The Potential of Pigment *Syngonium podophyllum* as Natural Dye in DSSC and The Effect of Solvent Extraction

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Abstract. The possibility of natural dye from the pigment of the pigment *of Syngonium podophyllum* leaves as natural photosensitizer in Dye Sensitized Solar Cells (DSSC) has been studied in this work. The dyes was extracted using various solvents, such as acetone, ethanol and the combination of acetone and ethanol. The effect of solvent extraction in absorbance spectra, band gap energy (HOMO-LUMO), and adsorbance on the surface of TiO_2 of the natural dye was explored. The uv-vis spectroscopy, Fourier Transform Infrared (FTIR), and Cyclic Voltametry (CV) were used to characterize the dyes. Our findings showed that the combination of acetone-ethanol give the highest peaks of the absorbance spectra. Based on FTIR analysis, all extracted dyes were adsorbed onto the surface of TiO_2. The ethanol solvent extraction gave smallest band-gap energy among the solvents.

Keywords: Dye Sensitized Solar Cells, Natural Dye, *Syngonium Podophllum*, Photosensitizer.

1 Introduction

Solar cells represent a promising candidate for addressing the global energy crisis. However, fossil fuels such as coal and diesel remain the primary energy sources due to their relatively low cost, ease of use, and widespread availability [1]. Solar cells are the technology to convert solar energy to electrical energy via photovoltaic effect. Dye sensitized solar cells (DSSCs) is the third generation of photovoltaic technology that has become an alternative renewable energy due to low costs manufacturing, simple fabrication process and stable conversion in low light and dark condition [2, 3]. DSSCs consist of nanoporous metal oxide materials doped onto conducting glass, which act as

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photoanodes; dyes as photosensitizers; electrolytes as the electron connectors between the photoanode and the counter electrode; and counter electrodes with electrocatalytic properties [4, 5].

The dyes components play an important role to improve the performance of DSSC. In recent years, ruthenium-based sensitizers, such as N3, N719, black dye, and others, have been widely used. These ruthenium dyes offer a significant advantage, namely high conversion efficiency, due to their broad light absorption spectrum, excellent stability, and superior light-harvesting and injection efficiencies [6]. However, ruthenium contains heavy metals that can cause environmental problems and involves a complicated synthesis process, which increases the cost of fabrication [7, 8]. Consequently, many researchers have developed natural dyes from chlorophyll, anthocyanin, carotene and other pigments which can be obtained from the extraction process from leaves, fruits, seeds, seems, flowers and others [9]. Several reasons researches are transitioning ruthenium-based dye to natural dyes include their ease of synthesis, cost-effectiveness and environmental sustainability [10, 11]. Regrettably, despite being easy to extract and environmentally sustainable, the resulting DSSC struggles to achieve high efficiency due to issues with resistance and incompatibility when integrated with other components [12]. Therefore, further research is required to explore and to optimize the new natural dye from the natural resources.

One of the development performance natural dyes is utilization of solvent extraction for preparation natural dye. Solvent extraction of natural dye can give the impact to the interaction and binding dye molecule on the surface of semiconductor TiO_2 and it can influence the overall performance of DSSCs [13, 10]. Previous research, have been investigated about the effect of different solvent to the performance of DSSC. Based on their results showed that the performance of DSSC depend on the parameter solvent extraction such as polarity, PH, and temperature [14]. The utilization of solvent extraction based on their polarity have been carried out by Adedukon, et.al [15]. *P.Granatum* dye that was extracted by protic polar solvent, produced an absorbance range of around 500 nm to 560 nm. The absorbance range of *P.Granatum* dye using polar solvent were around 450 nm. The result indicate that dye extracted from *P.Granatum* peels demonstrated greater solubility in polar solvents compare to the other solvents utilized. In addition, the use of different solvent extractions, such as ethanol, methanol, and a combination of ethanol-methanol, to extract anthocyanin and chlorophyll pigments from Roselle and green tea produced varying DSSC efficiencies: 0.000959%, 0.0016%, and 0.00142% for anthocyanin, and 0.0000257%, 0.0000752%, and 0.0000111% for chlorophyll [16].

In this study, we utilize a novel natural dye derived from pigment extract of *Syngonium podophyllum* leaves. This plant is a tropical climbing species classified under the *Araceae* family. They are commonly utilized as an ornamental plant due to its low maintenance requirements and abundant availability. *Syngonium podophyllum* as sensitizer has been reported by Halidun, et al. [17]. The efficiency of DSSC produced 0.074% with the purification process of natural dye. Lingga, et al reported that *Syngonium podophyllum*-based natural counter electrodes achieved a DSSC efficiency of 0.308% [18]. Therefore, this study aims to explore of the natural dye derived from *Syngonium podophyllum* as a photosensitizer, examining the impact of various solvents on its absorption spectrum, dye molecule interaction with the semiconductor, and the molecular orbitals of the natural dye.

2 Experimental Method

2.1 Extraction and Preparation of Natural Dye

This study employed natural dye extracted from *Syngonium podophyllum* leaves using the maceration technique. The dye extraction process utilized various solvents, including acetone, ethanol, and their combination. The procedure comprised three main stages: cleaning, preparation, and extraction. The stage of preparation of natural dye follows of Halidun, et al [17].

Cleaning stage. *Syngonium podophyllum* leaves were rinsed under running water to remove impurities such as dust and soil, followed by through washing with distilled water. Then, the leaves were kept in room temperature.

Preparation stage. The cleaned leaves were cut into smaller pieces and dried using a microwave at 30^0C until the moisture content was significantly reduced. The dried leaves were then ground into powder using an electric blender to produced *Syngonium podophyllum* powder.

Extraction stage. The powdered leaves were soaked in extraction solutions consisting of acetone, ethanol, and their combination, with a leaf-to-solvent ratio of 1:5 (v/v). The soaking process was conducted in a dark environment at ambient temperature for several days. The resulting dye solution was subsequently filtered using Whatman filter paper (110 mm) and centrifuged at 1500 rpm for 15 minutes.

2.2 Characterization and Measurement

The absorption characteristic of the extracted natural dyes was analyzed using UV-Vis spectrophotometer (Hawlett Packard 8453, Agilent Technologies, Europe/British), with the measurement conducted over a wavelength range of 200 – 800 nm. The binding vibration of the natural dye on the TiO_2 photoelectrodes were characterized using Fourier Transform Infrared (FT-IR) spectroscopy of Prestige 21 Shimadzu Japan over a wavenumber range 4500 – 400 cm^{-1}. Cyclic voltammetry characterization of the DSSC was conducted to determine the oxidation and reduction potentials of the dye using an eDAQ potentiostat with an e-coder 401 and Echem software version 2.1. The scan rate used in this measurement was 20 mV/s, with a potential range from -1600 mV to +1600 mV. The electrodes used in the measurement included a carbon paste working electrode, a platinum counter electrode, and an Ag/AgCl reference electrode. The HOMO, LUMO and redox potential gap were determined through this measurement with the Eqs. (1) to (3) [19].

$$HOMO = -(E_{ox} + 4{,}4) \quad (1)$$

$$LUMO = -(E_{red} + 4{,}4) \quad (2)$$

$$E_g = HOMO - LUMO \quad (3)$$

3 Results and Discussion

3.1 Absorption of Natural Dye

The UV-Vis spectrophotometer was used to determine the absorbance of the dye solution. Fig. 1 showed the absorbance of *Syngonium podophyllum* as natural dye. The wavenumber of the spectrum absorbance can indicate the pigment content of *Syngonium podophyllum* dye [20]. As shown in Fig.1, the absorbance peaks of dye were conducted in range around 400 nm and 650 nm. These absorbance peaks indicate that the pigment of Chlorophyll is present [21, 22].

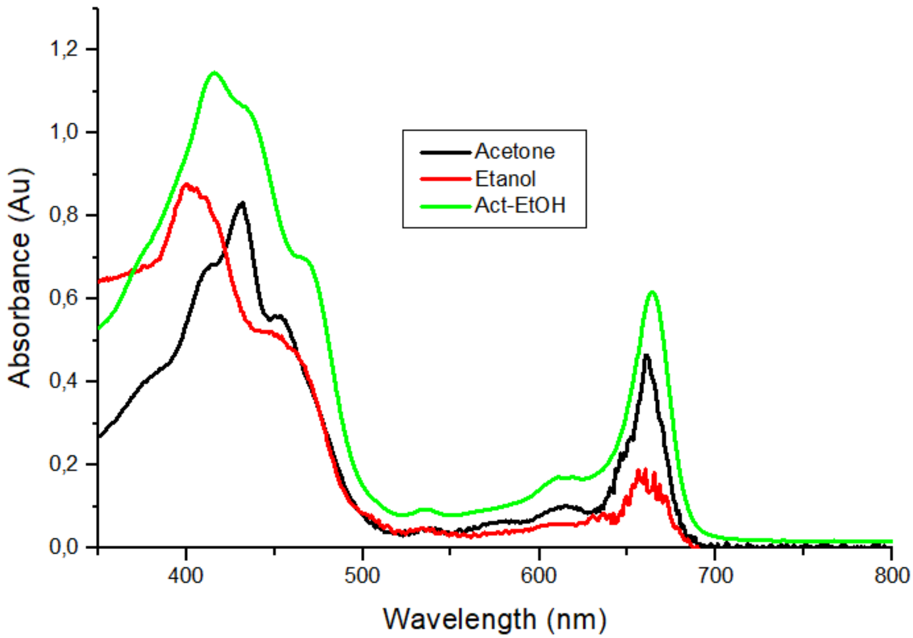

Fig. 1. Absorbance spectrum of *Syngonium podophyllum* dye

Chlorophyll is a green pigment involved in photosynthesis, found in plants, algae, and cyanobacteria. It has two primary absorption bands: the red band (Qy band) and the blue band (Soret band), which correspond to the light absorption ranges of 400–500 nm and 600–700 nm in the visible spectrum, respectively [23]. As seen in Fig. 1, all extracted dyes have abroad range in that spectrum. The broad absorption peak of *Syngonium podophyllum* dye was obtained using combination of ethanol and acetone solutions. This is attributed to the higher solubility of the solution compared to other [15].

3.2 FTIR Spectrum of Natural Dye on Semiconductor TiO_2

FTIR analysis is employed to examine the molecular bonding of the dye on the surface of the TiO_2 semiconductor. The FTIR spectra of TiO_2 before and after immersed in natural dye solution are shown in Fig.2.

All spectra have the characteristic vibration of Ti-O at range standard 450 – 1000 cm^{-1} [24]. The present peaks at 3429 cm^{-1} and 1627.37 cm^{-1} in all spectra is corresponding to the stretching and bending vibration of -OH group, respectively. The peaks of 2851 to 2921 cm^{-1} and 1627.37 in all spectra are represented to stretching of -CH vibration alkanes group and stretching vibration of C=C aromatic ring. The peak emerged at frequency of 2340-2366.4 cm^{-1} corresponding to the stretching vibration of C=C alkyne group. The present peak at 1383.2 in all spectra is due to nitrate ions derived from the nitric acid used for pH adjustment during synthesis of TiO_2 [25]. The transmittance value of TiO_2-natural dye is higher than pure TiO_2. It indicates that natural dye was adsorbed on the surface of TiO_2 [26, 15].

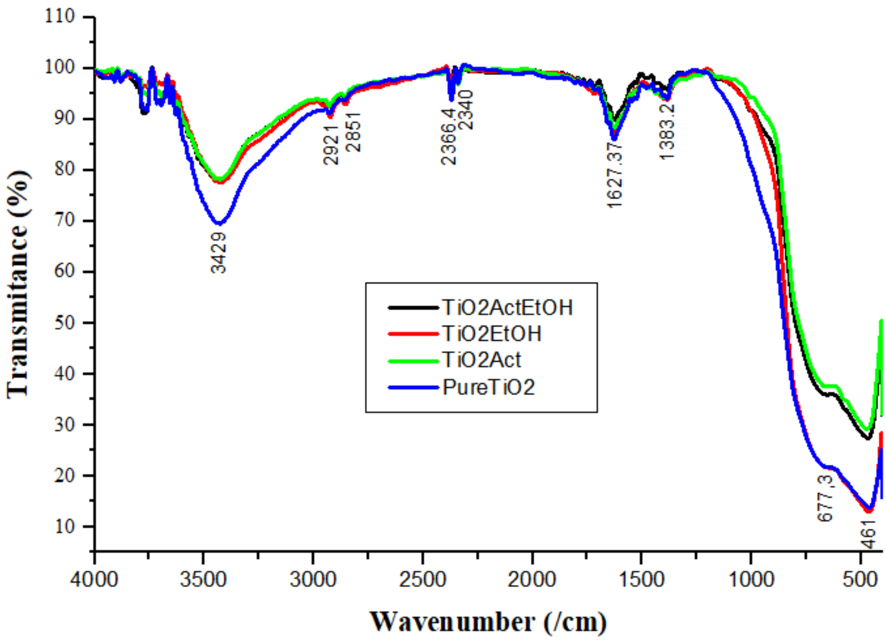

Fig. 2. FT-IR Spectra of TiO_2 before and after immersed in natural dye

3.3 Cyclic Voltammetry Analysis of Natural Dye

The determination of the HOMO and LUMO energy levels of the dyes was obtained from cyclic voltammetry measurement data. The onset data of the first reduction and oxidation potential peaks indicate the HOMO and LUMO energy levels of natural dyes based on the approach proposed by Bredas et al [27]. The voltammetry characteristics diagram of *Syngonium Podophyllum* leaf pigments extracted with ethanol, acetone, and their combination is presented in Fig. 3.

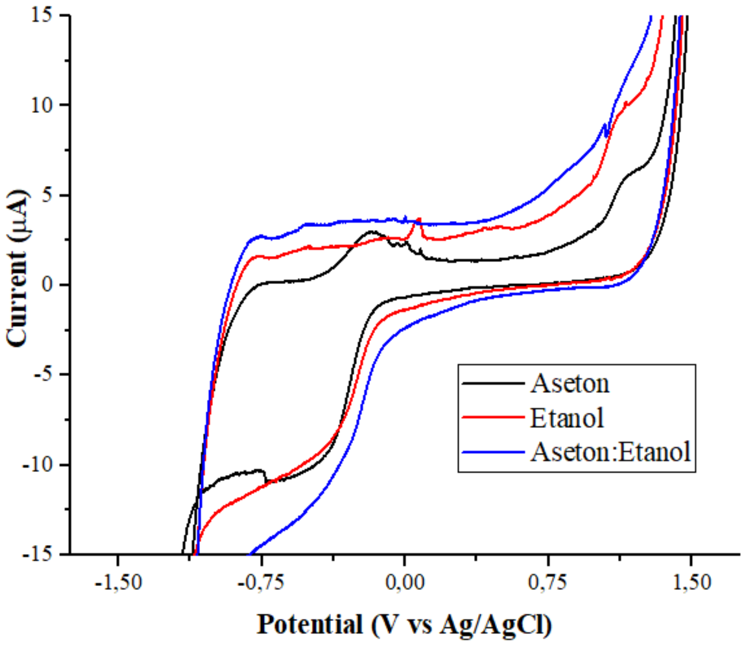

Fig. 3. Cyclic Voltametry of Syngonium Podophyllum with various Solvent Extraction

Table 1. The HOMO- LUMO Energy Levels and Gap Energy of *Syngonium Podophyllum*.

Solvents Extraction	E_{ox} (V vs Ag/AgCl)	HOMO (eV)	LUMO (eV)	E_g (eV)
Ethanol	1.15	-5.55	-3.72	1.83
Acetone	1.10	-5.50	-3.67	1.83
Acetone-Ethanol	1.14	-5.54	-3.72	1.82

Based on the cyclic voltammetry analysis, the HOMO and LUMO data of the natural dyes were obtained, as shown in Table 1. Each dye with different solvents extraction exhibits a LUMO energy level that is more positive than conduction band of semiconductor TiO2 (-4.0 eV) and a HUMO energy level that is more negative than iodide potential (-4.8 eV). This is consistent with the finding reported by Prima, et al [28]. The HOMO and LUMO energy levels play a critical role in determining the efficiency of electron transfer between the electrolyte, dye, and TiO_2 semiconductor. The difference value of gap energy due to difference solvent that used in extraction process, although the value gap is not much different. This is attributed to the similar polarity levels of each extraction solvent.

4 Conclusion

Natural dye derived from *Syngonium podophyllum* leaves extracted with various solvents such as ethanol, acetone and combination of acetone and ethanol have been investigated in this study. Absorbance analysis of natural dye showed that all extracted dye has absorbance peaks in range of 450-650 nm. This is corresponding to the chlorophyll pigment. The broad absorption peak of *Syngonium podophyllum* dye was obtained using combination of ethanol and acetone solutions. The adsorption of natural dye on the surface of TiO_2 has been studied by FTIR analysis. Based on FTIR analysis the transmittance of TiO_2 is increasing after immersed in natural dye solution. This indicate that all extracted natural dye adsorbed on TiO_2 surface. The electrical properties of *Syngonium podophyllum* dye that was extracted using ethanol, acetone and their combination has confirmed that a LUMO energy is must be positive that conduction band of TiO_2 with the value of LUMO energy at range 4,0 and a HUMO energy level that is more negative than iodide potential. The difference value of gap energy due to difference solvent that used in extraction process.

References

1. A Susanti, D., Nafi, M., Purwaningsih, H., Fajarin, R., Kusuma, G.E. 2014. The Preparation of Dye Sensitized Solar Cells From TiO2 and Tamarillo Extract. Procedia Chemistry (9), 3-9 (2014). doi: 10.1016/j.proche.2014.05.002
2. Etefa, H.F.; Dejene, F.B. Comparative Study on Optical, Structural, and Photovoltaic Properties of Binary and Ternary TiO_2 Nanocomposites for Efficient DSSCs. *Mater. Rep. Energy*, *4*, 100281 (2024).
3. Zhou, Y.P.; Wang, L.X.; Wang, B.Y.; Chen, Y.; Ran, C.X.; Wu, Z.B. Polarization Management of Photonic Crystals to Achieve Synergistic Optimization of Optical, Thermal, and Electrical Performance of Building-Integrated Photovoltaic Glazing. *Appl. Energy*, *372*, 123827 (2024).
4. Richariya, G., Kumar, A., Tekasakul, P., Gupta, B. Natural Dye for Sensitized Solar Cells: A Review. Renewable and Sustainable Energy Reviews 69, 705-718 (2017).
5. Kao, M.C., Wenng, J.H., Chiang, C.H., Chen, K.H., Lin, D.Y., Kang, T.K. 2024. Effect of Tungsten on The properties of Titanium Dioxide Dye Sensitized Solar Cells. *Energies*, *17*(20), 511, (2024) **https://doi.org/10.3390/en17205118**
6. Seithtanabutara V., Chumwangwapee N., Suksri A., WongwuttanasatianT. Potential Investigation of combined Natural Dye Pigments Extracted From ivy Gourd Leaves, Black glutinous rice and turmenic for dye-sensitised solar cell. Heliyon 9 e21533 (2023). https://doi.org/10.1016/j.heliyon.2023.e21533

7. Maddah, H.A., Berry, V., Behura, S.K., Biomolecular photosensitizers for dye- sensitized solar cells: Recent developments and critical insights. Renewable and Sustainable Energy Reviews. 121, 109678 (2020).
8. Pathak, C., Surana, K., Shukla, V.K., Singh, P.K. Fabrication and characterization of dye sensitized solar cell using natural dyes. Materials Today: Proceedings. 12,665–670 (2019).
9. Vinaayak, S. B., Balasubramani, V., Shkir, M., Manthrammel, M. A. & Sreedevi, G. Enhancing the performance of TiO2 basedN-DSSC using dye extracted from Cladophora Columbiana, Ludwigia repens and mixed sensitizer. Opt. Mater. 133, 112968. https://doi.org/10.1016/j.optmat.2022.112968 (2022).
10. Wu, T.L., Meen, T.H., and Yang, J.K. Using Various Solvents for extracting Grape Juice as Dye and Appliying It in Fabrication of Dye Sensitized Solar Cells. Applied Functional Materials, ISSN 2737-5323. Volume 3, Issue 3 (2024).
11. Pirdaus, N.A., Ahmad, N., Dahlan, N.Y., Redzuan, A.N., Zalizan, A.H., Muhammad-Sukki, F., Bani, N.A., Patah, M.F.A., and Wan-Mohtar, W.A.A.Q.I. 2024. Performance of Yellow and pink Oyster Mushroom dyes in dye sensitized solar cell. Scientific report 14 : 237537 (2024). https://doi.org/10.1038/s41598-024-73865-z
12. Ludin, N.A., Al-Alwani Mahmoud, A.M., Bakar Mohamad, A., Kadhum, A.A.H., Sopian, K., Abdul Karim, N.S. Review on the development of natural dye photosensitizer for dye-sensitized solar cells. Renew. Sust. Energ. Rev. 31, 386–396 (2014).
13. Tadesse S., Abebe A., Chebude Y., Garcia I.V., and Yohannes, T. 2012. Natural Dye-sensitized solar cells using pigments extracted from Syzygium Guineense. Journal of Phoyonics for Energy. Vol 2, (2012). http://photonicsforenergy.spiedigitallibrary.org/ on 05/17/2015 Terms of Use: http://spiedl.org/terms
14. 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 - Part A Mol. Biomol. Spectrosc., vol. 179, pp. 23–31, (2017). doi: 10.1016/j.saa.2017.02.026.
15. Adedokun, O., Sanusi, Y. K., & Awodugba, A. O. *Solvent Dependent Natural Dye Extraction and its Sensitization Effect for Dye Sensitized Solar Cells. Optik* (2018). doi:10.1016/j.ijleo.2018.06.064
16. Norhisamudin, N.A., Sabani, N., Shamimin, M.M., Juhari, N., Shaari, Ahmad, M.F, Zakaria, N. 2020. The Effect of Differnt Solvent in Natural dye from Roselle (Hibiscus Sabdarifa) and Green Tea Leaves (Cammellia Sinesis) for Dye sensitized Solar Cells. Journal of Physics: Conference Series 1755012024 (2021). doi:10.1088/1742-6596/1755/1/012024
17. Halidun, W.O.N.S., Prima, E,C. Yuliarto, B., and Suyatman. Fabrication Dye Sensitized Solar Cells (DSSCs) Using *β-Carotene* Pigment Based Natural Dye. MATEC Web of Conferences 159, 02052 (2018). https://doi.org/10.1051/matecconf/201815902052
18. Oktariza, L.G., Yuliarto, B., and Suyatman. Performance of dye sensitized solar cells (DSSC) using Syngonium Podophyllum Schott as natural dye and counter electrode. AIP Conf. Proc. 1958, 020022, (2018) https://doi.org/10.1063/1.5034553
19. Shafiee, A., Salleh, M.M., Yahaya, M., Determination of HOMO and LUMO of [6,6]-Phenyl C61-butyric Acid 3-ethylthiophene Ester and Poly (3-octyl-thiophene-2,5-diyl) through Voltametry Characterization. Sains Malaysia. 40, 173–176 (2011).
20. Prima, E.C., Rusliani, P.F., Suhendi, E., Yuliarto, B. 2024. Performance of dye-sensitized solar cells with mixed three natural pigments and reduced graphene oxide as a counter electrode. Results in Optics 14 100592 (2024) https://doi.org/10.1016/j.rio.2023.100592

21. D. Sengupta, B. Mondal, K. Mukherjee. Visible light absorption and photo-sensitizing properties of spinach leaves and beetroot extracted natural dye. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 148 (2015) 85 – 92. (2015).
22. Calogero G, Citro I, Crupi C, Di Marco G. Absorption spectra and photovoltaic characterization of chlorophyllins as sensitizers for dye-sensitized solar cells Spectrochim Acta A Mol Biomol Spectrosc 132:477-484. (2014).
23. Adhyaksa GWP, Prima EC, Lee DK, Ock I, Yatman S, Yuliarto B, Kang JK. A light harvesting antenna using natural extract graminoids coupled with plasmonic metal nanoparticle for bio-photovoltaic cells. Adv Energy Mater 4:1400470 (2014).doi:10.1002/aenm.201400470.
24. Ananth, S., Vivek, P., Arumanayagam, T., Murugakoothan, P. Natural dye extract of lawsonia inermis seed as photo sensitizer for titanium dioxide based dye sensitized solar cells. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 128 (2014) 420–426. http://dx.doi.org/10.1016/j.saa.2014.02.169 (2014)
25. Mir, N., & Salavati-Niasari, M. Preparation of TiO2 nanoparticles by using tripodal tetraamine ligands as complexing agent via two-step sol–gel method and their application in dye-sensitized solar cells. Materials Research Bulletin, 48(4), 1660–1667. (2013). https://doi.org/10.1016/j.materresbull.2013.01.006.
26. Hagfeldt, A., & Graetzel, M. Light-Induced Redox Reactions in Nanocrystalline Systems. Chemical Reviews, 95(1), 49–68 (1995). doi:10.1021/cr00033a003 .
27. Bredas J.L., Silbey R., Boudreaux D.S., Chance R.R. Chain Length Dependence of Electronic and Electrochemical Proprties of Conjugated systems; Polyacetlene, Polyphenylene, Polythiphene, and polypyrrole. J. Am. Chem. Soc. 1983, 105, 6555 – 6559. (1983)
28. Prima, E.C., Qibtiyah, M.A., Brian Yuliarto, B., Suyatman, Dipojono, H.K. Influence of Anthocyanin Co-Pigment on Electron Transport and Performance in Black Rice Dye-Sensitized-Solar-Cell. Ionics (2016). DOI 10.1007/s11581-016-1673-6.