Fabrication of Norbixin-Sensitized Solar Cell and The Effect of Light Intensity on Its Performance and Reusability

W Rahmalia*, E Crespo and T Usman
Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Tanjungpura, Jl. Prof. Dr. H. Hadari Nawawi, Pontianak 78124, West Kalimantan, Indonesia

*E-mail: winda.rahmalia@chemistry.untan.ac.id

Abstract. Dye-sensitized solar cell (DSSC) is a third-generation solar cell that has been developed as one of the clean and renewable alternative energies. This study aims to fabricate norbixin-sensitized solar cell (NSSC). Norbixin was obtained from the saponification followed by acidification of bixin and characterized using UV-Visible and FTIR spectroscopy. The solar cell was assembled using anatase-TiO$_2$ semiconductor, KI/I$_2$/MPII in acetonitrile as the electrolyte, and a platinum paste-based cathode. The UV-Visible spectrophotometry analysis results showed three peaks of carotenoid characteristics at 434, 457, and 486 nm. The formation of norbixin was proved by the absence of a spectral peak for the C=O-C ester group of bixin at 1254 dan 1159 cm$^{-1}$. The cells performance test showed that the maximum energy conversion efficiency of NSSC increased with increasing light intensity up to 0.08 W/cm$^2$. Exposure to the light above this intensity causes a decrease in the maximum energy conversion efficiency due to the temperature factor. The data also showed that the cell assembled was reusable. It still showed relatively good performance until the third day of analysis.

1. Introduction
Solar energy is one of the clean energy alternatives available all the time. Solar energy can be converted into electrical energy using an electronic device called a solar cell or photovoltaic cell. A solar cell produces electrical energy by converting photon energy from sunlight into electrons through the principle of the photovoltaic effect [1]. This conversion can be used to increase the amount of electrical energy supply due to the increasing need for electricity consumption and the development of human life.

One of the currently developed solar cell technologies is dye-sensitized solar cell (DSSC), the third generation of solar cells after silicon-based solar cells and thin-layer solar cells. The DSSC fabrication process is relatively easy, composed of materials with low toxicity and lower costs than previous generation solar cells [2]. Michael Grätzel and Brian O'Regan first developed DSSC. The photovoltaic conversion efficiency of DSSC using ruthenium complex as a sensitizer was reported to reach 12.3% [3].

The sensitizer is one of the essential components in the DSSC system, which functions to harvest light. The sensitizer based on ruthenium complex is reported to be toxic, has limited availability in nature, and is expensive. Therefore, the exploration of sensitizers from natural dyes is being developed. One of the natural dyes that have the potential as a sensitizer in DSSC is norbixin. Norbixin (C$_{24}$H$_{38}$O$_4$, \ldots)
Figure 1) is a carotenoid compound contained in the seeds of kesumba (*Bixa Orellana* L.), a shrub that grows a lot in the tropical area, including Indonesia [4]. Norbixin has nine conjugated double bonds and a carboxylate group on each end of the molecule structure. Due to its chemical structure, norbixin can absorb visible light from 350 to 550 nm with a molar absorptivity >10⁴ L mol⁻¹ cm⁻¹ [5]. It can bond chemically to the surface of the TiO₂ semiconductor through monodentate ester, carboxylate bonds, chelating bidentate, or bidentate bridging [6]. Norbixin can be extracted easily from kesumba seeds using alkaline solvents [5,7,8,9].

![Figure 1. Norbixin chemical structure](image)

Gómez-Ortíz et al.[7] reported the photoelectric conversion efficiency of DSSC using a norbixin sensitizer of 0.130 and 0.017%, when using a TiO₂ and ZnO-based semiconductor, respectively. Norbixin-sensitized solar cells fabricated by Carvalho et al. [10] showed that an efficiency of 0.001% and increased to 0.017% when added 2,2'-bipyridine as an additive in the electrolyte system. The efficiency value is obtained from changes of current and voltage generated by the cell under exposure to light with an intensity of 0.1 W/cm² (1.5 AM). In this paper, another parameter that is important in determining the performance of norbixin-based DSSC is reported, namely the value of short circuit current (Isc) and open-circuit voltage (Voc) under light intensity variations. In addition, the reusability of the cells is also reported for long-term use [11].

2. Materials and Methods

2.1. Materials
Kesumba seeds were obtained from Sintang Regency, West Kalimantan Province, Indonesia. Acetone (≥99.9%) was supplied by Mallinckrodt Chemicals, iodine (I₂) by VWR Chemicals, plastisol by Solaronix, transparent conductive oxide (TCO) glass with fluorine-doped tin oxide (FTO) type thermal evaporation coating, 7–8 ohm/sq (TEC-7) conductive glass by SOLEM. Anatase nanopowder titanium dioxide (TiO₂<25 nm particle size, 99.7% trace metals basis) and 1-methyl-3-propylimidazolium iodide (MPII) were supplied by Sigma Aldrich. Acetonitrile (≥99.8%), ethyl acetate (≥99.9%), potassium iodide (KI), triton-x-100, acetylacetone, and absolute ethanol were supplied by Merck.

2.2. Methods

2.2.1. Norbixin Extraction. Norbixin extraction was carried out by a small modifying method of Gómez-Ortíz et al.[7]. Dried kesumba seeds (100 g) were added to a beaker glass with 500 mL of aqueous 0.1 M NaOH, and stirred for 1 hour. The solution was filtered and adjusted to pH 2 with 0.27 M HCl. The resulting suspension was kept and filtered under a nitrogen atmosphere, and the solid product was stored at 4°C until further application.

2.2.2. DSSC Assembly. DSSCs were assembled by adopting the method of Rahmalia et al.[12]. TCO glasses measuring 2×2 cm² were immersed in 70% ethanol, sonicated for 30 minutes, and dried at a temperature of 100°C for 1 hour. The conductive side of the glasses was determined using a multimeter. Photoanode was prepared by mixing anatase-TiO₂ (2.5 g), absolute ethanol (15 mL), triton-x (16 drops), and acetylacetone (12 drops) by stirring magnetically for 24 h continued by sonicating for 3 hours to form a paste. The electrolyte composition in this work consists of KI (1.66 g), I₂ (0.127 g, 0.05 M), and 0.4 M of MPII mixed in 20 mL acetonitrile.

DSSC was prepared by doctor blading using TEC7 FTO-covered glass as follows. TiO₂ paste and plastisol paste were deposited on FTO glass with 1 cm² active side forming photoanode and cathode.
separately. The photoanode was heated in the furnace at 450 °C for 30 minutes, while the cathode was heated at 400 °C for 5 min. Photoanodes were immersed in norbixin solution concentrated of 3 g/L (in acetone solvent) for 24 h. Furthermore, one drop of electrolyte was added to the photoanode, then covered with a cathode to form a layer like a sandwich. The DSSC assembled using a norbixin sensitizer is then called a norbixin-sensitized solar cell (NSSC).

2.2.3. **NSSC Measurement Performance.** The NSSC was tested for performance ($I_{sc}$ and $V_{oc}$) using a scientific multimeter of 6.5 digits Agilent 34461A. The light source used in the test is a 500 W halogen lamp. The test conditions were carried out with variations in light intensity of 0–0.01 W/cm$^2$. The distance between the light and the DSSC was 20 cm, and the lamp's intensity was adjusted using a lighting control dimmer.

3. **Results and Discussion**

Norbixin was extracted from kesumba seeds which have been dried at 50 °C for 7 hours. The drying process aims to eliminate the water content. Water is a medium for the growth of fungi or bacteria that can accelerate the degradation of organic compounds. In addition, the drying process will also increase the interaction of seeds with the solvent used, thereby increasing the extraction yield. Norbixin extraction was carried out by saponification method of bixin pigment with alkaline NaOH solution, followed by acidification using HCl.[7]

![Figure 2. Norbixin formation mechanism][13]

When the ester group in the bixin pigment reacts with NaOH, it will form a natrium-norbixinat salt compound, where there is a substitution of the methyl group on the ester with Na$^+$ ions. The addition of HCl aims to convert natrium-norbixinat complex salt compound into norbixin compound. In this case, there is an exchange of cations between H$^+$ ions and Na$^+$. This cation exchange will continue until the compound norbixin was formed under acidic conditions. The presence of a precipitate that occurs is an indicator of the formation of norbixin. Stringheta et al.[13] have reported the mechanism of norbixin formation from bixin, as shown in Figure 2. Norbixin obtained from the extraction process in this study was 20.11 mg/100 grams of dried kesumba seeds.

In this study, the extracted norbixin was characterized using UV-visible and Fourier-transform infrared (FTIR) spectroscopy. The results of the analysis are presented in Figures 3 and 4. The UV-visible spectrum of norbixin in acetone (Figure 3) showed a strong absorption around 400 nm. The transition is mediated by $\pi \rightarrow \pi^*$ excited electrons in the conjugated double bond chain of the norbixin molecule[9]. The electronic transition occurs from the lowest vibrational level in the ground state to the lowest vibrational level in the excited state (HOMO→LUMO)[6]. As with carotenoid compounds,
norbixin showed three characteristic peaks at 434, 457, and 486 nm. This result agrees with the norbixin spectra reported by Rahmalia & Naselia[5] and Gómez-Ortíz et al.[7].

![Absorption spectra of norbixin in acetone](image)

**Figure 3.** Absorption spectra of norbixin in acetone

Analysis using FTIR was carried out in the wavenumber range of 400-4000 cm\(^{-1}\). Specific vibrations at certain wavenumbers are an indication of the presence of certain specific functional groups as well. Based on Figure 4, the extracted norbixin in this study have bands in the wavenumber region as follows: 3435 cm\(^{-1}\) which indicates stretching vibrations for O-H of the carboxylate group; 2923 and 2845 cm\(^{-1}\) for \(-\text{CH}_2\)- stretching vibrations, 1712 cm\(^{-1}\) for C=O carboxylate stretching vibrations, 1612 cm\(^{-1}\) for C=C stretching vibrations of alkenes, 1437 cm\(^{-1}\) for C\(_{\text{sp}2}\)-H deformation or \(=\text{CH}\) in-plane bending, and 976 cm\(^{-1}\) for C\(_{\text{sp}2}\)-H deformation (olefins) [8]. This spectral pattern shows the absence of an ester group as found in the bixin molecular structure, indicated that bixin had been successfully converted to norbixin. The results are also in agreement with the pattern of FTIR spectra for norbixin reported by Rahmalia & Naselia[5], Gómez-Ortíz et al.[7], and Fontinele et al.[8].

![FTIR spectrum of norbixin](image)

**Figure 4.** FTIR spectrum of norbixin

The extracted norbixin was then applied as a sensitizer in DSSC. The solar cell prepared with TiO\(_2\) semiconductor acquired a deep orange color upon immersion in norbixin solution. Figure 5 shows the parameters affecting DSSC performance. The \(V_{oc}\) is the maximum voltage available from a DSSC that occurs at zero current, \(I_{sc}\) is the current through the DSSC when the voltage across the DSSC is zero. While the maximum energy conversion efficacy describes the performance of a DSSC, how much solar energy (photons) can be converted into electrical energy without considering the value of the fill factor. It is the ratio between power generated by DSSC and the power of the light source[10].
Based on Figure 5, there is a relationship between $V_{oc}$, $I_{sc}$, and the maximum energy conversion efficiency to the light intensity. The variation of the illumination intensity significantly affects the $I_{sc}$ and $V_{oc}$. Any change of the irradiation causes a proportional change in the $I_{sc}$ and $V_{oc}$. There are linear increases in $I_{sc}$, both on the first-, second- and third-day measurements, with irradiation in the range 0-0.10 W/cm$^2$. The light-generated current is proportional to the flux of photons; therefore, $I_{sc}$ is directly proportional to the light intensity[14]. In contrast, open-circuit voltage increases logarithmically with light intensity, according to the trend reported by Cuce et al.[14] and Tobnaghi et al.[15]. An increase in temperature accompanies an increase in light intensity. An increase in temperature reduces the bandgap of solar cells, affecting the solar cell output parameters[16]. Tobnaghi et al.[15] also reported that the parameter most affected by temperature is $V_{oc}$.

![Graphs showing performance parameters of DSSC](image)

**Figure 5.** Performance parameters of DSSC at first (◊), second (○), and third (□) day of measurement

**4. Conclusion**

Norbixin is a potential sensitizer that could be developed for DSSC system. There is a relationship between $V_{oc}$, $I_{sc}$, and the maximum energy conversion efficiency to the light intensity. The $I_{sc}$ increases linearly, while the $V_{oc}$ increases logarithmically with light intensity with the maximum energy conversion efficiency of 0.024% under 0.08 W/cm$^2$ of light intensity. The DSSC assembled in this is reusable. Their energy storage and charging function worked well until the third-day measurement.
References
[1] Ananth S, Vivek P, Kumar G S, and Murugakoothan P 2015 Performance of Curcumin from Curcuma longa L. as photo-sensitiser for dye sensitized solar cells *Spectrochimica Acta A: Molecular and Biomolecular Spectroscopy* 137 345-350
[2] Devadiga D, Selvakumar M, Shetty P, Santosh M S 2021 Dye-sensitized solar cell for indoor applications: a mini-review *Journal of Electronic Materials* 50 3187-3206.
[3] Nazeeruddin Md K, Baranoff E, and Grätzel M 2011 Dye-sensitized solar cells: a brief overview *Solar Energy* 85 1172-78.
[4] Rahmalia W, Nurlina, Septiani, and Naselia U A 2021a *Bixin dari Biji Kesumba (Bixa Orellana L.): Metode Ekstraksi, Karakterisasi, dan Aplikasi* (Pontianak: UNTAN Press).
[5] Rahmalia W, and Naselia U A 2021 Transition energy, spectral fine structure, and absorption coefficient of norbixin (9'-cis-6,6'-diapocarotene-6,6'dioic acid) in different polar solvents *Journal of Physics: Conference Series* 1751: 012085.
[6] Rahmalia W, Fabre J F, Usman T, and Mouloungui Z 2016 *Bixin adsorption characteristic on TiO2* Proc. Int. Conf. on The IRES 28th 6th February 2016 (Jakarta, Indonesia) ISBN: 978-93-85973-19-2.
[7] Gómez-Ortíz N M, Vázquez-Maldonado I A, Pérez-Espadas A R, Mena-Rejón G J, Azamar-Barrios J A, and Oskam G 2010 Dye-sensitized solar cells with natural dyes extracted from Achiote seeds *Solar Energy Materials & Solar Cells* 94 40-44
[8] Fontinele L P, Sousa R, Viana V, Farias E, Queiroz E L, and Eiras C 2018 Norbixin extracted from urucum (*Bixa orellana L.*) for the formation of conductive composites with potential applications in electrochemical sensors *Surfaces and Interfaces* 13 92–100
[9] Silva M G, Garcia A L, Brito E S, and Carvalho P R N 2018 The Annatto Carotenoids and the Norbixin Absorption Coefficient *Rev. Inst. Adolfo Lutz* 77 1-8.
[10] Carvalho I C, Barbosa M L, Costa M J S, Longo E, Cavalcante L S, Viana V G F, and Santos R S 2021 TiO2-based dye-sensitized solar cells prepared with bixin and norbixin natural dyes: effect of 2,2’,-bipyridine additive on the current and voltage Optik 218 1-10.
[11] Rahmalia W, Silalahi I H, Usman T, Fabre J F, Mouloungui Z, and Zissis G 2021b Stability, reusability, and equivalent circuit of TiO2/treated metakaolinite-based dye-sensitized solar cell: effect of illumination intensity on Voc and Isc values *Materials for Renewable and Sustainable Energy* 10 1-10.
[12] Rahmalia W, Septiani, Naselia U A, Usman T, Silalahi I H, and Mouloungui Z 2021c Performance improvements of bixin and metal-bixin complexes sensitized solar cells by 1-methyl-3-propylimidazolium iodide in electrolyte system *Indonesian Journal of Chemistry* 21 669-678.
[13] Stringheta P C, Silva P I, and Costa A G V 2018 Anatto/Urucum-Bixa orellana *Exotic Fruits* ed Rodrigues S et al (Amsterdam: Elsevier) p 23-30.
[14] Cuce E, Cuce P M, and Bali T 2013 An experimental analysis of illumination intensity and temperature dependency of photovoltaic cell parameters *Applied Energy* 111 374-382.
[15] Tobnaghi D M, Madatov R, and Farhadi P 2013 *Investigation of light intensity and temperature dependency of solar cells electric parameters* Proc. Electric Power Engineering & Control Systems 21st-23rd November 2013 (Ukraine).
[16] Singh P, Singh S N, Lal M, and Husain M 2008 Temperature dependence of I–V characteristics and performance parameters of silicon solar cell *Solar Energy Materials & Solar Cells* 92 1611-16.
[17] Cheegaar M, Hamzaoui A, Namoda A, Petit P, Aillerie M, and Herguth A 2013 Effect of illumination intensity on solar cells parameters *Energy Procedia* 36 722-9

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