Hybrid Solar Cell using Conjugated Chlorophyll from Pandanus Amaryllifolius as Photosensitizers


Abstract: Solar energy is one of all few sources to renewable power and it is considerably critical in our each day lifestyles usage thus resulted to ensure the practicality and usefulness of the devices which regularly used to capture and manipulate solar energy. In this work, studies the effect of conjugated chlorophyll (iCHLO) on power conversion efficiency with relation of iCHLO where optical and electrical properties were investigated. These hybrid solar cells consist of combination of organic (Poly (3, 4-ethylenedioxathiophene): poly (styrenesulfonate) and iCHLO) and inorganic (Titanium Dioxide, TiO$_2$) materials. These hybrid solar cells were fabricated bilayer of ITO/TiO$_2$/PEDOT: PSS/iCHLO/Al. Chlorophyll compound (CHLO) was extracted from the Pandanus amaryllifolius leaves. CHLO undergoes conjugate process by oxidation polymerization using Ferric Chloride (FeCl$_3$) as catalyst. Different percentage of FeCl$_3$ was varied by 5%, 10% and 15% of CHLO molecular weight. Result shows that UV-Vis absorption spectra of CHLO was absorbed in the range of 400 nm – 600 nm (CHLO-PA) and 240 nm - 360 nm (iCHLO-PA). The highest power conversion efficiency (PCE) was obtained at 1.33% and electrical conductivity is 0.135 Scm$^{-1}$ for ITO/TiO2/PEDOT: PSS/iCHLO-PA 10% hybrid solar cell.

Index Terms: efficiency, conjugated chlorophyll, hybrid solar cell, PEDOT: PSS, TiO$_2$

I. INTRODUCTION

Nowadays, global energy demand is continuously growing and commonly dependent on fossil fuels, natural gas, coal and oil [1]. By relying on fossil fuel, besides being pricy it is also inefficient plus it is continuously causing pollution by releasing gaseous which sometimes affects human health. Therefore, renewable energy resources are needed to replace the depleted fossil fuels because of low cost, abundant of sources and environmental friendly [2]. Renewable energy can be simply said as energy collected from natural resources such as wind, solar, biomass and hydropower. Solar energy is used to harness sunlight and it is very useful for human in their daily life such as generating electricity, lighting and also industrial usages. An electrical device that converts energy of light directly into electricity through photovoltaic effect also known as photovoltaic. Hence, it will not produce pollution including disturbing noise, toxic substances and greenhouse emission [3-5]. With photovoltaic cells and solar electric panel system, electricity consumption in human daily life can easily be reduced thus automatically reduces cost [6-9].

In addition, PEDOT: PSS is the most widely utilized polymer as a hole-conducting layer of OLED and photovoltaic cells. The advantages of these materials include low in temperature, excellent in stability, large area processing, low in production cost, and flexibility. However, the efficiency of this material is limited by its low carrier mobility [15]. The natural dye was used as sensitizers because of sensitizers having a broad absorption band in conjunction with oxide films of nanocrystalline morphology permits to harvest a large fraction of sunlight. Besides, natural dyes are easily available and can be used with an acceptable efficiency besides can be extracted with simple procedures [16-19]. The extraction of chlorophyll from Pandanus amaryllifolius shows a broad range and frequency between 410 nm – 700 nm which is located within the visible range [20]. With the ability to absorb this high light, it can convert the absorbed light energy to electrical energy with the higher amount of energy. Besides, commonly known that chlorophyll is the green colour pigment and they are a lot of sources in nature and non-toxic [21]. However, the colour absorption of chlorophyll is weak and the chemical bonding can easily break, thus limited the amount of charge carriers to produce electricity in application of solar cell. At the same time, chlorophyll in market are sensitive to the light, which makes the main reason for the common chlorophyll from the green plant has been chosen [22]. To date, this problem also supported by Han et al., and Setyawati et al., [23, 24] stated that, the absorption of the nature chlorophyll is weak and insufficient for its practical application. On the other hand, natural dyes are easily available and can be used with an acceptable efficiency [25]. Thus, Pandanus amaryllifolius were chosen as natural dyes and undergo the conjugated chlorophyll in this research. To the best author knowledge, photosynthesis concept and conjugated chlorophyll using FeCl$_3$ is the first study to the photosensitizers to apply in hybrid DSSC. The predictions of conjugated chlorophyll are also discussed in this paper.
Hybrid Solar Cell using Conjugated Chlorophyll from Pandanus Amaryllifolius as Photosensitizers

II. METHODOLOGY

A. Extraction Chlorophyll from Natural Dye

Organic dye was taken from natural plant, Pandan leaves. Pandan leaves or scientifically known as Pandanus amaryllifolius were plucked around Kuala Neru, Terengganu. These natural dyes were cut into smaller pieces, dried and weighted. 10 g of weighted dried pandan leaves were immersed into 150 ml of ethanol for overnight before filtered the next day. After, the solution was filled into a blue reagent bottle.

B. Conjugated Chlorophyll

The 20 ml of chlorophyll was combined with 5 % of FeCl₃, and 200 ml of chloroform was diluted in in a three-neck flask. The solution was supplied with nitrogen gas, and refluxed at a temperature of 50–60°C with moderate stirring continuously for 48 hours. Replacing the chloroform was vaporized, chloroform was added from time to time. This process continues until there is brown-black precipitate was formed. Then, methanol was added to allow precipitation of conjugated dye occur. The deposition process is for 48 hours without stirring. The product was filtered from the remaining polymerization solution containing FeCl₃ using vacuum filtration. The precipitate rinsed with 2 times 100 ml of methanol until no discoloration in methanol, followed by 50 ml of de-ionized water. Finally, 50 ml ethanol was added into the solution to form the product of conjugated dye [26]. Then, the steps were repeated with different 10% and 15% of FeCl₃.

C. Fabrication of Thin Film

The simulation software, Hybrid solar cells were fabricated bilayer using a few technique; doctor’s blade for TiO₂ solution, spin coating method for polymer (PEDOT: PSS) and dip coating method for dye. For the first layer, 0.2 M of TiO₂ paste was blended together by mixing with 50 ml ethanol, TritonX-100 and then followed by a few drop of diluted acetic. The TiO₂ solution were additionally diluted with ethanol until acquired solution. So that, the solution was mixed on stirrer in room temperature for 24 hours [27, 28]. Temperature used for annealing TiO₂ was at 450 °C for 30 minutes on a hot plate. The annealing step was an important step to rein-forced the attachment of TiO₂ layer with ITO substrate. In addition, the solvent can be removed thus enhanced the mobility of charge carrier in sample. Deposition of second layer of PEDOT:PSS solution was mixed by 2 ml of 5% dimethyl sulphoxide (DMSO) and 0.5% Triton 100, and spin coated at 2000 revolutions per minute (rpm) for 10 s and subsequently 3000 rpm for 40 s, then dried on a hotplate at 150 °C for 15 minutes [29]. Efficiencies of Hybrid solar cell were measured using Autolab Potentiostat PGSTAT 302. Efficiency of hybrid solar cell was then calculated using equations (3) and (4).

\[ \sigma = \frac{R_s}{P_{in}} \times 100 \]  
\[ \eta = \frac{P_{out}}{P_{in}} \times 100 \]

III. RESULTS AND DISCUSSION

A. UV-Visible Analysis

Fig. 2 shows the representative UV-Vis absorption spectra for the extracts of Pandanus amaryllifolius. Chlorophyll Pandanus amaryllifolius (CHLO-PA) exhibits two absorption peaks at 434 nm and 664 nm. While conjugated chlorophyll Pandanus amaryllifolius, iCHLO-PA shows three maximum peaks with shifted to the left with shorter wavelength known as red shift (bathochromic shift). According to the graph, 5% iCHLO-PA, 10% iCHLO-PA and 15% iCHLO-PA are sharing the same peak of λmax at 311 nm and 360 nm; respectively with different absorbance. These absorptions assigns to their identical components, commonly known as chlorophyll. Usually there are two types of chlorophyll would be found widely which are chlorophyll a and b and are used as the absorber of the light [30, 31]. Furthermore, the absorption peak for iCHLO-PA was red.
shifted compared to the CHLO-PA as this shift could be due to the chemical adsorption surface, for which the surface of the narrow band between the treatments pigment molecules. Thus, the energy of the electron transition is reduced and the absorption spectrum is extended to the visible region [32, 33]. Therefore, the iCHLO-PA absorption spectrum divisions increase energy absorption as a cause to improve the efficiency of solar hybrid cells.

![Figure 2](image)

**Fig. 2. UV-Vis absorption Pandanus amaryllifolius chlorophyll (CHLO-PA) and conjugated chlorophyll (iCHLO-PA) with 5\% (red), 10\% (blue) and 15\% (green) percentages of FeCl\textsubscript{3}.**

### B. Optical Energy Gap

The optical band gap of CHLO and iCHLO can be observed from optical absorbance measurements. From the Table I presents the energy gap of PA. Energy gap before undergoes conjugating process is PA 1.831 eV and after the process, the value of optical energy gap shows slightly increased to the value iCHLO-PA (5\%) 3.205 eV, iCHLO-PA (10\%) 3.192 eV and iCHLO-PA (15\%) 3.195 eV. Comparing the result between CHLO and iCHLO, iCHLO has the higher energy gap but the higher energy gap, the more difficult for a carrier charge to be excited across the band gap. However, from this energy gap can determined that after conjugating process, the changes of organic to inorganic material can be occurred as mention in Costa et al. [34] and Choi et al. [35]. But this study, conjugated chlorophyll (iCHLO) is more suitable to be used as sensitizer to capture light and Ludin et al. [36] stated that conjugated chlorophyll have bigger molecule structure and it is last longer compare to chlorophyll (CHLO).

### C. FTIR Analysis

As shown in Fig. 3, referring to the first peak from left, pure compounds; chlorophyll Pandanus amaryllifolius' wavenumber (black) is at 3307.92 cm\(^{-1}\). This broad and medium peak was created by O-H groups which contain in the sample. The peak becomes greater and bigger as dyes were added proving that the dyes itself enhance the reaction of compounds. Although the reaction does not consist of any O-H group, but O-H group may be present as a result from the reaction between dyes and the sample. Referring to the peaks at 2973.92 cm\(^{-1}\), 1361.67 cm\(^{-1}\) and 877.89 cm\(^{-1}\) respectively, it appears to acknowledge the presence of C-H bonding in the samples. Besides, the waves were shifted to the right as exhibits in the graph as there were changes in the frequency and energy transmittance in the C-H bond which causing the differences in wavenumbers thus affect the numbers of peaks appearance. Since wavenumbers along the range of 2000 cm\(^{-1}\) to 2500 cm\(^{-1}\) only play the supporting role to proof that there was a definite presence of the double bond there. These facts were being confirmed by the 1637.56 cm\(^{-1}\) peak which generally determined the presence of the alkene group C=C aromatic. The wave becoming stronger at the peak of 1638.64 cm\(^{-1}\) and 1631.51 cm\(^{-1}\) and undoubtedly more obvious parallel to the adding of the dyes. This shows that these dyes were obviously great as catalysts in enhancing absorption. Concerning on the CHLO-PA (black) line, the first and second wave appeared was C-H bend at 877.89 cm\(^{-1}\) and 1361.67 cm\(^{-1}\) respectively. The iCHLO-PA (red, blue and green) lines shows that there were C-C bends appeared to the right at 922.86 cm\(^{-1}\). The peak appearance after catalyst represents C=C at a wavenumber ranging from 2262 cm\(^{-1}\) to 2250 cm\(^{-1}\). This occurred due to lack of hydrogen atom resulted in the bonded process of carbon-carbon atoms. The peaks that appeared at the right hand side of the C-O is the C-H peak which play as supporting role to the appearance of C-H compounds in the samples. It can be seen that the peaks ranging from 450 cm\(^{-1}\) – 480 cm\(^{-1}\) resembles the presence of Fe-O compounds. Although this study does not involves any Fe-O compounds, but Fe-O compounds may be appeared as a results of reaction between samples and dyes that added as shown in Fig. 4 the prediction of bonding appear after conjugating process using FeCl\textsubscript{3} as a catalyst [24]. This appearances of Fe-O also indicates that the reactions were excellently conducted thus producing other compounds.

### Table-I: Energy gap of dye conjugated chlorophyll

<table>
<thead>
<tr>
<th>Samples Name</th>
<th>Energy Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHLO-PA</td>
<td>1.831</td>
</tr>
<tr>
<td>iCHLO-PA (5%)</td>
<td>3.205</td>
</tr>
<tr>
<td>iCHLO-PA (10%)</td>
<td>3.192</td>
</tr>
<tr>
<td>iCHLO-PA (15%)</td>
<td>3.195</td>
</tr>
</tbody>
</table>

![Figure 3](image)

**Fig. 3. IR Spectrum of CHLO-PA, iCHLO-PA, iCHLO-PA (5 \%), iCHLO-PA (10 \%) and iCHLO-PA (15 \%).**
Thus, this hybrid solar cell droxyl groups of the dye molecule and the sensitizer in photosynthesis respectively. Before undergoing the layer of dye was not - .% d - .eep coating only obtained 0.067% and - tivity decreased with the values of 3 .um conjugated chlorophyll will (%) have potential to provide more continues plus efficient pathway for charge transport with the help of optimum TiO and PEDOT: PSS consequently leading to the deterioration of film performance [3, 37]. In addition, the most effective time for dye deep coating is 10 minutes compared to 5 minutes and 15 minutes. With longer immersion time, the thickness of dye onto the samples increases and lead to the lower performance of efficiency. With shorter immersion time, the layer of dye was not sufficient to acts as sensitizers and give the low performances too. Besides, this condition may affect the bonds between the carbonyl and hydroxyl groups of the dye molecule and the surface of TiO and PEDOT: PSS. When the immersion time too short or longer, the efficiencies were lower [38]. Therefore in this study, 10 minutes the most effective of immersion time was taken to the further investigation of thin films.

Table II: Efficiency of dye at different immersion of time

<table>
<thead>
<tr>
<th>Samples</th>
<th>Times (min)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/TiO/PEDOT:PSS/</td>
<td>5</td>
<td>0.003</td>
</tr>
<tr>
<td>CHLO-PA (0%)</td>
<td>10</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.0002</td>
</tr>
<tr>
<td>ITO/TiO/PEDOT:PSS/</td>
<td>5</td>
<td>0.001</td>
</tr>
<tr>
<td>iCHLO-PA (5%)</td>
<td>10</td>
<td>0.067</td>
</tr>
<tr>
<td>ITO/TiO/PEDOT:PSS/</td>
<td>5</td>
<td>0.001</td>
</tr>
<tr>
<td>iCHLO-PA (10%)</td>
<td>10</td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.007</td>
</tr>
<tr>
<td>ITO/TiO/PEDOT:PSS/</td>
<td>5</td>
<td>0.075</td>
</tr>
<tr>
<td>iCHLO-PA (15%)</td>
<td>10</td>
<td>0.226</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.210</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.131</td>
</tr>
</tbody>
</table>

E. Electrical Conductivity of Thin Film

Fig. 5 shows the fabrication of thin film ITO/TiO/PEDOT: PSS/ Pandanus amaryllifolius and the result below show the conductivity of sample with or without conjugated chlorophyll. Electrical conductivity of ITO/TiO/ PEDOT: PSS/PA thin films determined by the equation 2. From that, it was found that ITO/ TiO/ PEDOT: PSS/CHLO-PA conductivity decreased with the values of 0.091 Scm⁻¹ before conjugated dye. After conjugated dye, the lowest value of electrical conductivity are 0.126 Sm⁻¹ for ITO/TiO/ PEDOT: PSS/iCHLO-PA 5% and 0.124 Sm⁻¹ for ITO/TiO/ PEDOT: PSS/iCHLO-PA 15%; respectively. The highest electrical conductivity can briefly explain that ITO/ TiO/ PEDOT: PSS/ iCHLO-PA (%) have potential to conduct electric with 0.135 Scm⁻¹ where it shows similar efficiency pattern when exposed to the light. Therefore, with the presence of optimum conjugated chlorophyll will increase the performance of Hybrid DSSC. Based on this result, it observed that the percentages of FeCl₃ during conjugated process affected the conductivities of these hybrid DSSC. The result shows that iCHLO-PA 10% was the most effective due to the properties of chlorophyll which performed as an effective photosensitizer in photosynthesis that can absorb maximum in the wide range, thus it is attractive potential compound as a photosensitizer in the visible region [17].

Fig. 5. The conductivities of the thin film

F. Absorption Spectrum of Thin Film

According to the Fig. 6, showing the combination of absorption thin films of ITO/TiO/PEDOT: PSS/ PA. The efficiency of HSC can be determine with looking the highest absorbance value with the 10 minutes of optimal immersion time and this absorption spectrum enhanced the power conversion efficiency (PCE). Before conjugating dye shows CHLO (dyes) maximum peak at 415 nm – 434 nm and 664 nm – 668 nm [39]. Besides, Fig. 6 also show...
ITO/TiO₂/PEDOT at the range 300 nm to 400 nm and PEDOT: PSS in the range from 360 nm to 500 nm and was supported by Wu et al. [2]. Based on the figure below, the highest absorption is ITO/TiO₂/PEDOT: PSS/ iCHLO-PA (10%) with the spectrum range from 300 nm to 700 nm. From this, iCHLO-PA (10%) dye may absorb much more energy. The lowest absorption is ITO/TiO₂/PEDOT: PSS/ iCHLO-PA (5%) and ITO/TiO₂/PEDOT: PSS/ iCHLO-PA (15%) together with the absorption of dye without the conjugated of dye ITO/TiO₂/PEDOT: PSS/ CHLO-PA. This shows broader and stronger absorption of spectrum could give a huge impact to the performance of power conversion efficiency (PCE) [40-42].

![Combination of UV-Vis absorption thin film of natural dyes](Image)

**Fig. 6. Combination of UV-Vis absorption thin film of natural dyes**

**IV. CONCLUSION**

Combining organic/inorganic hybrid solar cell with the architecture of Titanium Dioxide (TiO₂) and organic material of PEDOT: PSS and Pandanus amaryllifolius as dyes were successfully prepared. The absorption of these dyes was investigated via UV-Vis Spectrum and contributes to the enhancement of efficiency for hybrid solar cell. The chlorophyll Pandanus amaryllifolius (CHLO-PA) shows two absorption peaks at 434 nm and 664 nm. While conjugated chlorophyll Pandanus amaryllifolius (iCHLO-PA) shows two maximum peaks shifted to the left at 311 nm and 360 nm with a shorter wavelength known as red shift. This proves that, combination of these materials can increase the absorption over a wide range of light spectrum. Different percentages of conjugated chlorophyll exhibits different value of efficiency where, it were increasing up to 10% of FeCl₃ of conjugated chlorophyll Pandanus amaryllifolius at 1.33% and EC 0.135 Scm⁻¹. This result indicates there was interaction of charge transport for conjugated chlorophyll from the dye. This proves, conjugated chlorophyll from Pandanus amaryllifolius act as sensitzers or light harvesting materials together with environmental friendly benefit as well with simple manufacturing technique.

**ACKNOWLEDGMENT**

The authors would like to thank all the laboratory staff in Faculty of Ocean Engineering Technology and Informatics, Universiti Malaysia Terengganu and financial support from Malaysian Ministry of Education through FRGS grant, FRGS/1/2018/TK10/UMT/02/4, Vot 59511.

**REFERENCES**

24. Setyawati, H., et al., Effect of metal ion Fe(III) on the performance of chlorophyll as

**International Journal of Recent Technology and Engineering (IJRTE) ISSN: 2277-3878, Volume-8 Issue-4, November 2019**

Published By: Blue Eyes Intelligence Engineering & Sciences Publication

Retrieval Number: D4361118419/2019©BEIESP
DOI:10.35940/ijrte.D4361.118419 10146
Hybrid Solar Cell using Conjugated Chlorophyll from Pandanus amaryllifolius as Photosensitizers

AUTHORS PROFILE

Nurhayati ISHAK received B.Sc in Physic, Electronic and Instrumentation in 2016 from Universiti Malaysia Terengganu (UMT). After that, she continued her study in master level as a full time research student in Physics in 2017 at the same university. During her postgraduate studies she works on fabrication and characterization on hybrid dye sensitized solar cell.

Hasnah SALLEH received received B.Sc (Nuclear Science) in 1993 and M.Sc (Physics) in 1998 from the National University of Malaysia, Malaysia. She appointed as research assistant started 1994 - 1996. She began working as a tutor in 1997 and a lecturer in 1998 to 2001 at Universiti Malaysia Sabah (UMS). She continue served as a lecturer at Universiti Malaysia Terengganu (UMT) since 2002. Then thin film technology, solid state physics, organic electronic materials and organic solar cells are her specialties. She focused in thin film research for organic solar cell fabrication.

Ahmad Nazri DAGANG received B.Eng in 2000 and M.Eng in 2004 both in Electrical and Electronic Engineering from Ehime University, Japan. In between he worked as engineer in Sharp electronics Malaysia from 2000 to 2002. In 2007 he received Dr.Eng in Plasma Engineering from the same university. He was appointed as a researcher at University of Toulouse, France from 2008 to 2011. His expertise is in electrical discharge, plasma and light applications. He is currently working as a senior lecturer at Universiti Malaysia Terengganu (UMT).

Salisa ABDUL RAHMAN received the B.E. and M.E. in Electrical & Electronics Engineering from University of Technology Petronas (UTP), Perak, Malaysia in 2004 and 2006, respectively while Ph.D. in Optimal Energy Management Strategy for the University of Technology Sydney Plug-In Hybrid Electric Vehicles from University of Technology Sydney (UTS), Australia. She is currently working as a senior lecturer at University Malaysia Terengganu, Malaysia. Her research interests are in Hybrid Electric Vehicles, innovation powertrain, simulation and modeling, energy management strategy, driving cycles, fuel economy, emissions and optimization.

Nurul Huda KAMARULZAMAN in 2000, she pursued her study in Universiti Teknologi MARA (UTM), Shah Alam and received her diploma in science in 2003. A graduate of Universiti Teknologi MARA, Shah Alam with undergraduate degree in Physics, in 2005. She also completed her master in applied physics at Universiti Kebangsaan Malaysia (UKM). After that, she continued her study in PhD level in physics field in 2015-2019 at Universiti Malaysia Terengganu (UMT). She began her career in education at Universiti Teknologi MARA, Terengganu in 2009 as a lecturer.

Salmah Mohd GHAZALI received B.Sc in Material Science in 2009 from Universiti Kebangsaan Malaysia (UKM), Malaysia. After that, she continued her study in master level in coursework program for her Master and graduated her Master in Energy Technology in 2011 at the same university. She entered PhD program at Universiti Malaysia Terengganu (UMT) in 2013-2019. There, it was her privilege to carry out her research in solar cell which focused on hybrid solar cells composed of organic and inorganic materials with natural dyes as the novel materials.

Nurhaziqah ABD MAJID received B.Sc in Physics, Electronic and Instrumentation in 2016 from Universiti Malaysia Terengganu, Malaysia (UMT). After that, she continued her study in master level as a full time research student in Physics field in 2017 at the same university. During her postgraduate studies she was appointed as a graduate research assistant at Universiti Malaysia Terengganu, Malaysia from 2017 to 2019.

Zakiah AHMAD graduated with her first degree in Material Science from Universiti Putra Malaysia (UPM) in 2010. She worked on Optic Study for her degree and her project title was Refraction Index of Rhombodamine 6g Dyes. Subsequently she continued to pursue her Master Degree in the same field in Universiti Malaysia Terengganu (UMT) and successfully graduated in 2013. Just recently she obtained her PhD from UMT with her study on Natural Dyes of Hybrid Solar Cells in 2019.