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Hayat Azwar, Putra A. Erwin E., Amaliyah Novriany, Hayase Shuzi, Pandey Shyam S.

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**Piper Ornatum** and **Piper Betle** as Organic Dyes for TiO$_2$ and SnO$_2$ Dye Sensitized Solar Cells

Azwar Hayat$^1$, A. Erwin E. Putra$^1$, Novriany Amaliyah$^1$, Shuzi Hayase$^2$ and Shyam. S. Pandey$^2$

$^1$Mechanical Engineering Department, Faculty of Engineering, Hasanuddin University, Poros Malino Km. 6 Gowa, South Sulawesi, Indonesia.
$^2$LSSE, Kyushu Institute of Technology, Japan, 2-4 Hibikino, Wakamatsu-ku, Kitakyushu-shi, Fukuoka, Japan.

E-mail: azwar.hayat@unhas.ac.id

**Abstract.** Dye sensitized solar cell (DSSC) mimics the principle of natural photosynthesis are now currently investigated due to low manufacturing cost as compared to silicon based solar cells. In this report, we utilized Piper ornatum (PO) and Piper betle (PB) as sensitizer to fabricate low cost DSSCs. We compared the photovoltaic performance of both sensitizers with Titanium dioxide (TiO$_2$) and Tin dioxide (SnO$_2$) semiconductors. The results show that PO and PB dyes have higher Short circuit current ($J_{sc}$) when applied in SnO$_2$ compared to standard TiO$_2$ photo-anode film even though the Open circuit voltage ($V_{oc}$) was hampered on SnO$_2$ device. In conclusion, from the result, higher electron injections can be achieved by choosing appropriate semiconductors with band gap that match with dyes energy level as one of strategy for further low cost solar cell.

1. **Introduction**

Solar energy is one of the greenest types of energy resources. It is free and abundant that makes this energy form one of candidate to replace fossil fuel. Silicon based solar cells have dominated the installed solar cell today. However, Silicon based solar cell required huge energy resources to purify the silicon and high production cost in order to achieve high efficiency cell. Low cost solar cells, such as Dye sensitized solar cells (DSSCs) are gaining more and more attention owing to their high efficiency and relatively lower cost of production [1]. A DSSC consist of two sandwiched electrodes, working and counter electrode, made from transparent conducting glass which mainly made of Fluorine doped tin oxide (FTO). Working electrode is made of thin layer of semiconducting material such as titanium dioxide (TiO$_2$), tin dioxide (SnO$_2$) Zinc oxide (ZnO) etc, coated with dyes as photo anode on top of FTO [2-9]. Counter electrode is made of FTO with thin layer of platinum or carbon [10-13]. Electrolyte is placed between both electrodes to connect and maintain electrons transfer. One of the main components to enhance the Photo-conversion efficiency (PCE) is dye sensitizer. The most widely used in DSSCs research area are Ruthenium based sensitizer. In the recent past Ruthenium based as well as metal free dyes have been reported having nearly quantitative photon harvesting mainly in the visible region of solar spectrum [14-17]. High quality ruthenium dyes are produced in sophisticated ways that increase the production cost of the DSSC. Most of sensitized dyes need anchoring groups in order to attach in nanoporous surface. Although attachment dyes on the nanoporous oxide semiconductor via a suitable anchoring group is common practice in DSSCs but...
Introduction of such anchoring groups in dye structure at suitable position is synthetically cumbersome. In order to attach dyes on nanoporous oxide semiconductor surface, it could be achieved by several types of bonding, for example hydrophobic or electrostatic interactions and co-valent bonding [18]. Natural dye has widely used in textiles industry and recently in DSSC as sensitizer due to easier to prepare and low in cost [19-23]. In this works, the extracts of Piper ornatum and Piper betle as dye sensitizer in DSSC. The absorption spectra of PO and PB dyes solution in ethanol was measured with UV-VIS Spectrophotometer. The DSSC was made using two types of semiconductors which are TiO$_2$ and SnO$_2$. The current-voltage (I-V) characteristics were measured along with Incident photon-to-current Efficiency (IPCE) to determine the photo-conversion efficiency and internal quantum efficiency.

2. Experimental

2.1. Dye preparation

The natural dyes used in this work extracted from Piper Ornatum (PO) and Piper Betle (PB) leafs. PO and PB fresh leafs was cleaned with distilled water and dried in shaded place for more than 3 weeks. After dried, the dried leaf ware crushed with Food grinder FTC-Z100 with output fineness 20-180 mesh. Powdered PO and PB ware diluted in ethanol. 1 gr of powdered leafs was immersed in 10 ml of ethanol and stored for 48 hours in dark place. After that, dye solution was filtered from remained powder using vacuum pump. Dye solution was kept in dark container to protect it from direct light exposure.

2.2. Preparation of dye sensitized solar cell

DSSCs were fabricated with standard sandwich-like structure. Working electrode was prepared using Fluorine doped Tin Oxide (FTO) glass coated with 7 µM thick TiO$_2$ (30NRD) and SnO$_2$ followed by backing at 450°C for 30 minutes. Baked working electrode immersed in dye solution for 20 hours (figure 2). The cell area was 0.25 cm$^2$. The thickness of the spacer used to create a gap between working electrode and counter electrode was 25 µm (Solaronix Spacer). Counter electrode using Platinum (Pt) sputtered on FTO glass and electrolyte containing 500 mM LiI, 50 mM I$_2$, 600 mM Ethylmethylimidazolium dicyanoimide (MeEtIm-DCA), and 580 mM tert-butylpyridine (TBP) in Acetonitrile was used to fabricate the DSSCs. Natural dye solution in ethanol was used for sensitizer on the TiO$_2$ and SnO$_2$ surface. Photovoltaic characterization the DSSCs were made using a solar simulator (Bunko-Keiki Co. Ltd., Model Solar Simulator CEP-2000SRR) and black metal mask used to avoid the effect of optical reflection on photovoltaic measurement.

Figure 1. Absorption spectra of Natural dyes: Piper Ornatum in solution (red solid lines) and Piper Betle in solution (green dashed lines).
3. Results and Discussions

Two kinds of Natural dyes (PO and PB) have been utilized as sensitzers in the present work. Two kind of semiconducting materials (TiO$_2$ and SnO$_2$) ware utilized to accommodate energy level of the dyes. Both PO and PB dyes used in the present work exhibits intense light absorption having absorption maximum at 667 nm and 671 nm in ethanol solution for the PB and PO dyes respectively. Light absorption spectra of dyes were characterized using UV-VIS spectrophotometer (Jusco V-670) to confirm the dye absorption (figure 1). Due to lower solubility of the natural dyes, it has been found that 48 hours are required to immerse in ethanol solution before proper usage in DSSC fabrication.

![Figure 2. Immersion of semiconductor films on PO and PB dye.](image)

### Table 1. I-V Characteristic of DSSCs with PO and PB dyes.

|        | PO- TiO$_2$ | PO- SnO$_2$ | PB- TiO$_2$ | PB- SnO$_2$ |
|--------|-------------|-------------|-------------|-------------|
| Efficiency [%] | 0.032       | 0.022       | 0.034       | 0.014       |
| FF     | 0.553       | 0.357       | 0.598       | 0.325       |
| Voc[V] | 0.463       | 0.238       | 0.455       | 0.202       |
| Jsc[mA/cm$^2$] | 0.124       | 0.261       | 0.125       | 0.207       |

Figure 3 exhibits the current-voltage characteristics of the DSSCs fabricated using these two dyes as sensitizers. It can be clearly seen that PO and PB exhibits relatively same PCE on TiO$_2$ as compared to the SnO$_2$ fabricated under similar experimental conditions. This phenomenon occurred maybe due to deeper LUMO (Low Unoccupied Molecular Orbital) of these dyes that suppress the electron injection to semiconductor conduction band. The main factor controlling the efficiency is the short circuit density (Jsc) since open circuit voltage (Voc) and fill factors (FF) are nearly the same for PO and PB for each semiconductor. Table 1 shows result of PO-TiO$_2$ have Jsc of 0.124 mA/cm$^2$, Voc 0.463 V, FF 0.553 and PCE 0.032% and PB-TiO$_2$ have Jsc of 0.125 mA/cm$^2$, Voc 0.455 V, FF 0.598 and PCE 0.034% for device with TiO$_2$ semiconductor. The results were comparatively higher that dye from same genus reported before utilizing Piper Nigrum which was exhibit only 0.009% of PCE [24].
Device with SnO$_2$ semiconductor, PO-SnO$_2$ have Jsc of 0.261 mA/cm$^2$, Voc 0.238 V, FF 0.357 and PCE 0.022% and PB-SnO$_2$ have Jsc of 0.207 mA/cm$^2$, Voc 0.4202 V, FF 0.325 and PCE 0.014%. The results are interpreted in terms for facile dye regeneration in SnO$_2$ film was higher as compared to TiO$_2$ film due to its deeper conduction band. IPCE graph shown that photon to current density on SnO$_2$ film was higher. Higher electron injection was confirmed from peaks shown in 600 to 700 nm wavelength that agreed with absorption peak of the dyes shown in figure 4. Cells fabricated with SnO$_2$ film have lower Voc due to high traps on SnO$_2$ semiconductor lead to higher recombination that affect the Voc and FF.

4. Conclusions
DSSCs using Natural dyes Piper Ornatum and Piper Betle were fabricated for with two type semi conducting material Titanium dioxide and Tin dioxide. Fabricated cells produced relatively same PCE on TiO$_2$ film. Deeper conduction band of SnO2 compared to TiO2 lead to higher dye regeneration in SnO$_2$ film. IPCE graph confirmed that photon to current density on SnO$_2$ film was higher shown from peaks shown in 600 to 700 nm wavelength. Traps on SnO$_2$ semiconductor lead to higher recombination that affect the Voc and FF make both parameters lower compared on TiO$_2$ film. In conclusion, from the result, higher electron injections can be achieved by choosing appropriate semiconductors with band gap that match with dyes energy level as one of strategy for further low cost solar cell.

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References
[1] Brian O and Grätzel M 1991 A Low-cost, High-efficiency Solar Cell Based on Dye Sensitized Colloidal TiO$_2$ Films *Nature* **353** 6346 737-740
[2] Chandiran A K, et al 2014 Analysis of Electron Transfer Properties of ZnO and TiO$_2$ Photoanodes for Dye-sensitized Solar Cells *ACS nano* **8** 3 2261-2268
[3] Ahn S H, et al 2013 One-Dimensional Hierarchical Nanostructures of TiO$_2$ Nanosheets on SnO$_2$ Nanotubes for High Efficiency Solid-State Dye-Sensitized Solar Cells *Advanced Materials* **25** 35 4893-4897
[4] Niu H, et al 2014 Dye-sensitized Solar Cells Employing a Multifunctionalized Hierarchical SnO$_2$ Nanoflower Structure Passivated by TiO$_2$ Nanogranulum *The Journal of Physical Chemistry C* **118** 7 3504-3513
[5] Thapa A, et al. 2014 TiO$_2$ Coated Urchin-like SnO$_2$ Microspheres for Efficient Dye-sensitized Solar Cells *Nano Research* **7** 8 1154-1163

[6] Lv H, Xiaowei Y and Can C 2017 Enhancing the Photovoltaic Performance of Dye-sensitized Solar Cells by Modifying TiO$_2$ Photoanodes with Layered Structure g-C3N4 *AIP Conference Proceedings* **1820** 1

[7] Dongre J K 2017 A Comparative Study on the CDS Sensitized and Dye-sensitized ZnO Photoelectrodes Based on Solar Cell Performance *IJAR* **3** 3 504-507

[8] Abdalla J T, et al. 2017 TiCl$_4$ Surface-treated SnO$_2$ Photoanodes for Self-powered UV Photodetectors and Dye-sensitized Solar Cells *Materials Technology* **32** 7 443-450

[9] Samsuri S A M, et al. 2017 Influence of ZnO Growth Temperature on the Performance of Dye-sensitized Solar Cell Utilizing TiO$_2$-ZnO Composite Film Photoanode *Ironics* 1-12

[10] Ahmad I, et al. 2014 Carbon Nanomaterial Based Counter Electrodes for Dye-sensitized Solar Cells *Solar Energy* **102** 152-161

[11] Zheng M, et al. 2015 Flowerlike Molybdenum Sulfide/Multi-walled Carbon Nanotube Hybrid as Pt-free Counter Electrode Used in Dye-sensitized Solar Cells *Electrochimica Acta* **173** 252-259

[12] Ma J, et al. 2014 3 D Single-Walled Carbon Nanotube/Graphene Aerogels as Pt-Free Transparent Counter Electrodes for High Efficiency Dye-Sensitized Solar Cells *ChemSusChem* **7** 12 3304-3311

[13] Arbab A A, et al. 2017 A Complete Carbon Counter Electrode for High Performance Quasi Solid State Dye Sensitized Solar Cell *Journal of Power Sources* **343** 412-423

[14] Parisi A, et al. 2017 Anomalous Performance Enhancement Effects in Ruthenium-based Dye Sensitized Solar Cells *Clean Electrical Power (ICCEP) 2017 6th International Conference on IEEE*

[15] Parisi A, et al. 2017 Electro-optical Characterization of Ruthenium-based Dye Sensitized Solar Cells: A study of light soaking, ageing and temperature effects *Optik-International Journal for Light and Electron Optics* **135** 227-237

[16] Nagarajan B, et al. 2017 Novel Ethynyl-pyrene Substituted Phenothiazine Based Metal Free Organic Dyes in DSSC with 12% Conversion Efficiency *Journal of Materials Chemistry A* **5** 21 10289-10300

[17] Chiu K Y, et al. 2017 A New Series of Azobenzene-bridged Metal-free Organic Dyes and Application on DSSC *Dyes and Pigments* **146** 512-519

[18] Kalyanasundaram K and Grätzel M 1998 Applications of Functionalized Transition Metal Complexes in Photonic and Optoelectronic Devices *Coordination chemistry reviews* **177** 1 347-414

[19] Lim A, et al. 2016 Co-dominant Effect of Selected Natural Dye Sensitizers in DSSC Performance *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **167** 26-31

[20] Jinchhu I, et al. 2016 Photovoltaic Parameters of DSSCs Using Natural Dyes with TiO$_2$ Nanopowder and Nanofiber as Photoanodes: A Comparative Study *Electrical, Electronics, and Optimization Techniques (ICEEOT) International Conference on IEEE*

[21] Teoli F, et al. 2016 Role of pH and Pigment Concentration for Natural Dye-sensitized Solar Cells Treated with Anthocyanin Extracts of Common Fruits *Journal of Photochemistry and Photobiology A: Chemistry* **316** 24-30

[22] Sathyajothi S, Jayavel R and Dhanemozhi C A 2017 The Fabrication of Natural Dye Sensitized Solar Cell (DSSC) Based On TiO$_2$ Using Henna And Beetroot Dye Extracts *Materials Today: Proceedings* **4** 2 668-676

[23] Yoon S I, et al. 2016 Deprotonated Curcumin as A Simple and Quick Available Natural Dye for Dye Sensitized Solar Cells *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* **38** 2 183-189

[24] Abdel-Latif M S, El-Agez T M, Taya S A, El-Ghamri H S and Batniji A Y 2015 Dyes Extracted
from Biota orientalis, Piper nigrum, and Glycyrrhiza glabra as Photosensitizers for Dye-Sensitized Solar Cells *International Journal of Renewable Energy Research (IJRER)* 5(4) 1034-1040