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Research paper

Enhanced Hybrid Solar Cells Efficiency by Plant Wastes (Terminalia Cattapa) as a Sensitizer to Titanium Dioxide (TiO_2) Combined with PEDOT: PSS

Nurul Huda Kamarulzaman[1,4], Hasiah Salleh[2,*], Ahmad Nazri Dagang[1], Mohd Sabri Mohd Ghazali[2], Nurhayati Ishak[1],Salmah Mohd Ghazali[1]

[1]School of Ocean Engineering, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia,
[2]Centre for Fundamental and Liberal Education, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia,
[3]School of Fundamental Science,Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia,
[4]Faculty of Applied Sciences, Universiti Teknologi MARA, 23100, Dungun, Terengganu, Malaysia
**Corresponding author E-mail: hasiahsalleh1@gmail.com*

Abstract

Synthetic dyes possess good efficiency; however these dyes suffer from stability, price and toxicity. Due to abundance of waste materials in Malaysia, natural dyes were chosen to replace synthetic dyes in hybrid solar cell (HSC). The main purpose of this research is to study the performance of integrating *Terminalia catappa* (Ketapang's leaves) into HSC. To this date, no research on HSC was presented using this plant as natural dye. Process started with an extraction of *Terminalia cattapa* and the colour obtained was strong brown dye. ITO/TiO_2/PEDOT: PSS/TC/Al was fabricated using blade techniques, followed by spin coating and dye loading technique. FTIR and UV-Vis Spectrometer were used to characterize samples. A four point probe was used to measure electrical properties of the samples. Their performance in HSC was then recorded by IV test Autolab Potentiostat PGSTAT 302 under light radiation. From results, electrical conductivity of TiO_2/PEDOT: PSS/TC was recorded at 0.37 Sm^{-1} as compared to TiO_2/PEDOT: PSS. The efficiency of TiO_2/PEDOT: PSS/TC was 0.24% and it can be conclude that *Terminalia cattapa* was suitable to be used as a natural dye for third generation solar cell.

***Keywords**: efficiency; hybrid solar cell; natural dye; Titanium dioxide; Terminalia cattapa*

1. Introduction

Depletion of fossil fuel reserves was increasing in public awareness of energy consumption throughout countries, worldwide. Range of energy consumption is 7.5% in 2012 and predicted to increase at 6% to 8% in future [27]. Due to low efficiency and high production cost of materials, the development of solar cells was yet feasible. Therefore, dye sensitized solar cells (DSSCs)[7, 10, 25, 28] and hybrid solar cells (HSCs) [4] were developed to match the solution of this renewable energy global demand problems.

Additionally, natural dye was used extensively as an organic material and alternative to synthetic dye. Synthetic dye such as Ruthenium obtained higher efficiency but it is undesirable in safety side and higher production cost [18]. Therefore, natural dyes have the potential of becoming the leading photosensitizer material in solar energy. However, it is new in Malaysia. Natural dyes extracted from waste namely, ketapang's leaves (*Terminalia cattapa*) were selected as the organic material in this research.

Natural and clean environment in the river are the best environment to tropical fishes. Ketapang or commonly known as tropical almond produces a poison in its leaves as a form of protection against insect parasites. The dried leaves provide a strong brown dye and acts as a 'black water extract' when it falls into the river. It will release organics compounds and effectively reduces the PH levels in water [6]. The pigments formed in this leaves were violaxanthin, lutein, zeaxanthin and flavonoids (like kaempferol or quercetin) due to its pinkish-red-brown colour [32]. Besides that, dried leaves will help to create a very calm and soothing environment to fishes and give impact in absorbing harmful chemical from the river. It was widely used in India folk medicine to treat dermatitis and usually used as anticancer, wound healing, anti-diabetic, anti-inflamma-tory and analgesic[3-6].

Combination of organic and inorganic materials is one of the fastest growing renewable energy technologies. Metal oxide semiconductor consist of titanium dioxide (TiO2) [21], zinc oxide (ZnO)[5, 19], copper (II) sulfate (CuSO4)[14] and Iron (II) Oxide (FeO)[11] have been studied extensively in hybrid solar cells. Among them, TiO2 are the most promising acceptor materials for hybrid solar cells, owing to its environment-friendly and easy availability. Titanium dioxide nanoparticle is widely used as photo anode inorganic semiconductors to improve the electron transport through the film[33].

Up to now, a variety of polymers (e.g., P3HT,PEDOT: PSS, P3OT and P3DT) have been explored as conjugated polymers and are suitable to be used as an organic material for hybrid solar cells with impressive performance efficiency, PCE. Currently, one of the most promising conductive polymers is Poly(3,4-ethylenedioxythiophene): polystyrenesulfonate (PEDOT: PSS) because of its higher light transmittance, easy device processability with potential applications in photovoltaic[31]. In addition, PEDOT: PSS is low cost in material preparation compared to other conjugate polymers.

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The aim of this study focuses on the study of natural dyes (*Terminalia cattapa*) in application for hybrid solar cells devices. *Terminalia cattapa* was chosen for this research to investigate the ability of waste as a natural dye towards electrical properties for the purpose of solar application. Hybrid solar cells are formed with inorganic materials (titanium dioxide) and conjugated polymer of PEDOT:PSS. To this date, no research on hybrid solar cells using *Terminalia catappa* as photosensitizer. Hopefully, this technology could be proven to be a strong alternative system to fossil fuel.

2. Experimental method

Experimental method can be divided into preparation of plant waste, fabrication and characterization of hybrid solar cells.

2.1 Extraction of plant wastes

Distilled water was used to clean dried leaves of *Terminalia cattapa* before drying it at 60˚C. 10 g sample of powdered leaves were crushed and placed into 100 ml of ethanol (R&M Chemical). The mixture was then kept for a week at room temperature. Subsequently, filter paper was used to filter the solution and dark brown extract were collected. Then, solution was cleaned in an ultrasonic bath (JEIOTECH model, Chrom ScienceSdn. Bhd) for 10 minutes to appear more concentrate. The concentrated solution was eventually used as a dye to TiO_2 nanoparticles for the fabrication of solar cell [1, 2].

2.2 Preparation of working electrode

Indium Tin Oxide (ITO) coated glass substrates (sheet resistance 7Ω/sq with dimension 2 cm x 2 cm) which were used as working electrode were clean with distilled water and detergent for 10 minutes. ITO must be cleaned with acetone (R&M Chemical) subsequently for 10 minutes. Later, ITO coated glass substrates were dried using dryer before being kept in a Petri dish.

2.3 Fabrication of hybrid solar cells

0.2 M concentration of TiO_2 colloid was prepared using TiO_2 powder (anatase, 25 nm by Sigma Aldrich Chemical) with ethanol (95%, HmbG Chemicals) and a few drops of Triton X□100. TiO_2 was deposited on ITO glass plate using doctor blade techniques. Temperature used for annealing TiO_2 was at 450 ˚C for 30 minutes on a hot plate. The annealing step was an important step to reinforced the attachment of TiO_2 layer with ITO substrate. In addition, the solvent can be removed thus enhanced the mobility of charge carrier in sample. A layer of PEDOT:PSS was deposited onto TiO_2 surface by spin coating technique with 2000 rpm in 30 seconds. 10 minutes dip coating techniques was used to deposit natural dye on the surface of PEDOT:PSS. A thin layer of Aluminium (Al) was then deposited on top of the natural dye as a counter electrode. Bilayer heterojunction was used to fabricate HSC.

2.4 Characterization of hybrid solar cells

Four point probe, UV-Vis and Fourier Transform Infrared (FTIR) were used to characterize the hybrid solar cells samples. Primary technique for measuring electrical conductivity is four point probe method (FPP), which is performed using four point probe (FPP Jandel RM3 Test Unit). It is commonly used in dark condition and under different light illumination. Fourier-transform infrared (FTIR) spectroscopy (IR Tracer-100, Shimadzu) was used to study the functional group of *Terminalia cattapa*. Absorption spectrum was studied using UV-Vis spectrophotometer (Model Lambda 25 with UV Winlab V2.85 software, Perkin Elmer).

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) level were studied through cyclic voltammetry method using Autolab Potentiostat. The cyclic voltammetry, (CV) analysis were prepared using three electrode system where platinum rod was used as counter electrode while a saturated calomel electrode used as a reference electrode. The CV measurements were studied via the scan rate of 0.05 V/s and step potential of 0.01 V. The photocurrent density-voltage curves (I-V) were measured by an Autolab Potentiostat PGSTAT302 with 100 $mWcm^{-2}$ of light intensity.

3. Result and discussion

3.1 Performance of hybrid Solar Cells

Performance of HSC was generally evaluated by current–voltage (I–V) measurements [28, 29]. As a next step, fill factor (FF) is also calculated as a critical parameter that is important in determining the performance of hybrid solar cell. The value of FF can be obtained from equation (1) :

$$FF = (V_{max} . I_{max}) / (V_{oc} . I_{sc}) \quad (1)$$

Hence, efficiency can be calculated using equation (2):

$$PCE\ (\%) = (J_{max} \times V_{max}) / P_{in} \quad (2)$$

3.1.1 Effect of immersion time on hybrid solar cell performance

Table 1 shows power conversion efficiency (PCE) for TiO_2/PEDOT:PSS/TC at different dye loading period. Immersion time of thin film layer was varied for 5, 10 and 15 minutes in order to find the optimal dye loading period. Surface dye loading period has become one of the most importance factors in photovoltaic response of HSC. Furthermore, film absorption ability of dye molecule depends on the dye loading period [13, 15, 22]. Thus, more electrons were excited to transfer and emitted. Efficiency at immersion time of 5 minutes and 15 minutes were observed at lower performance compared to 10 minutes of immersion time.
This comparison shows that the immersion time successfully leads to the increment of PCE. Interestingly, it is proven that all samples exhibited the same trends and 10 minutes was the optimum time of dye loading period. This results was due to lower dye concentration requires longer immersion time and for higher dye concentration, the immersion time become shorter [8]. If immersion time is longer, thickness of the sample increases and corresponds to low performance of efficiency. Therefore, through this approach 10 minutes of immersion time was taken to be proceed for next investigations.

Table 1: Efficiency of TiO2/PEDOT:PSS/TC at different dye loading period

Samples	Immersion Time (mins)	PCE (%)
TiO_2/PEDOT:PSS/TC	5	0.08±0.04
	10	0.24±0.14
	15	0.07±0.02

Cell parameters obtained are tabulated and shown in Table 2. An open circuit voltage of 0.4V and efficiency of *Terminalia catappa* was obtained at 0.24% with fill factor of 15%. It was reported that photoelectric conversion efficiency and the fill factor are the most important parameters to describe solar cell performance [3]. The value of FF and voltage at open circuit (V_{oc}), were decreased equivalent to the low performance of PCE. This is cause by the interfacial recombination losses as stated by Hochbaum et.al in their study [12]. It was mentioned that TiO_2/PEDOT:PSS/TC has the highest efficiency due to its better photon response in visible spectrum thus avoiding the recombination of electron – hole as well as being the best electron transportation in the device [23].

Table 2: Photoelectrochemical parameters of hybrid solar cells

Samples	I_{sc} (μA)	V_{oc} (μV)	Fill Factor (FF)	PCE (%)
TiO_2/PEDOT:PSS	0.125	0.4	0.17	0.005±0.001
TiO_2/PEDOT:PSS/TC	12.0	0.4	0.15	0.24±0.14

3.1.2 Electrical conductivity

The measurement of electrical conductivity was carried out in dark and under light condition. It was calculated using equation (3)

$$\sigma = \frac{1}{R_s} \quad (3)$$

As can be seen in Figure 1 below, electrical conductivity under light condition of TiO_2/PEDOT:PSS and TiO_2/PEDOT:PSS/TC were 0.028 S/cm and 0.037 S/cm, respectively. It was due to anthocyanin in *Terminalia cattapa* that absorbs more light from the sunlight and convert it into electricity. In dark condition (0 Wm^{-2}), sample shows a minimum electrical conductivity. This occurred due to the absorption of light by the samples itself. Anthocyanin in natural dyes has involved in photosystem assembly and was used to absorb light energy in the visible region. However, the sunlight transmits the light to the samples thus TiO_2 absorbs the light in infrared region. Light was needed to absorb energies using natural dyes. Electrical conductivity was increased in light condition because samples absorbed light energy and change it into electrical energy [24].

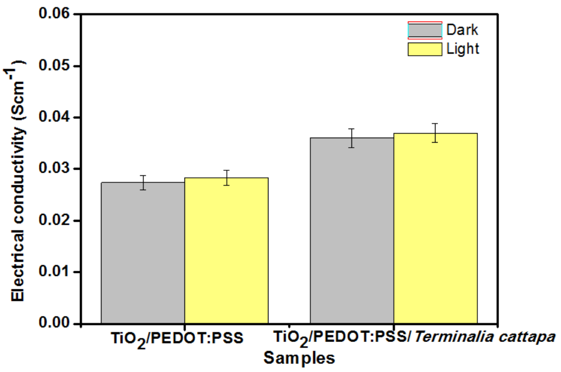

Fig. 1: The electrical conductivity of HSC

3.2 Dyes Structure

The functional group for *Terminalia cattapa* was reported using FTIR as indicate in Figure 2 below. FTIR spectrum exhibits the spectrum of anthocyanin characteristic. Absorption peak is assigned to alkanes at 1442 cm^{-1} for *Terminalia cattapa* which indicates the presence of C=C of aromatic group. At a wavenumber of 1053 cm^{-1}which is specify as higher values in this dye, strong sharper peaks are observed corresponds to C□O. In the catchment area of 1645 cm^{-1}, it was belong to the peak of anthocyanin. Absorption peak at 1645 cm^{-1} was recorded to the functional groups of stretching carbonyl C=O. During the observation, OH group was recorded at the wavenumber of 3379 cm^{-1} represents benzene ring at anthocyanin structure with strong and broad signal.

As referring to FTIR analysis, excited state can be stabilized with the appearance of carbonyl (C=O) and hydroxyl group (□OH) in anthocyanin and maximum absorption was developed by having lower energy [30]. The excitation of electrons was obtained due to the absorption of light photon by all pigments in anthocyanin [1]. Both aromatic and aliphatic can influence the durability and colours presence in plants tissues [9, 16]. Other than that, carbonyl group (C=O) assigned by an absorption peak at 1640 cm^{-1} to 1715 cm^{-1} in aliphatic hydrocarbon, which has been generally coordinated to Ti (IV) sites on TiO_2 surface. Several carbonyl and hydroxyl groups in dye structure were capable to complexion with TiO_2 surface. Consequently, this plant was suitable to be combined with TiO_2 and exhibit higher performance in power conversion efficiency.

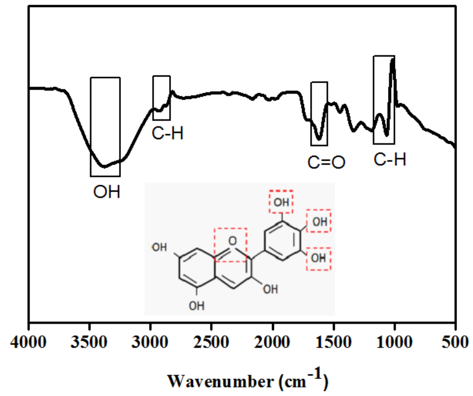

Fig. 2: FTIR spectra of natural dye solution extracted from Terminalia cattapa

3.3 Optical absorption of natural dyes

Figure 3 exhibits absorption spectrum for *Terminalia cattapa* and the highest peak can be observed at 375 nm. The spectrum range was recorded at 360 nm to 500 nm and the broadest peak was 450-480 nm. This result is also similar to the report by Vadwala et. al [32]. It is assumed that enhancement in absorption spectrum of *Terminalia cattapa* is due to the pigments in anthocyanin. On the other hand, yellowish brown colour was observed for *Terminalia cattapa*. Their color absorption was from blue to green blue which is in the range of 435 nm to 500 nm. Quercetin was observed in this spectrum at 375 nm and the yellow colour presented in hydroxyl derivative is from flavones [32]. The hydroxyl group contains in flavones was increasing anthocyanin's stability [17, 32]. Similarly, it absorbs more visible light thus therefore it can be attributed to the performance of solar cell.

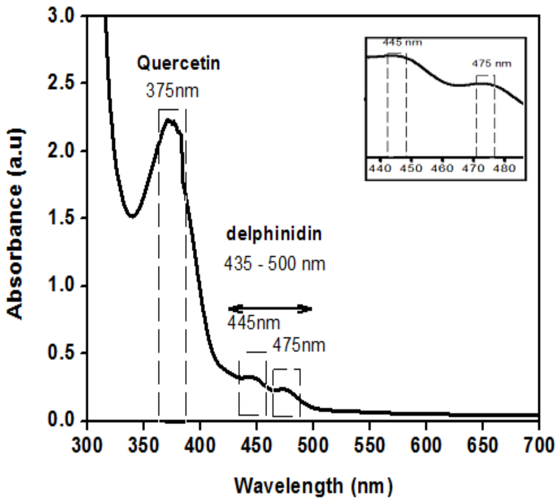

Fig. 3: Uv-Vis Absorption of natural dye solution extracted from *Terminalia Cattapa*

3.4 Optical energy gap in hybrid system

Energy of photon is inversely proportional to the wavelength as shown in Equation (4); where *h* is the plank's constant (6.62517 X 10^{-34} JS^{-1}), λ is the wavelength in photoluminescence spectrum (in meter unit) and c is the velocity of light (3.0 x 10^8 ms^{-1}).

$$E_p = \frac{hc}{\lambda} \quad (4)$$

Thus, optical energy gap (E_g) is;

$$E_g = \frac{E_p}{1.60217653 \times 10^{-19}} \quad (5)$$

Optical energy gap was used in analyzing performance of hybrid solar cell which related to the absorption of solar energy. *Terminalia cattapa* optical energy gap was observed at 2.54 eV. Meanwhile, the highest occupied molecular orbital (HOMO) levels and lowest occupied molecular orbital (LUMO) levels can be calculated using Leeuw's formula according to the first oxidation potential [26]. The electrochemical HOMO level of *Terminalia catappa* was calculated as −5.16 while the LUMO level of *Terminalia catappa* was calculated as −2.71. As can be seen from Figure 4, value of LUMO level is higher than polymer and TiO_2. Energy level for conduction band (CB) of TiO_2 and HOMO level of PEDOT:PSS were obtained at -7.4 eV and -5.1 eV respectively. Meanwhile, valence band (VB) for TiO_2 and LUMO level for PEDOT:PSS were recorded at -4.2 eV and -3.5 eV respectively as shown in Table 3.
Low energy gap helps electron to interact faster from HOMO level to LUMO level. Therefore, less energy is needed to combine these electrons. Electron jumps from pigment anthocyanin (dye molecule) which is from HOMO to LUMO and the positive charge remain in HOMO (Figure 5). Consequently, molecule oxidation process was performed by the resulting hole. Electron was transferred from LUMO dye to LUMO PEDOT: PSS and injected into TiO_2.
The main cause of this condition was due to the strong bridge in chemical interaction inside TiO_2 particles, conducting polymer and dye molecules [20, 34]. HOMO level and LUMO level considered as the most important developments for dye regeneration and electron injection. Recently, Sevim et.al reported on the enhancement of electron transfer, referring to the closeness of LUMO level and conductivity bands [26]. This again shows that there is sufficient mobility force from LUMO level to conduction band. Figure 4 indicates CV curves of these complexes.

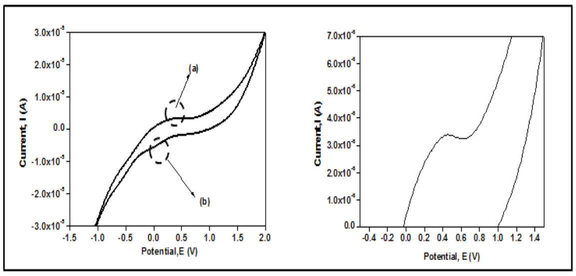

Fig.4: CV curve for *Terminalia cattapa*

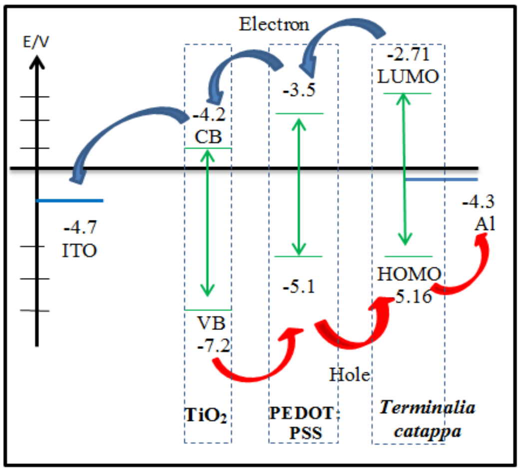

Fig. 5: Formalism showing sensitization mechanism

Table 3: Electrochemical parameters of natural dyes in *Terminalia cattapa (TC)*

Dye	Peak Absorbance (nm)	Absorption Range (nm)	Optical Band Gap (eV)	E homo (eV)	E Lumo (eV)
TC	380	350-480	2.45	-2.71	-5.16

4. Conclusion

In summary, *Terminalia cattapas* were successfully extracted from leaves and UV Visible spectrum was used to investigate the absorption of its dyes. Characterization by FTIR proved that the carbonyl and hydroxyl group presence in *Terminalia cattapa* was suitable to combine with TiO_2. Additionally, *Terminalia Cattapa* has the lowest energy band gap and possess proper alignment in energy level of TiO_2 and PEDOT:PSS. The efficiency obtained for TiO_2/PEDOT:PSS/TC in range of 0.24%. *Terminalia Cattapa* is the best dye that can contribute to the development of hybrid solar cells.

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