porkalai, D.B. Anburaj, B. Sathya, G. Nedunchezhian, R. Meenambika. Mater. Sci. Eng. **9**:01499405**(**2017). https://doi.org/10.2412/mmse.77.37.39.
21. M.R.A. Karim, M.B. Ahmed, E.U. Haq, K. Mahmood, A. Hussain, S.U. Iqbal, et al. Key Eng. Mater. **778**:91–99(2018). https://doi.org/10.4028/www.scientific.net/KEM.778.91.