Jurnal
Teknologi

Full Paper

NATURAL DYE'S PHOTODEGRADATION EFFECT TOWARDS OPTICAL PROPERTIES FOR SOLAR ENERGY APPLICATIONS

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Article history
Received
23 June 2022
Received in revised form
13 October 2022
Accepted
20 October 2022
Published Online
26 December 2022

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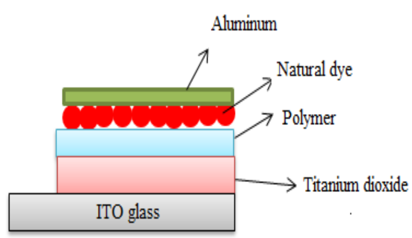
Graphical abstract



Abstract

Photodegradation effect to natural plant waste under solar irradiation was investigated. Five plants waste namely, *Averrhoe Bilimbi*, *Eugenia Clavifora*, *Elaies Guineensis*, *Terminalia cattapa* and *Clidemia hirta* were selected from all over the states. Main purpose of this research was to study the stability of natural dye in presence of sunlight radiation for future solar cell applications. FTIR and UV-Vis absorption were used to investigate the optical properties of dye. *Eugenia Clavifora* was clearly revealed that it took more than 10 weeks to degrade and required 64% of degradation percentage. Optical energy gap was observed at 2.04 eV before exposure, while 2.15 eV after exposure of sunlight. Efficiency of *Eugenia Clavifora* hybrid solar cells was leading at the highest performance of 1.33%. This clearly shows that *Eugenia Clavifora* can be used as a natural photosensitizer thus enhancing the efficiency of any solar cell applications.

Keywords: Photodegradation, plant waste, natural dye, hybrid solar cells, absorption spectrum, functional group

Abstrak

Kesan fotodegradasi kepada sisa tumbuhan semula jadi di bawah penyinaran suria telah dikaji. Lima sisa tumbuhan iaitu, Averrhoe Bilimbi, Eugenia Clavifora, Elaies Guineensis, Terminalia cattapa dan Clidemia hirta telah dipilih dari seluruh negeri. Tujuan utama penyelidikan ini adalah untuk mengkaji kestabilan pewarna semula jadi dengan kehadiran sinaran cahaya matahari untuk aplikasi sel suria pada masa hadapan. Penyerapan FTIR dan UV-Vis digunakan untuk menyiasat sifat optik pewarna. Eugenia Clavifora jelas mendedahkan bahawa ia mengambil masa lebih daripada 10 minggu untuk merendahkan dan memerlukan 64% peratusan kemerosotan. Jurang tenaga optik diperhatikan pada 2.04 eV sebelum pendedahan, manakala 2.15 eV selepas pendedahan cahaya matahari. Kecekapan sel solar hibrid Eugenia Clavifora mendahului prestasi tertinggi sebanyak 1.33%. Ini jelas menunjukkan bahawa Eugenia Clavifora boleh digunakan sebagai fotosensitizer semula jadi sekali gus meningkatkan kecekapan sebarang aplikasi sel suria.

Kata kunci: Fotodegradasi, sisa tumbuhan, pewarna semula jadi, sel solar hibrid, spektrum penyerapan, kumpulan berfungsi

1.0 INTRODUCTION

Energy crisis in these days appears as one of the main issues to the worldwide nation. In 2015, around 90187 kilotonnes of crude oil were consumed daily and if this trends continue, world energy consumption will increase by 26.84% [1]. Since then, green technology has become a new focus. The most obvious benefits are; it can help to reduce field emissions, reduces waste and consumes less energy compared to conventional technology. Owing to such problems, it is a suitable need to the present time; with low cost of preparation techniques, environmental friendly materials, abundant in resources and easy to handle energy production process [2-5]. As known, the sun provides an abundant supply of energy arriving to earth. Spectrum of its solar radiation extends only a minimal UV light which is covered from 5 to 7% while the visible light and infrared radiation consist of 46% and 47% respectively [6, 7]. The visible light energy and infrared radiation are inversely proportional to the wavelength as shown in Equation (1) where h is the plank's constant (6.62×10^{-34}Js), λ is the wavelength in photoluminescence spectrum and c is the speed of light (3×10^8 m/s).

$$E=hc/\lambda \quad (1)$$

Interestingly, investigation of various dyes obtained were from waste material. Natural dyes extracted from waste namely *Eugenia Clavifora, Averrhoe bilimbi* (AB), *Elaies guineesis* (EG), *Terminalia cattapa* (TC) and *Clidemia hirta* (CH) are the plants used in this study as shown in Figure 1. The stability problem of dye was occurred because of degradation of dye in the presence of sunlight radiation. Five different colours of natural dyes extracted from various part of plant such as leaves, seeds, fruits and pulps were used. They were chosen based on their colour absorption which were red, purple, yellow, brown and greenish blue. *Averrhoe bilimbi* or also known as Belimbing Buluh's flower in Malaysia is commonly used in traditional and Malay cuisine [8-10]. Direct sunlight and seasonally humid climate are considered to be beneficial for this flower to bloom in yellowish green to reddish colour [10]. *Terminalia cattapa* (Ketapang) or commonly known as tropical almond, produces poison in its leaves as a form of protection against insect parasites. These dried leaves provide a strong brown dye and acts as a 'black water extract' when it falls into the river.

A well-known natural dye: anthocyanin was investigated as a photosensitizer. These pigments extracted from Jambu Arang or scientifically called *Eugenia Clavifora* was chosen here as one of the natural dyes. The colour of this fruit is black purple and cyanidin-3-O-glucoside [11] was observed as chemical structure in this fruit. Its commonly known benefits are for the use of traditional medicine. This fruit is commonly abundant in resources, safe and grow easily around villages and forests.

Senduduk Bulu or scientifically known as *Clidemia hirta* is a species mostly grown in oil palm plantation area and usually affect the production of oil palm's fruit [12] .This plant was immune to the herbicides and is the fastest growing plant on the ground. The effects of having *Clidemia hirta* on crop productions are not easily quantify but almost 6 to 20% loses of oil palm plantations is due to the strong competition resulted from this species [13, 14].

Mesocarp fibre from palm oil *(Elaies guineesis)* was chosen as biomass waste, which then utilized for hybrid solar cell development. Commonly, palm tree belongs to a family of plants known as Palme or Palmeceae which contains high concentration of oil, abundant in resources, safe and reputative application involving food, biodiesel, fat and related products [15, 16].

Despite its impressive application list, the colour of matured plant used in this study was found to be the most susceptible towards its permanent colour plus the colour will not change within 7 days. The reason why its colour cannot easily change was most probably due to the solvent used which consequently long lasted its colour up till one year. Chemical structures of anthocyanin and flavanoid were shown in Figure 1 including cyanidin-3-O-glucoside [11], delphinidin3,5-O-diglucoside [17], delphinidin [18] and mesocarp fiber.

Solar energy integrated with plants is not fully utilized in Malaysia yet. Therefore, this research was focused to study the stability of natural dye in the presence of sunlight radiation. The findings, data and knowledge acquired were assisted in the development of a hybrid solar cell for green energy application. Most plants that could be used as sensitizers for solar cell application undergo rapid photodegradation [19].

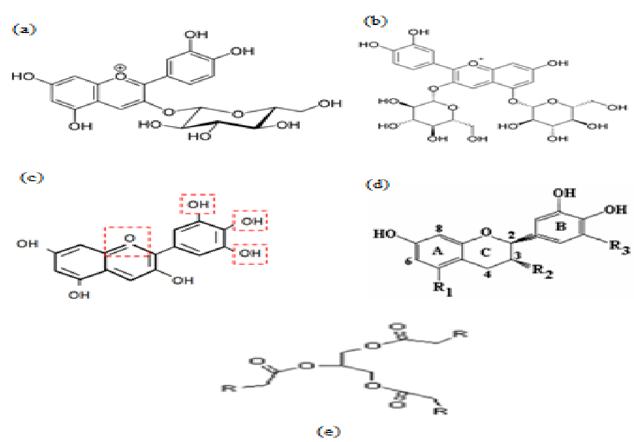


Figure 1 Structure of (a) *Eugenia Clavifora (*cyanidin-3-O-glucoside) (b) *Clidemia hirta (*delphinidin3,5-O-diglucoside) (c) *Terminalia cattapa* (delphinidin) (d) *Averrhoe bilimbi* (flavonoid) (e) *Elaies guineesis* (fiber) [11, 17, 18]

2.0 METHODOLOGY

2.1 Sample Collection and Extraction of Plant

Averrhoe Bilimbi flowers, *Eugenia Clavifora* fruits, *Terminalia catappa*'s leaves and *Clidemia hirta* fruit were collected from a small village in Terengganu. Mesocarp fiber of *Elaies Guineensis* was collected from Johor. They were chosen based on their colour absorption which were red, purple, yellow, brown and greenish blue as shown in Figure 2. They were chosen based on their colour absorption which were red, purple, yellow, brown and greenish blue. After that, they were cleaned using tap water and then rinsed with distilled water. Then, they were crushed into fine powder and immersed in ethanol. Subsequently, the solution was filtered and placed in ultrasonic bath to maximize the efficiency of natural colorant extraction [20, 21].

Figure 2 Extraction of pure dyes (a) *Eugenia Clavifora* (b) *Averrhoe Bilimbi* (c) *Clidemia hirta* (d) Terminalia Cattapa and (e) *Elaies Guineensis*

2.2 Photodegradation Experiments

10 ml of reactions solution was filled into a vial bottle made from pyrex glass and was then exposed to sunlight. The power of sunlight was determined to be 200 to 1000 W/m^2 using pyrannometer with data logger. The absorption spectrum (wavelength 200nm to 1000nm) was recorded using UV-Vis Spectrophotometer Perkin Elmer [22]. Then data were collected every week to determine the rate of decoloration. The irradiation experiments were carried out between 10 am to 3 pm for ten weeks.

2.3 Fabrication of Hybrid Solar Cells

In order to produce the solar cell, a bilayer heterojunction device was fabricated on the film. The principal scheme for heterojunction solar cells was presented in Figure 3.

Titanium dioxide (TiO_2) was deposited onto the ITO substrate using doctor blade technique. Deposition blade angle was fixed at 45^o [23]. These films was then annealed at 450 ^{o}C for 15 minutes on a hot plate in ambient atmosphere. The annealing step was an important step to reinforced the attachment of TiO_2 layer with ITO substrate.

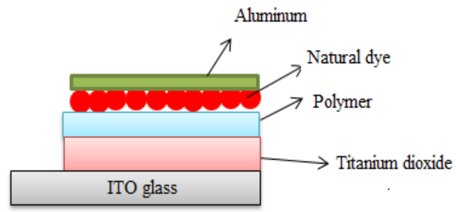


Figure 3 Bilayer heterojunction structure of hybrid solar cells

In addition, this solvent can be removed thus enhancing the mobility of sample charge carrier. After cooling to room temperature, samples were then transferred to a glove box for subsequent procedures. Spin coating Model Laurell WS-400/500-Lite Series was used in this study. PEDOT:PSS was deposited by spin coating technique at 2000 rpm in 10 seconds [24, 25] with a thickness of 28 nm approximately. The thickness of the sample was measured using Surface Profiler located at Universiti Kebangsaan Malaysia. The sample was then dried at 120 ^{o}C for 15 minutes on a hot plate [26]. All films were allowed to cool down to room temperature before next process was performed. In this study, after deposition of TiO_2 and PEDOT:PSS, samples were then immersed in natural dye solution. Finally the Aluminum was deposited as an electrode for all samples using Physical Vapour Deposition, (PVD) techniques [27]. The model used for this research was Edwards Auto 306 located at Universiti Malaysia Terengganu.

2.4 Characterization of Thin Film

UV-Vis, FTIR were used to characterize the hybrid solar cells sample. UV-Vis was used as an easy technique to estimate band gap of organic and inorganic materials. The optical properties including HOMO-LUMO energy gaps of conjugated systems were evaluated by UV-Vis spectroscopy. Direct band gap occured if the momentum of electrons and holes is similar in both conduction and valence band. The most important criterion for hybrid solar cells is the power conversion efficiency. It can be measured using Autolab Potentiostat PGSTAT 302 with 100 mWm^{-2} light intensity. Performance of hybrid solar cell is generally evaluated by the current–voltage (I–V) measurements [28, 29].

3.0 RESULTS AND DISCUSSION

3.1 Photodegradation Effect on Natural Dyes

The photodegradation is performed on dye to study the effect of sunlight exposure and stability of dye when exposed to sunlight.

3.2 Observation Colour of Natural Dye After Sunlight Exposure

The result of photodegradation on natural dye under sunlight radiation was shown in Table 1. The colour changed from its natural dye was observed after ten weeks of direct sunlight exposure. This colour change occurred because natural dyes had gone through the decay process caused by sunlight.

Table 1 Observation of color changes for all plants before and after sunlight exposure

Natural dyes	Before sunlight exposure	After sunlight exposure	Observation of colour
***Averrhoe Bilimbi* (flower)**			The colour changed from red maroon to brown
***Eugenia Clavifora* (skin of fruit)**			The colour changed from dark purple to light purple
***Elaies Guineensis* (mesocarp fiber)**			The colour changed from yellow to clear solution
***Terminalia cattapa* (leaves)**			The colour changed from brown to light brown
***Clidemia hirta* (fruit)**			The colour changed from blue-green to light brown

3.3 Evaluation of the Photodegradation Activities of Natural Dyes

Table 2 illustrates the color and UV-Visible spectra of five experimented dyes. The absorption was found to be in the range of 400 nm to 700 nm and the chemical compound obtained for all natural dyes were anthocyanin and carotenoid. As shown in Figure 4, two absorption peaks of natural dye compound in *Averrhoe Bilimbi's* flower were observed to be in visible range between 400 nm and 650 nm. Figure 5, 6, 7 and 8 shows the absorption spectrum for *Eugenia Clavifora, Elaies Guineensis, Terminalia cattapa* and *Clidemia hirta* are 380 nm – 600 nm, 380 nm - 520 nm, 300 nm – 500 nm and 400 nm – 700 nm respectively. This proves that *Averrhoe Bilimbi* is an attractive compound that can be used as natural sensitizer with two strong absorption peaks in the visible region located at 411 nm to 660 nm wavelengths [30].

Table 2 Wavelength for the strong absorption peak based on different color of natural dyes

Natural dyes	The color of natural dye	Wavelength for the Strong Absorption Peaks (nm)
Averrhoe Bilimbi (AB)	red maroon	545 and 665
Eugenia Clavifora (EC)	dark purple	550
Elaies Guineensis (EG)	yellow	446
Terminalia cattapa (TC)	brown	371 and 450
Clidemia hirta(CH)	blue green	411 and 660

Degradation percentage (%) can be calculated by using Equation (2).

$$\text{Percentage }(\%)=\left(\frac{A-A_0}{A_0}\right)x100\% \quad (2)$$

Where: A_o= initial absorption and A=final absorption

Absorption was related to the concentration of dye in the solution. Higher concentration of dye, higher absorption would become. As can be seen in Figure 4 and 5, *Averrhoe Bilimbi* and *Eugenia Clavifora* resulted in degradation percentage of 92% and 64.7% respectively after sunlight exposure. However, *Terminalia cattapa* and *Elaies Guineensis* were recorded at 70% and 90% respectively in the same time frame as shown in Figure 6 and 7. Figure 8 shows the percentage for *Clidemia hirta* was 91.5% and it was shown that *Clidemia hirta* was slightly different with *Averrhoe Bilimbi* by 0.5%. Figure 9 shows the percentage of photoreduction of all plants.

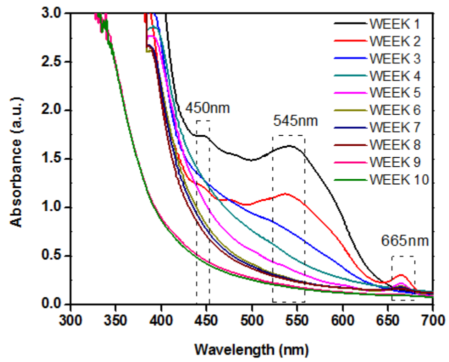


Figure 4 Absorption spectrum of *Averrhoe Bilimbi* after sunlight exposure from week 1 to week 10

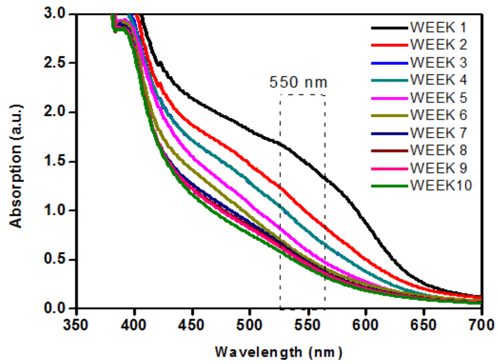


Figure 5 Absorption spectrum of *Eugenia Clavifora* after sunlight exposure from week 1 to week 10

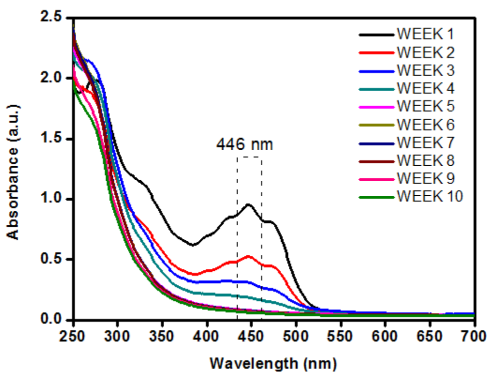


Figure 6 Absorption spectrum of *Elaies Guineensis* after sunlight exposure from week 1 to week 10

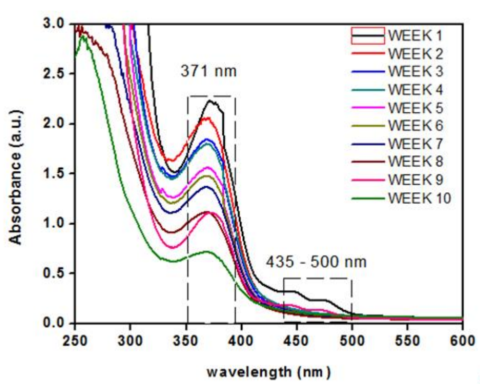


Figure 7 Absorption spectrum of Terminalia cattapa after sunlight exposure from week 1 to week 10

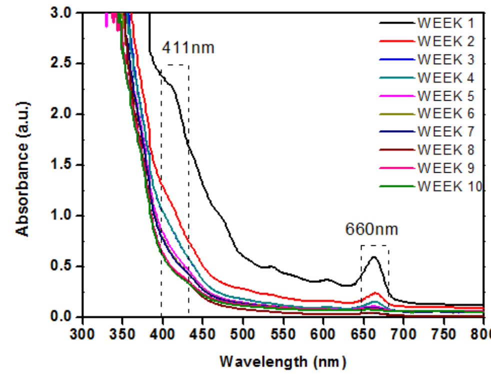


Figure 8 Absorption spectrum of *Clidemia hirta* after sunlight exposure from week 1 to week 10

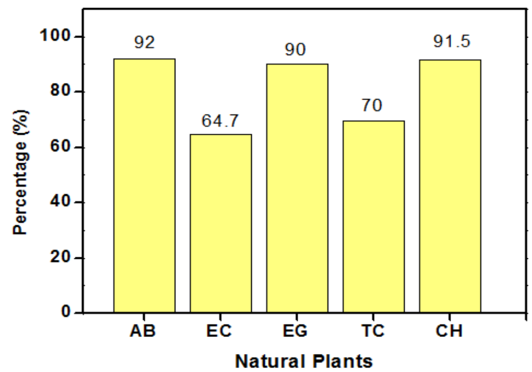


Figure 9 Percentage of photodegradation of all natural dyes

Refering to Table 1, this changes in colour for all dyes were observed after directly being exposed to sunlight radiation. The influence of sunlight exposure on natural dyes compounds can be observed via absorption spectrum in UV-Vis analysis. As can be seen from Table 1, the colour of *Elaies Guineensis* degraded from yellow to colorless solution (with 90% of degradation) after directly exposed to sunlight within 10 weeks. *Elaies Guineensis* contains pigment of β-carotene and generally, degradation occured due to heat, oxidation and light absorption [31]. Besides that, according to Khoo (2011), β-carotene was very unstable when directly expose to sunlight radiation, easily isomerized into cis-isomers and the degradation occurs to all trans- β-carotene [32]. Previous researches also mentioned that *Elaies Guineensis* are hydrophobic (do not react with water), therefore the structure was unstable with 90% of degradation [33].

This statement also agreed by Wrostald et.al (2005), the stability of dye can be affected by reducing water from pigments. Anthocyanin pigments undergo degradation reaction and their stability was affected by their structure and presence of ascorbic acid will increase the degradation process [33]. Hence, degradation percentage of *Averrhoe Bilimbi* and *Clidemia hirta* were higher compared to other dyes which are 92% and 91.5%, respectively. In addition, reduced water content and dried condition of anthocyanin significantly enhanced the stability of natural dyes.

Anthocyanin mostly extracted from flowers, leaves and fruits. These different parts of natural dye sources obviously influence the stability of dye molecules. According to Delgado (2000), fruits are more suitable to be used compared to flower corresponding to their synthetic ability [34]. Thus, referring to Table 1, part of natural dyes for *Eugenia Clavifora* are more stable compared to *Averrhoe Bilimbi*. It was strongly agreed due to the degradation percentage of *Eugenia Clavifora* was obtained around 64.7% (as shown in Figure 9) and exhibits slightly degraded when irradiated with sunlight. *Eugenia Clavifora* demonstrated photodegradation clearly (Figure 5), it took more than 10 weeks to degrade at similar rate compared to other natural dyes. This smaller degradation of *Eugenia Clavifora* ascribed to the stability of anthocyanin pigments. Furthermore, its stability is highly variable and dependable on the matrix composition in their structure [33, 35].

Each sample for all dyes has their own absorbance region depending on their individual pigmentation. The natural occurrence of the photodegradation in all natural dyes revealed that the pigment composition destructed when exposed to sunlight. This significant difference in colour can be attributed to the lack of pigmentation in dye molecule (the tone of colour become lighter). These pigments absorbs energy of radiation and possess protective effect in enzymes on the other molecule system [31, 36]. However, the pigment destruction can be prevented by coating with metal. Anthocyanin with cyanidin (*Eugenia Clavifora*), delphinidin (*Terminalia cattapa*) and petunidin glycosides exhibit remarkable stability interaction with metal [37]. The energy adsorption of anthocyanins is successfully employed to occur because of the interaction between alcoholic – bound protons with hydroxyl group embedded in TiO_2 architecture. This interaction was reported by Ludin et. al (2014) and Jaafar et.al (2017) [38, 39]. These efficient interactions promotes in excitation and electrons transfer from anthocyanin to TiO_2 films [40, 41].

3.4 Optical Energy Gap for Natural Dye after Exposing to Sunlight Radiation

Table 3 presents the optical energy gap after exposing to sunlight radiation. Optical energy gap of *Eugenia Clavifora* was observed to be 2.15 eV followed by 3.76 eV for *Terminalia cattapa*. 4.8 eV, 3.2 eV and 3.25 eV were calculated for *Elaies Guineensis* (EG), *Averrhoe Bilimbi* (AB) and *Clidemia hirta*(CH), respectively. Optical energy gap for TC, AB, EG and CH were slowly changed to UV region after sunlight exposure. However, EC remained in the same region (visible) as before exposure.

The increasing of optical energy gap after sunlight exposure radiation was depending on the colour source (part of the plant extract) which are from fruits, leaves and flower as shown in Table 2. The effect of sunlight radiation shows the optical energy gap from flower (*Averrhoe Bilimbi*) and fruit (*Eugenia Clavifora*) were slightly increased along with the percentage of 1 and 5%, respectively. However, for leaves (*Terminalia cattapa*) and fiber (*Elaies Guineensis*), they exhibit obvious increase with ~50%. Referring to FTIR result (Figure 13), it shows that the appearing of C-H bond for *Terminalia cattapa* is in the range of 2000 to 2450 cm^{-1}. Due to the strong bond of C-H, more energy from dye molecule is needed to transmit electron from the ground state to higher state. Therefore, it has a large optical energy gap after exposing to sunlight radiation. As can be seen from the result of *Elaies Guineensis* (Table 3), the increase of optical energy gap due to the strong steric hindrance by long chain alkenes that inhibit dye attachment [39]. Thus, it needs more energy to break the chain in degradation process.

As a comparison, *Eugenia Clavifora* had slightly increased (5%) in optical energy gap from 2.04 eV to 2.15 eV after exposed to sunlight. This dye shows the lowest energy gap for both radiations. Eventhough only an increment of 1% before (3.15 eV) and after (3.20 eV) exposure, the optical energy gap for *Averrhoe Bilimbi* was higher compared to *Eugenia Clavifora*. The difference of this photodegradation percentage causes by anthocyanin pigment in *Eugenia Clavifora* is effective in electron transfer [39]. The lowest optical energy gap will promote electron from dye molecule easily excites from ground state to higher energy state. This results also supported with the results from Figure 5 which is reported that, EC obtained the lowest percentage of photodegradation (64.7%). As a conclusion, EC was the suitable photosensitizer compared to other dyes to be fabricated for HSC.

Table 3 Optical energy gap for all dyes before and after expose to sunlight

Natural dyes	**Optical energy gap, E_g (eV)**	
	Before expose to sunlight	**After expose to sunlight**
Averrhoe Bilimbi	3.15	3.20
Eugenia Clavifora	2.04	2.15
Elaies guinennsis	2.50	4.80
Terminalia cattapa	2.45	3.76
Clidemia hirta	3.11	3.25

3.5 Functional Group (FTIR)

Figure 10 shows there are few peaks observed for *Averrhoe Bilimbi* at 3336 cm^{-1} and 2950 cm^{-1} before and after sunlight exposure. The hydroxyl peak at 3336 cm^{-1} becomes broader after exposed compared to before exposed. However, at wavenumber 1430 cm^{-1}, the C-H peak become sharper after being exposed to sunlight. In the wavenumber of 1050 cm^{-1}, a sharp peak corresponds to the C-O alkoxyl group observed after exposure. The peak at 1640 cm^{-1} in Figure 10 was assigned to stretching vibrations of carbonyl groups for anthocyanin molecule. The chain of C=O peak at 1640 cm^{-1} was break to peak C-O and C-H allocated at 1050 cm^{-1} and 2450 cm^{-1}, respectively.

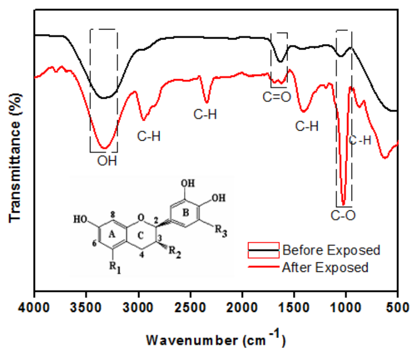


Figure 10 FTIR *Averrhoe Bilimbi* before and after exposure to sunlight

Figure 11 shows the infrared spectra for *Eugenia Clavifora* in the wavenumber of 1050 cm^{-1} with a sharp peak corresponds to the C-O alkoxyl group before and after exposure to sunlight. At region 1500 to 1800 cm^{-1}, it shows that the interaction of carbonyl group (C=O) stretching vibration along photodegradation test. *Eugenia Clavifora* displays carbonyl groups and hydroxyl group -OH) at 1670 cm^{-1} and 3386 cm^{-1}, respectively. The absorption of sunlight energy on dye molecules had reduced down to 25% in peak intensity taking place at C-O, C-H and C=O band.

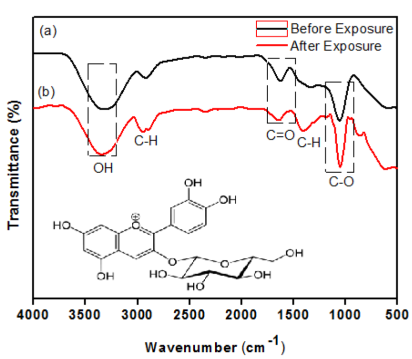


Figure 11 FTIR *Eugenia Clavifora* before and after exposure to sunlight

In *Elaies Guineensis*, there are three sharp peaks observed in the region from 500 cm^{-1} to 2000 cm^{-1}. The peaks appeared at 1060 cm^{-1}, 1423 cm^{-1} and 1676 cm^{-1} as shown in Figure 12. As can be seen from this figure, hydroxyl group was allocated at 3000 to 3500 cm^{-1} regions. The peak at this region was associated as broader before exposure compared to after exposure. In addition, the change of C=O to the sharp peak of C-O (1060 cm^{-1}). Consequently, the intensity of C=O was slightly reduced before and after exposing to sunlight.

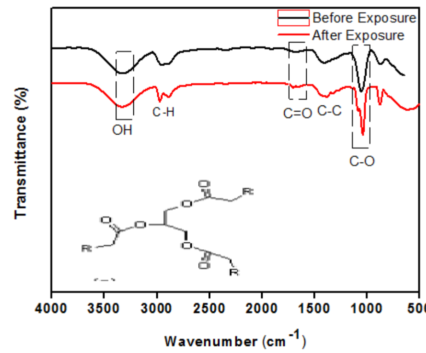


Figure 12 FTIR *Elaies Guineensis* before and after exposure to sunlight

There existed few peaks for *Terminalia cattapa* in the range of 1000 cm^{-1} to 3500 cm^{-1} as shown in Figure 13. Those peaks were assigned to -OH, C-O and C=O at 3450 cm^{-1}, 1060 cm^{-1} and 1645 cm^{-1}, respectively. It can be clearly seen before exposing to sunlight, a broader peak was assigned to -OH group. In the anthocyanin molecule, the band C=O was assigned to stretching vibration of carbonyl groups. A sharper peak of C=O was observed before exposing compared to after exposing. After exposure, C=O was probably suggested to be changed into C-O and the peak of C-O becoming more intense.

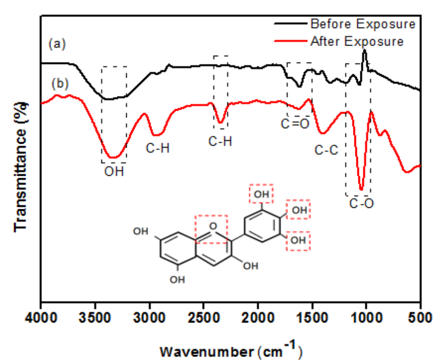


Figure 13 FTIR *Terminalia cattapa* before and after exposure to sunlight

In the region from 500 cm^{-1} to 1800 cm^{-1}, there are few peaks of infrared spectra clearly observed in *Clidemia hirta* (Figure 14). The disappearing of stretching vibration C=O (before expose to sunlight) resulted appearing the sharp peak of C-O observed (after expose to sunlight) at 1650 cm^{-1} and 1050 cm^{-1}, respectively. The broader peak of -OH also capture between before exposed and sharper peak occured after exposed to sunlight at 3450 cm^{-1}. Another C-H peak appear at region 2000 cm^{-1} to 2500 cm^{-1} was observed between after expose to sunlight.

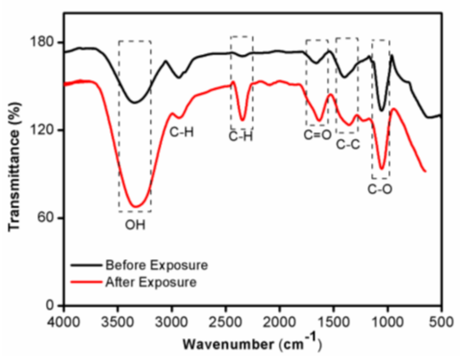


Figure 14 FTIR *Clidemia hirta*before and after exposure to sunlight

The existence of hydroxyl group stretch region can be seen from Figure 10 to 14. The region of -OH group was observed between 3000 to 3500 cm^{-1}. A broader peak observed in -OH group as can be seen for *Averrhoe Bilimbi, Eugenia Clavifora, Elaies Guineensis, Terminalia cattapa* and *Clidemia hirta*. -OH group for all natural dyes mostly take placed around 3380 cm^{-1} inhibited to the attachment with TiO_2 film.

Other than that, carbonyl group at 1640 to 1715 cm^{-1} regions in aliphatic hydrocarbon, which has good attachment to Ti (IV) sites on TiO_2 film. The presence of several carbonyl and hydroxyl groups in dye structure were capable to complexion the TiO_2 surface. Consequently, all natural dyes were suitable to be combined with TiO_2. This interaction exhibits higher performance in power conversion efficiency.

Summing up, after exposing to sunlight, intensity of C=O band shows decreasing patterns for all natural dyes. Meanwhile C-O shows increasing pattern. This vice versa pattern, suggested that the change of C-O bond breaks into C-O due to the interaction between natural dye with sunlight energy absorption. This interaction includes reaction in molecular's decomposition by C=O and the reaction in molecule's combination of C-H and C-O.

Nevertheless, the reduction of natural dye's tone colour was affected by the decomposition of C=O bond illustrated in FTIR spectrum. This was applied to the condition in *Terminalia cattapa*. At this point, C=O breaks into C-O and referring to UV-Vis results, the photodegradation occurred in the range of 375 nm and 435 nm to 500 nm (Figure 7). Hence, it can be suggested that C=O bond is contributed to the photodegradation process. This statement was agreed by Marcin et. al (2008) and Delgado et. al (2000) that both aromatic and aliphatic can influence the durability and colours presence in plants tissues [9, 34].

As mentioned, for *Eugenia Clavifora* (Figure 11) there was a slight decreased in peak intensity of -OH and C=O bond before and after exposure to sunlight. The effect of sunlight exposure on dye molecules (-OH, C-O, C-H and C=O) had reduced to 25% of peak intensity. This results also supported with photodegradation test from Figure 5 and it was also calculated at lower percentage of photodegradation (64.5%) as can be seen from Figure 9. The presence of hydroxyl and carbonyl groups in *Eugenia Clavifora* suggested to be a good sensitizer for hybrid solar cell through this work. Thus, based on these observations, chemical reactions and mechanism for anthocyanin dye molecule occur during the photodegradation process can be presented in Figure 15 and Figure 16. There are three steps for mechanism process for anthocyanin after exposed to sunlight: i) Hydrolysis of anthocyanin ii) Elimination of H_2O and iii) Rearrangement of aromatic ring.

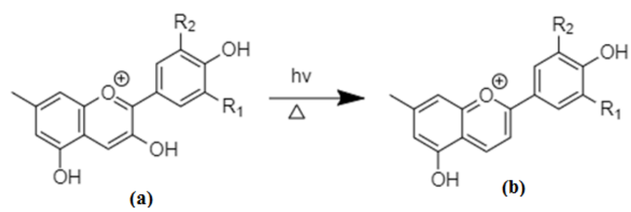


Figure 15 Chemical reaction for anthocyanin dye molecule during photodegradation process: (a) before expose to sunlight (b) after expose to sunlight

Mechanism:

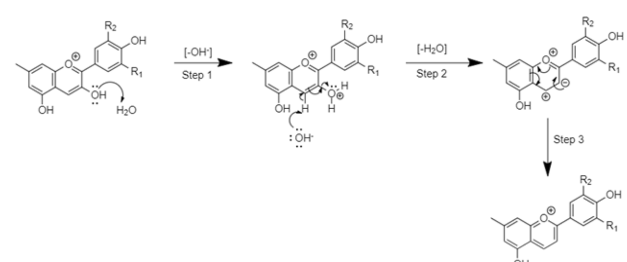


Figure 16 Mechanism for anthocyanin dye molecule during photodegradation process: with different steps after expose to sunlight: i) Hydrolysis of anthocyanin ii) Elimination of H_2O and iii) Rearrangement of aromatic ring

3.6 Performance of Hybrid Solar Cells

In conclusion, dye molecules in the *Eugenia Clavifora* are stable in photodegradation when exposed to sunlight compared to other selected natural dyes. Through photodegradation analysis, *Eugenia Clavifora* was suggested to be the best photosensitizer with TiO_2 attachment in HSC. This result also agreed by performance of HSC. Their efficiencies (PCE) were presented in Table 4 and TiO_2/PEDOT:PSS/EC obtained the best performance thus leading to an efficiency of 1.33%. It was reported that PCE of TiO_2/PEDOT:PSS/AB, TiO_2/PEDOT:PSS/EG, TiO_2/PEDOT:PSS/TC and TiO_2/PEDOT:PSS/CH of 0.01%, 0.10%, 0.24% and 0.05%, respectively.

Table 1 Power conversion efficiency for TiO_2/PEDOT:PSS with dye EC,TC,AB, CH and EG

Samples	PCE(%)
TiO_2/PEDOT:PSS	0.005±0.001
TiO_2/PEDOT:PSS/EC	1.33±0.39
TiO_2/PEDOT:PSS/TC	0.24±0.14
TiO_2/PEDOT:PSS/AB	0.01±0.008
TiO_2/PEDOT:PSS/CH	0.05±0.009
TiO_2/PEDOT:PSS/EG	0.10±0.01

4.0 CONCLUSION

These results indicated that photodegradation of plants was mostly dependent on specific wavelengths in the range of 400nm to 700nm. It is due to the interaction of electronic structure in plant pigment to the sunlight [42, 43]. *Eugenia Clavifora* is clearly demonstrated that it took more than 10 weeks to degrade compared to other plants. *Eugenia Clavifora* resulted in degradation percentage of 64.7%. *Eugenia Clavifora* had slightly increased (5%) in optical energy gap from 2.04 eV to 2.15 eV after exposed to sunlight.Molecules in the *Eugenia Clavifora* dye are more stable when exposed to sunlight than other dyes. PCE for hybrid solar cells in *Eugenia Clavifora* also leading at the highest efficiency (1.33 %) compared to other dyes. This clearly shows that *Eugenia Clavifora* can be used as natural photosensitizer that can enhance the efficiency of solar cell application.

Improvement of solar cell efficiency possibly be achieved by following recommendation. The arrangement of inorganic materials and organic materials component in thin film alter their electrical and optical properties plus the design also depends on selection of material. The reliability of other plant pigment such as chlorophyll, caratenoid, betalain and flavoid can act as a more desirable alternative of photosensitizer to thin film solar cells.

Acknowledgement

The authors would like to thank Universiti Malaysia Terengganu (UMT), Fundamental Physics Laboratory UMT's members and Nano Research Team (UMT) for supporting in this research. We also acknowledge the financial support from UiTM and Ministry of Education Malaysia (SLAB/SLAI).

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