Eco-Friendly Hybrid Solar Cells using Eugenia Claviflora as New Alternatives Sensitizer to TiO₂/PEDOT:PSS

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Abstract. Studies on HSCs have been focusing on exploration of natural dyes obtained from Eugenia claviflora (EC). This work mainly aimed to enhance device efficiencies related to new dye sensitizer particularly Eugenia claviflora. These samples were then characterised based on morphology, thickness, optical absorption, electrical conductivity and solar cell’s performance in term of efficiency, voltage and current using various techniques including FESEM, EDS, profilometer, UV-Vis, FTIR and autolab with irradiance of 100 mW/m². TiO₂/PEDOT:PSS/EC obtained an open circuit voltage (Voc) of 0.43 V with fill factor of 0.2 leading to an efficiency of 1.33%. The absorption of TiO₂/PEDOT:PSS/EC was located at 550 nm (between 450 nm to 755 nm) which exhibited an intense broad band in visible light. Hence, fabrication of HSCs was successful thus improving its performance.

1. Introduction
Numerous researches focused on Hybrid Solar Cell (HSC) and Dye-Sensitized Solar Cell (DSSC) in photovoltaic systems. The performance of DSSC and HSC were still limited as compared to silicon solar cell. This possibly is enhanced by using proper selection of material, design and energy gap. Problems also can be filtered out by the development of dye (sensitizer) in the HSC. Rutheniums are usually used in DSSC and HSC research’s as synthetic dye and are reported to be more efficient plus possessed higher efficiency when combined with nanoporous TiO₂ electrode [1]. Meanwhile, Rutheniums are undesirable to environment safety due to the chemical used and varieties of procedure to be done. It is time consuming thus production become very expensive. Due to this problem, natural dye has been discovered as the most promising material presents to next generation of solar cells.

As compared to such synthetic dye, dye extracted from natural resources are more desireable due to its abundant in resources, natural extraction i.e stems, flowers, fruits and etc. Additionally, the advantages also include less effect to environment, simple preparation technique applications’, low production cost, easier handling process and low toxicity [2]. Interestingly, investigation of various dyes
obtained is from waste material. To date, *Eugenia claviflora* was used as a new sensitizer, eventhought the efficiency is still limited due to degradation of dye. It can be overcome by selection of the dye itself plus the architectural design of HSC. Stability problem of dye is because of degradation of dye in the presence of sunlight radiation. It has been also suggested that combination of dye with semiconductor material and conductive polymer will provide high conductivity and stability [3]. Recently, this understanding allows further development in designing thin film to improve performance of HSC. Hybrid solar cell is the combination of organic and inorganic material, and is one of the major concerns in solar energy technologies. Metal oxide semiconductor consist of TiO$_2$ [4], ZnO [5, 6], CuSO$_4$ [7] and FeO$_3$ [8] have been studied extensively in hybrid solar cells. Among them, TiO$_2$ is the most promising acceptor materials for hybrid solar cells, owing to its environment-friendly and easy availablility. Currently, one of the most promissing conductive polymer is Poly(3,4-ethylenedioxythiophene): polystyrenesulfonate (PEDOT: PSS) because of its higher light transmittance, low cost in production process, easy device processability with potential applications in photovoltaic [9].

This work mainly aimed to enhance device efficiencies related to new dye sensitizer particularly *Eugenia claviflora*. However, understanding solar cell mechanism and moderate energy conversion efficiencies evolved as major challenges encounted in application of thin film solar cells based HSCs. *Eugenia claviflora* was chosen for this research to investigate the ability of this waste as a natural dye towards electrical properties for the purpose of solar application. Dye extraction from *Eugenia claviflora* was a rich source of anthocyanin which is widely used as antioxidant properties. These pigments differ from other flavonoid due to its positive charge in the central ring structure that provides color intensity to plants and fruits. Hybrid solar cells are formed with inorganic materials (titanium dioxide) and conjugated polymer of PEDOT:PSS. To this date, there is not yet a research on hybrid solar cells using *Eugenia claviflora* as photosensitizer. Recently, this understanding allows further development in designing the thin film to improve performance of HSCs.

2. Experimental Details

2.1. Material’s Preparation

First, ITO substrates (sheet resistance 7Ω/sq with dimension of 2 cm x 2 cm) were cleaned in detergent, acetone (R&M Chemical), isopropanol (R&M Chemical) and distilled water. And they were ultrasonic (JEIOTECH) cleaned to remove residual organics. Later, the ITO coated glass substrates were dried using dryer before being kept in a Petri dish. Natural dye, *Eugenia claviflora* (EC) was chosen based on colour observed which was purplish blackish (figure 1). Then, the skin of EC were cleaned with distilled water and dried at 60°C. After, they were crushed into fine powder and 10 g sample of powdered pulp were placed into 100 ml of ethanol (R&M Chemical). The mixture was then kept for a week at room temperature, filtered and extraction’s solution was collected. The solution was then placed in an ultrasonic bath for 10 minutes around temperature of 30°C leaving it to become apparently concentrated. The concentrated solution was eventually used as a dye to TiO$_2$ nanoparticles for the fabrication of solar cell [1, 3].

![Figure 1. Eugenia claviflora fruits](image-url)
2.2. Fabrication and Characterization of HSC

0.2M of TiO$_2$ colloid was prepared using TiO$_2$ powder (anatase, 25 nm by Sigma Aldrich Chemical) with ethanol (95%, HmbG Chemicals). This sample was then deposited using doctor blade technique onto the ITO glass at 45o angle. These substrates were afterward annealed for 30 mins at 450 oC on a hot plate. Sample was allowed to cool at room temperature and then transferred to glove box for subsequent procedures. PEDOT:PSS was spin coated on a prepared TiO$_2$ film at 2000 rpm for 10 s with a thickness of 28 nm approximately [13, 35]. The films were dried for 15 mins and then immersed into EC’s solution for 5, 10 and 15 minutes respectively. Lastly, Aluminum (Al) electrode was deposited on top of the films. Physical vapour deposition (PVD) was used to control evaporation thickness. Figure 2 shows schematic diagram of hybrid solar cell.

Fourier-transform infrared (FTIR spectroscopy IRTracer-100, Shimadzu) was used to study the functional group. Surface morphology images of the films were characterized using FESEM. Absorption spectra and thickness of these films were measured via UV-Vis spectrometer (Model Lambda 25 with UV Winlab V2.85 software, Perkim Elmer) and Dektak 150 surface profiler, respectively. The electrical conductivity was measured with four point probes, under dark and light condition.

![Schematic diagram of hybrid solar cell](image)

3. Experimental Details

3.1. Absorption Spectra

Optical properties of Eugenia claviflora were investigated using UV-Vis spectrometer. Figure 3 presents the absorption spectra for EC dye extract, TiO$_2$/PEDOT and TiO$_2$/PEDOT:PSS/EC. Figure 3 clearly shows that Eugenia claviflora exhibits broad absorption band at wavelength from 450 nm to 600 nm with its peak allocated at 530 nm. The color observed by Eugenia claviflora was purple however; the pigment absorbs green color in the range of 500 nm to 560 nm. Cyanidin 3-glucoside was a pigment in anthocyanin found in Eugenia claviflora. In addition, the highest concentration of cyanidin found was in seeds and skin of the fruits [10]. The broadest absorption spectrum was Eugenia claviflora due to colour ranges that produce difference absorption characteristics [11]. Wu et al stated that wavelength of TiO$_2$ was recorded 380 nm in ultraviolet (UV) light spectrum [12]. TiO$_2$ showed high transparency in visible region and a sharp fall in UV region yet it does not absorb in visible region. Hence, absorption observed at 350 nm to 600 nm was due to PEDOT:PSS.

The absorption of anthocyanin onto the surface of TiO$_2$/PEDOT:PSS was due to the presence of carbonyl and hydroxyl group on anthocyanins. Electrons from dye molecule were excited to transfer to conduction band of TiO$_2$. Thus, it will enhance the efficiency of hybrid solar cell. The absorption of EC dye was obtained to be red shifted at 550 nm upon chelation to TiO$_2$/PEDOT:PSS.
3.2. Energy Gap of TiO₂, PEDOT:PSS and EC dye

Figure 4 exhibits formalism showing sensitization mechanism. Energy gap of EC dye was calculated at 2.04 eV with anthocyanin pigments that are effective in electron transfer [3]. The lowest energy gap will promote electrons from dye molecule easily excite to another level. Absorption of the ultra-violet radiations results due to the excitation of the electrons to transfer from ground state to higher energy state.

The attachment of EC dye and TiO₂ has been suggested to possess an effect on HOMO and LUMO level of anthocyanin due to the decreasing of energy gap which results in the red shifted’s absorption peak. The energy level of the *Eugenia claviflora* (-2.81 eV) was far closer to HOMO energy level of PEDOT:PSS (-3.5 eV) and conduction band of TiO₂ (-4.2 eV). The closeness of the energy levels between the *Eugenia claviflora*, PEDOT:PSS and TiO₂ are beneficial for a better hole extraction to the ITO. An efficient hole extraction reduces charge recombination thus improving hole collection efficiency.

The lowest unoccupied molecular orbital (LUMO) energy levels of *Eugenia claviflora* calculated as 2.87 eV. Energy of conduction band (CB) for TiO₂ and HOMO energy for PEDOT:PSS were obtained at -7.4 eV and -5.1 eV, respectively. The valence band (VB) and LUMO energy for TiO₂ and PEDOT:PSS were recorded at -4.2 eV and -3.5 eV, respectively. When dye molecules (*Eugenia claviflora*) on TiO₂ absorb incident photons, electrons in the molecules become excited and promoted from photosensitizer (*Eugenia claviflora*) which is HOMO to LUMO [3, 13]. Then, positive charge (electron hole) remained in HOMO. Consequently, molecule oxidation process were performed by these resulting holes. Then, electrons were transferred from dye molecule (*Eugenia claviflora*) to the conductive polymer (PEDOT:PSS) and TiO₂ conductive band (CB). It can be concluded that *Eugenia claviflora* exhibits proper alignment of excited state’s energy level between dye and conduction band edge. This means, decreased of energy gap were enhanced by the photo response of titania thin film and due to the excellent conjugated polymer of PEDOT:PSS.
3.3. Dyes Structure

_Eugenia claviflora_ presents C-H aliphatic and 3335 cm\(^{-1}\) as shown in Figure 5. Observed strong bands at 1080 cm\(^{-1}\) correspond to the symmetric vibrational mode of C-O stretching mode. Structure of dye provides the significant impact to both dyes' efficiencies. However, the stability of anthocyanin was reduced due to the methoxyl contained in isoflavones. Meanwhile, hydroxyl group (-OH) exists in flavones increased anthocyanin’s stability [14, 15]. As referring to FTIR analysis, Carbonyl (C=O) and -OH contained in anthocyanin able to stabilize excited state and develop maximum absorption by having lower energy [16]. Al-Alwani et. al also was agreed with the statement of all pigments in dye can absorb light photon and lead to production of excited electrons [17]. Consequently, the broadest region in -OH group was quite important to maintain the stability of all dyes and can be promoted to be applied in excitation of electron.

_Figure 4. Formalism showing sensitization mechanism_

_Figure 5. FTIR Spectra of Natural Dye Solution Extracted from _Eugenia claviflora_
3.3.1 Morphological Studies of EC Dye in Hybrid Thin Film. Particles’ size are estimated to be in a range of 60 nm to 100 nm as observed in figure 6. It can be seen that the surface morphology differs a bit in TiO$_2$/PEDOT:PSS and TiO$_2$/PEDOT:PSS/EC. Moreover, uniform distribution of surface potential in TiO$_2$/PEDOT:PSS implies that the nanomaterial is coated uniformly by PEDOT:PSS in accordance with observation from FESEM images.

Thickness of TiO$_2$/PEDOT:PSS increased to 74 nm. Meanwhile, thickness of TiO$_2$/PEDOT:PSS/EC was recorded at 162.9 nm. This increase was due to the amount of Eugenia claviflora loading onto the surface of TiO$_2$/PEDOT:PSS. Therefore it can be confirmed that Eugenia claviflora was detected during fabrication of thin film. Table 1 shows sulphur and carbon elements were observed clearly in the EDS analysis. Therefore, both elements were detected in TiO$_2$/PEDOT:PSS. Other than that, mass percentage of carbon were also increase for TiO$_2$/PEDOT:PSS/EC compared to TiO$_2$/PEDOT:PSS which was depicted in table 1. Hence, a highly magnified FESEM image of TiO$_2$/PEDOT:PSS/EC suggests that it consist of PEDOT:PSS and Eugenia claviflora in the fabrication of thin film. This results were also supported by the thickness incrementation for TiO$_2$/PEDOT:PSS and TiO$_2$/PEDOT:PSS/EC.

Fabrication of all devices with each layer thickness was recorded below than 100 nm, leading to a shorter exciton diffusion length. This shorter exciton length was necessary in connection with strong light absorption and due to this requirement, the interface between electron accepting and hole accepting material received more volume heterojunction. Consequently, this allows the highest performance of power conversion efficiency to be achieved in this fabrication [18].

![Figure 6](image)

**Figure 6.** (a)Surface morphology of TiO$_2$/PEDOT:PSS without dye (b) cross section of TiO$_2$/PEDOT:PSS without dye (c) surface morphology of TiO$_2$/PEDOT:PSS with dye EC (d) cross section of TiO$_2$/PEDOT:PSS with dye EC

According to Kalaiselvi and Murtaza, high efficiency can be achieved if the thickness of active layers is less than 500 nm because of enough sunlight absorption by the sample. [18-20]. If immersion time is longer, thickness of the sample will increased and correspond to low efficiency performance. Sengupta et.al also agreed with the statement and stated that, with respect to the thickness of hybrid solar cells,
the focus has been done to control the absorption of dye molecules within semiconductor, electronic charge transport as well as may contribute to enhance in power conversion efficiency of the device [21].

| Element | TiO$_2$/PEDOT:PSS without dye | TiO$_2$/PEDOT:PSS/EC dye |
|---------|-----------------------------|--------------------------|
| In      | 34.0                        | 37.2                     |
| O       | 22.9                        | 19.7                     |
| C       | 12.1                        | 14.3                     |
| Si      | 8.5                         | 11.2                     |
| Ti      | 16.5                        | 10.8                     |
| Sn      | 5.7                         | 6.4                      |
| S       | 0.3                         | 0.4                      |

3.4. Electrical conductivity
Figure 7 illustrates the electrical conductivity under light condition for bilayer heterojunction thin film of TiO$_2$/PEDOT:PSS and TiO$_2$/PEDOT:PSS/EC with conductivity being calculated at 0.028 Scm$^{-1}$ and 0.045 Scm$^{-1}$ respectively. Electrical conductivity of the TiO$_2$/PEDOT:PSS/EC was the highest compared to TiO$_2$/PEDOT:PSS with increment of 60.7%. This is due to the absorption of light by the samples since anthocyanin in *Eugenia claviflora* absorb more light from the sunlight and convert it into electricity. Electrical conductivity was increased under light condition because the samples absorbed light energy and change it into electrical energy [22]. This light energy was absorbed in the visible region by anthocyanin pigment. Meanwhile, TiO$_2$ absorbed energy from sunlight in infrared region.

3.5. Performance of Hybrid Solar Cells
Performance of HSC was carried out and the performance of hybrid solar cell is generally evaluated by the current–voltage (I–V) measurements [28, 29].

3.5.1 Effect of Dye Loading Period on the Photovoltaic Performance. Table 2 represents power conversion efficiency (PCE) for TiO$_2$/PEDOT:PSS/EC at different dye loading period. Immersion time for natural dye plays an important role in determining the best efficiency. After deposition of TiO$_2$ and PEDOT:PSS, samples were immersed in natural dye solution for three consecutive time; i) five minutes, ii) ten minutes and, iii) fifteen minutes. Futhermore, film absorption of dye molecule depends on the dye loading period [23-25]. Thus, more electrons were excited to transfer and emit. Lower performance
obtained at 5 minutes and 15 minutes compared to 10 minutes caused by reduction in dye concentration [26]. Thickness sample will increase with longer immersion time and may also worsen cell performance. Therefore, through this approaches 10 minutes of immersion time was proceed to next investigations.

**Table 2. Efficiency of TiO$_2$/PEDOT:PSS with and without dye EC at different dye loading period**

| Samples           | Dye loading period (mins) | PCE (%)   |
|-------------------|---------------------------|-----------|
| TiO$_2$/PEDOT:PSS | 0                         | 0.005±0.001 |
| TiO$_2$/PEDOT:PSS/EC | 5                        | 0.57±0.25   |
|                   | 10                        | 1.33±0.39   |
|                   | 15                        | 0.21±0.07   |

Photovoltaic parameters includes short circuit current ($I_{sc}$) [27], open circuit voltage ($V_{oc}$), fill factor (FF) [28] and efficiency (PCE) were presented in Table 3. As shown in Table 3, TiO$_2$/PEDOT:PSS/EC obtained the best performance with $I_{sc}$ of 2.5E-5 A, $V_{oc}$ of 0.43V, FF of 0.2 and leading to an efficiency of 1.33%. It was reported that photoelectric conversion efficiency and fill factor are the most important parameters to describe solar cell performance [28]. The value of FF, $V_{oc}$, and $I_{sc}$ were decreased equivalently to low PCE performance due to interfacial recombination losses [29]. Highest efficiency of TiO$_2$/PEDOT:PSS/EC cause by its better photon response in visible spectrum and reducing recombination of electron – hole throughout the device [30].

**Table 3: Power conversion efficiency of TiO$_2$/PEDOT:PSS with and without dye EC**

| Samples          | $J_{sc}$ (mA/cm$^2$) | $I_{sc}$ (µA) | $V_{oc}$ (V) | FF  | PCE (%) |
|------------------|---------------------|--------------|-------------|-----|--------|
| TiO$_2$/PEDOT:    | 0.058               | 0.125        | 0.4         | 0.17| 0.005±0.001 |
| PSS              |                     |              |             |     |        |
| TiO$_2$/PEDOT:    | 0.12                | 0.025        | 0.43        | 0.20| 1.33±0.039  |
| PSS/EC           |                     |              |             |     | 39     |

4. Conclusion

Low energy gap of TiO$_2$/PEDOT:PSS/EC was found as the best material with lower energy gap compared to other samples. In order to obtain greater understanding on performance of HSCs, efficiency measurement was performed. Among all devices, TiO$_2$/PEDOT:PSS/Eugenia claviflora demonstrated as the best device performance; with fill factor of 0.2 and an overall efficiency of 1.33%. The combination of TiO$_2$/PEDOT:PSS/Eugenia claviflora may reveals the best efficiency with increasing conductivity among all samples. Efficiency value is nearly dependent on the FF value which is directly related to device capability of light absorption.

Furthermore, performance of HSC also depends on a broader wavelength in absorption spectrum. Wavelength of TiO$_2$/PEDOT:PSS/Eugenia claviflora ranging from 400 nm to 750 nm exhibits higher efficiency due to higher broadband absorption value. Consequently, these devices are capable to generate more carriers. These carriers were important in excitement of electrons transferred from ground state to a higher state. Eventhough this device exhibits lower efficiencies than silicon solar cells, its efficiency is still encouraging and can be enhanced by further researches. Data and knowledge acquired
possibly be used for other researches in HSC. Studies on new sensitzers are still vastly unexplored which left for future exploration.

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