

**ELECTRICAL PROPERTIES, THICKNESS MEASUREMENT AND
EFFICIENCY OF BILAYER ORGANIC SOLAR CELL USING *GARCINIA
MANGOSTANA LINN* AND *ALLAMANDA CATHARTICA LINN* AS NATURAL
DYE: A SUBSTRATE TREATMENT**

A.R.N. Laily¹, S. Hasiah², N.A. Nik Aziz³,
Ahmad Nazri Bin Dagang¹, and Mohd Sabri Bin Mohd Ghazali³

¹*School of Ocean Engineering, Universiti Malaysia Terengganu,
21030 Kuala Terengganu, Terengganu, Malaysia*

²*Center for Foundation and Liberal Education, Universiti Malaysia Terengganu,
21030 Kuala Terengganu, Terengganu, Malaysia*

³*School of Fundamental Science, Universiti Malaysia Terengganu,
21030 Kuala Terengganu, Terengganu, Malaysia*

Corresponding author: norlaily.rashid@gmail.com

ABSTRACT

This paper describes the electrical conductivity, Hall effect study, thickness measurement and efficiency in bilayer hetero-junction organic solar cell (OSCs) using natural pigments from Mangosteen Pericarp (*Garcinia mangostana Linn*) and Yellow Bell (*Allamanda cathartica Linn*) Flower. In this work, Indium Tin oxide (ITO) glass as substrate was heated at 50°C to 200°C. The polymer used was Poly (3-Dodecylthiophene) (P3DT) thin film. The P3DT were deposited on the ITO substrate using electrochemistry method and spin coated technique at room temperature. The electrical conductivity of ITO deposited thin film was explored by four point probes (FPP) under dark and under light radiation (range of 10 Wm⁻² to 200Wm⁻²). FPP data revealed that electrical conductivity was increased by the increment of light intensity and temperature of substrate. Then, the samples were examined using Hall Effect measurement to obtain the type of sample, Hall mobility, and highest charge carrier in the sample of OSCs. Both samples detected was N-type from Hall effect measurement. The efficiency detected in range of 0.013% to 0.211%.

Keywords: Allamanda cathartica Linn; Garcinia mangostana Linn; Organic Solar Cell; Electrical Properties; Hall Effect; Heat treatment;

INTRODUCTION

The problems of worldwide energy shortage and environment pollution are becoming more and more serious, thus lots of attention has been paid to renewable and sustainable energy [1]. Today, the reduction of greenhouse gas emission from the conventional

thermal power plants is quite necessary. For the reduction of greenhouse gases from the electrical power sources, the power producers are now marching towards usage of renewable energy sources (RESs) [2]. Renewable energies are defined as the resources that are reproduced continuously by natural manners, can be reused due to their environment-friendly and sustainable properties [1]. It offer the promise of clean, abundant energy gathered from self-renewing resources such as the sun, wind, earth, and plants. Virtually all regions of the world have renewable resources of one type or another. It is expected that the global energy demand would increase by five times of the current demand by 2100 [3].

One of the solutions is to develop solar cells (SCs) since solar energy is unlimited and free to use. The organic solar cell (OSC) is a promising alternative in comparison to the conventional inorganic devices owing to their high performance and low production costs. In line to organic solar cells, the dye sensitized solar cell is the current focus and the natural dye ingredients could be utilized as dyes for OSC. The best performance is currently achieved with bilayer, polymer:fullerene bulk heterojunction (BHJ) or tandem cells [4]. Organic solar cells could alleviate the stated draw-backs through the use of natural pigments for the conversion of solar energy into electrical energy. Foremost, the natural dyes abundantly available in plant parts, like flowers, seeds, barks, leaves, and stem can be extracted by simple procedure. Several pigments have been the famous subjects of research such as chlorophyll [5, 6], carotenoid [7] anthocyanin [8] flavonoid [9], cyanine [10] and tannin [11]. Due to their cost efficiency, easily extractable using cheap organic solvents [12], non-toxicity, and eco-friendly [13, 14], natural dyes are still a popular subject of research. Some of the chemical dyes in use have been found hazardous to human life causing skin and lung diseases [15-17].

Malaysia provides the possible limitless options of renewable energy resources. Located in the tropical climate, all-year sunshine is one blessing that Malaysia owns [4]. Mangosteen fruit (*Garcinia mangostana* Linn) is native to South East Asian countries. It belongs to the family of Guttiferae and is named as 'the queen of fruits' in Malaysia [18]. Large amounts of mangosteen peels are discarded as waste domestically [19]. There are benefits of mangosteen pericarp such as good source of natural antioxidants due to rich of phenolic compounds [19, 20]. It is contains a variety of bioactive compounds with potential applications as therapeutic agents phenolic acids [21], tannins [22], xanthenes and anthocyanins [19]. However, xanthenes being the major bioactive compounds [23] in mangosteen and the purple colour of the mangosteen fruit pericarp is mainly due to anthocyanins. Xanthenes are heat stable molecules. Some of the most important Xanthenes found in mangosteen include Alpha-mangostin, Beta-mangostin, Gamma-mangostin, Garcinone, Garcinone A , Garcinone C , Garcinone D , Mangostanol , Gartanin. Several xanthenes isolated from *Garcinia mangostana* is in Figure 1.

Yellow Bell flower (*Allamanda cathartica* Linn) a widely growing perennial shrub. The leaves are smooth and thick [24]. The chemical formula of *Allamanda Cathartica* Linn is $C_{30}H_{48}O_3$. Its IUPAC name is 10-hydroxy-1,2,6a,6b ,9,9,12a-heptamethyl -

2,3,4,5,6,6a, 7,8, 8a,10, 11,12. The chemical structure of *Allamanda Cathartica* Linn is shown in Figure 2.

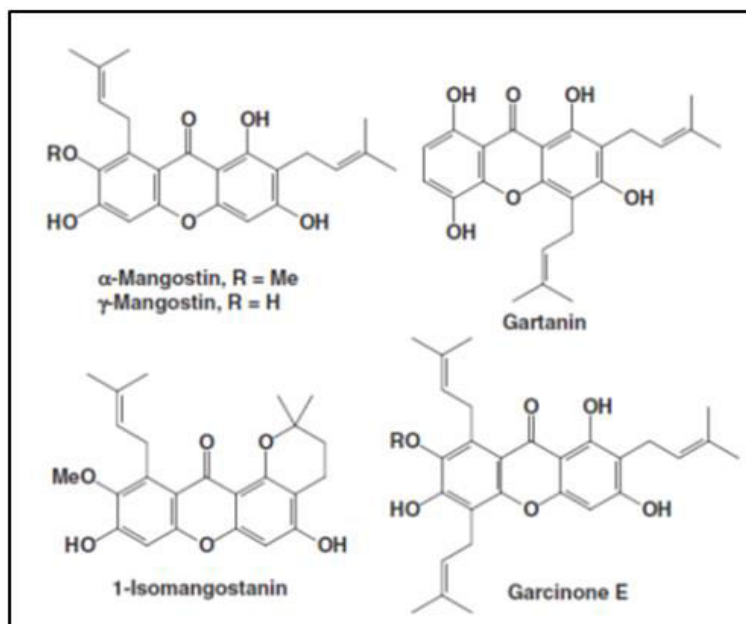


Figure 1: Several xanthenes isolated from *Garcinia mangostana* Linn [25]

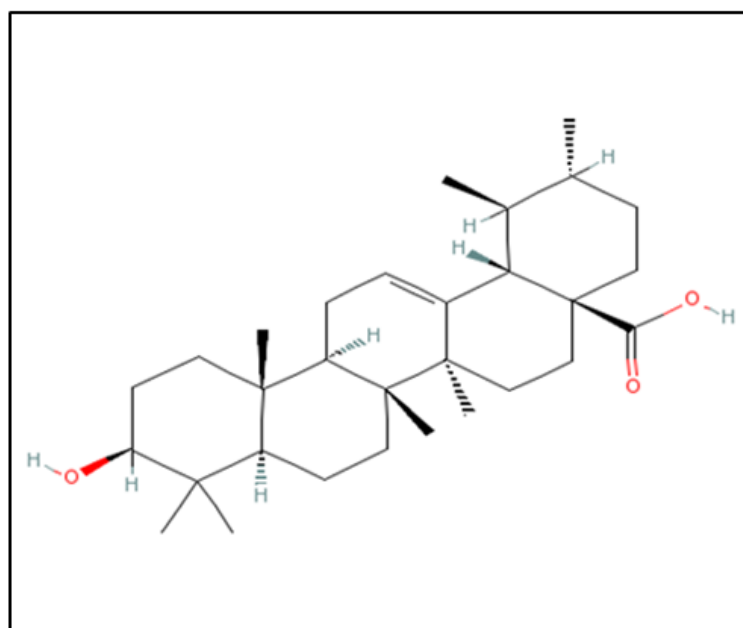


Figure 2: Chemical structure of *Allamanda Cathartica* Linn

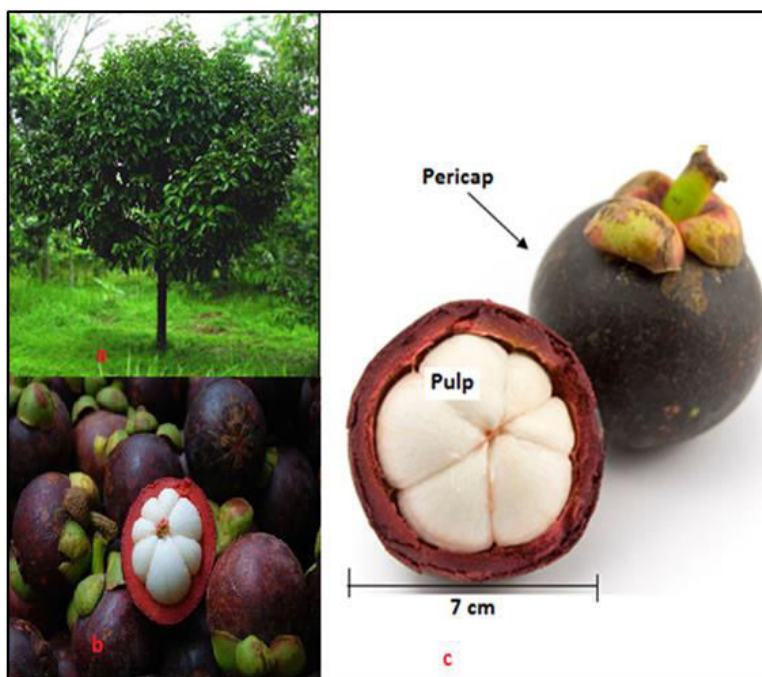


Figure 3: Plant (A), and fruits (B, C) of *Garcinia mangostana* Linn



Figure 4: Plant (A), and flower (C) of *Allamanda cathartica* Linn

EXPERIMENTAL

Sample collection and preparation.

The Mangosteen fruits were hand-picked from Dungun region, Terengganu. The collected fruits were placed in a plastic box, kept on ice and transported to the laboratory on the same day of collection. The fruits were then washed under the running tapwater and then rinsed with distilled water for three times.

Yellow bell flower was hand-picked from three separate plants located in Universiti Malaysia Terengganu (UMT), Terengganu. P3DT was prepared through polymerization of the Dodecylthiophene

Cleanup the ITO coated glass.

The ITO coated glass must be clean to make it free from dirt and dust and also to avoid any contamination. Cleanliness of ITO is very important to reduce any impurities present in the ITO because it will affect the accuracy of the results [26]. Ultrasonic vibrator (JEIOTECH, United Kingdom) was used to clean the ITO coated glass. Firstly, 2 cm² of ITO coated glass were immersed in 50ml beaker filled with detergent solution and put into the ultrasonic vibrator for 10 minutes at 30°C. Secondly, the ITO coated glasses were put in distilled water followed by acetone in order to remove any contaminations that might have been formed on the substrates [27]. Lastly, ITO coated glass were immersed in distilled water to remove stained of acetone [26] and were dried using the hair dryer before kept in a glass Petri dish. The dried ITO coated glass was heated from 50°C to 200°C.

Extraction of dye.

The 20g of mangosteen were immersed in 200mL of distilled water for 10 minutes. Then, it was crunched into small size and immersed in ethanol for 2 days. After that, it was shaken using ultrasonic bath for 24hours. It is for maximizing the efficiency of natural colorant extraction [28]. Finally, the solution was filtered to harvest the extraction of mangosteen pericarp. The same step was repeated to extract yellow bell flower.

Fabrication of Organic solar cell.

The thin films were prepared using two type of technique. The layer of conducting polymer (P3DT) was prepared using the electrochemistry method and the second layer was produced using spin coating technique.

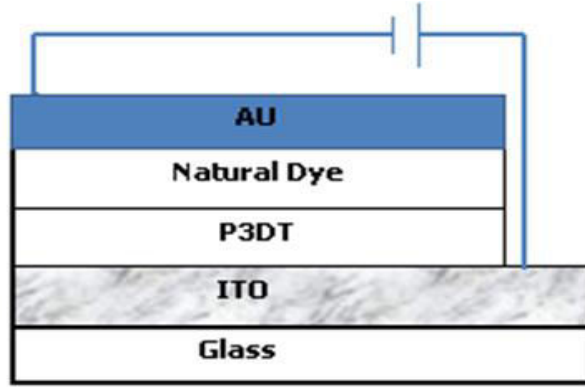


Figure 5: Structure of bilayer heterojunction organic solar cell

RESULTS AND DISCUSSION

Electrical conductivity.

The electrical conductivity of the samples was measured in two conditions: in the dark condition and under illumination of light. The resistivity produced by the prepared films was measured using FPP (Jandel RM3 Test Unit). The two outer probes supply a voltage difference that drives a current through the film. The two inner probes pick up a voltage difference, and the sheet resistivity is calculated from Equation (1) via a physical model of the current distribution. The unit of sheet resistance is ohms per square (Ω/m^2):

$$R_s = 4.532 \times V/I \quad (1)$$

Where, R_s is the sheet resistance, 4.532 is the correction factor, V is the voltage measured and I is the current applied from the test unit. Thus, electrical conductivity (σ) can be determined which it is the reciprocal of R_s , as described in Equation (2).

$$\sigma = 1/R_s \quad (2)$$

Hall Effect Measurement.

In HEM, the samples expected to have well-defined geometries and good ohmic contacts in order to obtain the accurate results. The samples must have van der Pauw (vdP) geometry. The Hall effect calculation was referring [29].

Hall voltage average, $V_{H\text{ avg}}$;

$$= [V(+31,42(+B)) - V(+31,42(-B)) + V(-31,42 - B)) - V(-31,42(+B)) \dots \\ - V(+42,13(+B)) - V(+42,13(-B)) + V(-42,13(-B)) - V(-42,13(+B))]/8 \quad (1)$$

The Hall coefficient average, $R_{H\text{ avg}}$ calculated by;

$$R_{H\text{ avg}} = \frac{R_{HC} + R_{HD}}{2} [\text{cm}^3 \cdot \text{C}^{-1}] \quad (2)$$

The unit of R_H will be m^3C^{-1} , if t is in meter, B in Tesla, Hall voltage and voltages in volt and current, I in ampere. When the thickness is unknown, the layer or sheet carrier concentration, $n_s = n$, is used instead of the bulk density,

$$n_s = \frac{8 \times 10^{-8} \times IB}{q V_{H \text{ (total)}}} \text{ cm}^{-2} \quad (3)$$

Then the Hall mobility (μ_H) is given by

$$\mu_H = \frac{|V_{H \text{ avg}}|}{\rho_{\text{avg}}} [\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}] \quad (4)$$

Lastly, a type of charge carrier is determined by the polarity sign of $V_{H \text{ avg}}$ from Equation (1) and polarity sign of $R_{H \text{ avg}}$ in (2). If the polarity sign is positive, the type of charge carrier is holes and called P-type. In contrast, if negative sign, it is electrons and called N-type.

Efficiency of organic solar cell.

The efficiency of organic solar cell can be calculated as follow:

$$\eta = \frac{P_{in}}{P_{out}} \times 100\% \quad (5)$$

$$P_{in} = \text{Intensity} \times \text{Effective Surface Area} \quad (6)$$

$$P_{out} = I_{max} \times V_{max} \quad (7)$$

Where, η is the efficiency, I is current and V is voltage.

Result and Discussion

Electrical conductivity

The electrical conductivity at different intensity of light is shown in the Figure 6 and Figure 7. The conductivity was proportional with the intensity of light for sample ITO/P3DT/Mangosteen (ITO/P3DT/MA) and ITO/P3DT/Yellow Bell (ITO/P3DT/YB). The electrical conductivity for both types sample increases with the increment of light intensity and substrate temperature. This happen because of the samples were absorbed the light energy and converted to the electrical energy [30].

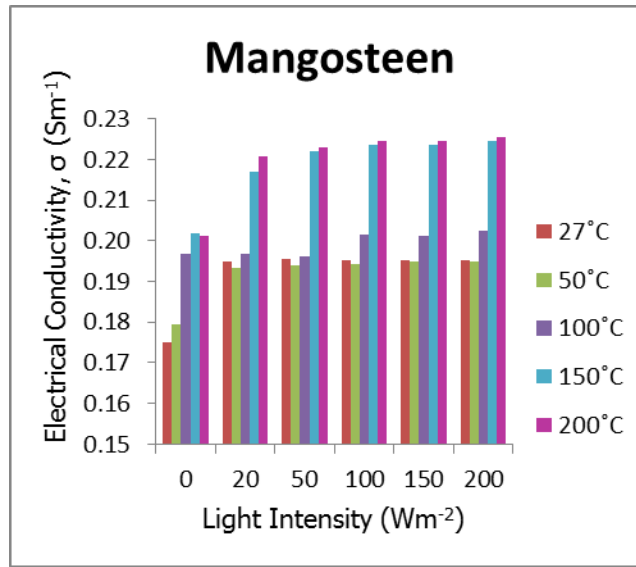


Figure 6: The electrical conductivity for ITO/P3DT/MA Organic solar cell

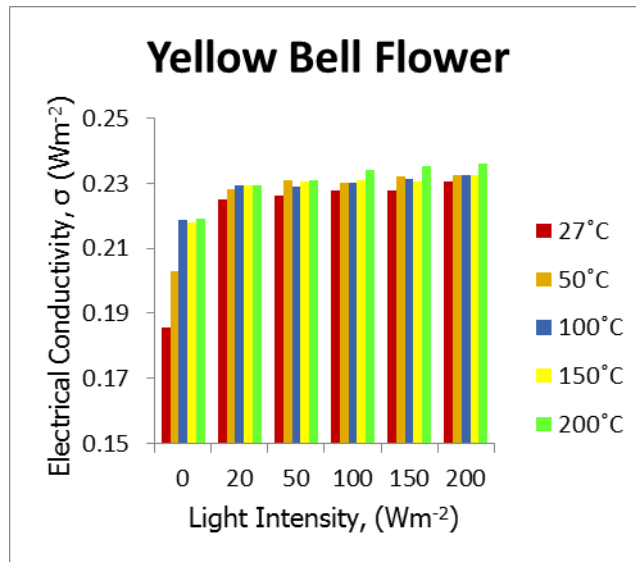


Figure 7: The electrical conductivity for ITO/P3DT/YB Organic solar cell

In Figure 6, it is rapidly increased from a low electrical conductivity at 100°C to the highest electrical conductivity at 200°C of substrate temperature. The unheated ITO substrate of P3DT/ MA/ITO (27°C) shows the electrical conductivity lower than heated substrate (50°C to 200°C). The highest electrical conductivity for unheated substrate detected was 0.201 Sm⁻¹ compared to heated substrate temperature was 0.225 Sm⁻¹. In Figure 7, unheated ITO substrate of ITO/P3DT/YB (27°C) shows the lowest electrical conductivity measured under dark condition (0 Wm⁻²) with 0.185 Sm⁻¹. While the

highest electrical conductivity obtained for P3DT/ YB/ITO was 0.236 Sm^{-1} deposited on 200°C of substrate temperature measured under 200 Wm^{-2} of light illumination. This is due to natural phenolic compound namely anthocyanin and xanthon. They are involved in photo system assembly and contribute to light harvesting by absorbing light energy in a region of the visible spectrum [31]. These plant pigments exhibit electronic structure that interacts with sunlight and alters the wavelengths that are either transmitted or reflected by the plant tissue. This process leads to the occurrence of plant pigmentation and each pigment is described from the wavelength of maximum absorbance (λ_{max}) and the color perceived by humans [32]. This is improving the electrical conductivity of commercial ITO.

The electrical conductivity was higher as substrate temperature increase. This is due after heat treatment, the particle size becomes larger, and the particle shape becomes more regular. Then, the film atoms more energetic at higher temperature to migrate and more un-perfect crystal nucleuses sufficiently grow, leading to the reconfiguration of the grains and the formation of particles with perfect crystal structure [33]. As a result, higher substrate temperature was led to the formation of lower resistance films, then causes a rises on electrical conductivity. This is basically due to the increase of the mobility and/or carrier concentration at higher substrate temperature. The increase in substrate temperature may have led to oxygen deficient films, resulting in an increase in carrier concentration as illustrated in Figure 8 and 10.

Hall Effect Measurement.

The Hall effects is a useful technique for making some electrical property measurements related to transport, such as the carrier concentration, Hall mobility, resistivity, and conduction type The Hall measurements were performed under room temperature for ITO/P3DT/YB and ITO/P3DT/MA blend thin film samples at different substrate temperature.

Carrier Concentration and Hall Voltage

The carrier concentration and Hall voltage was calculated according to the equation (3) and equation (1) respectively. The effect of temperature of substrate on carrier concentration for ITO/P3DT/MA and ITO/P3DT/YB sample is illustrated in Figure 8 and Hall voltage illustrated in Figure 9.

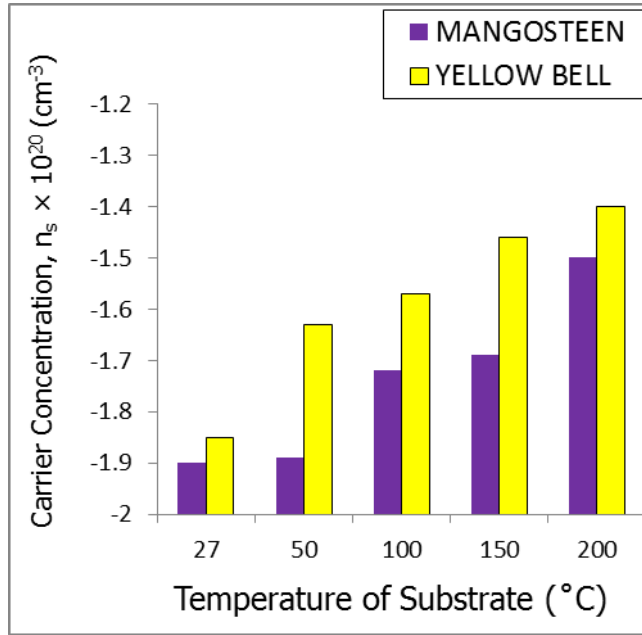


Figure 8: Carrier concentration for bilayer heterojunction organic solar cell

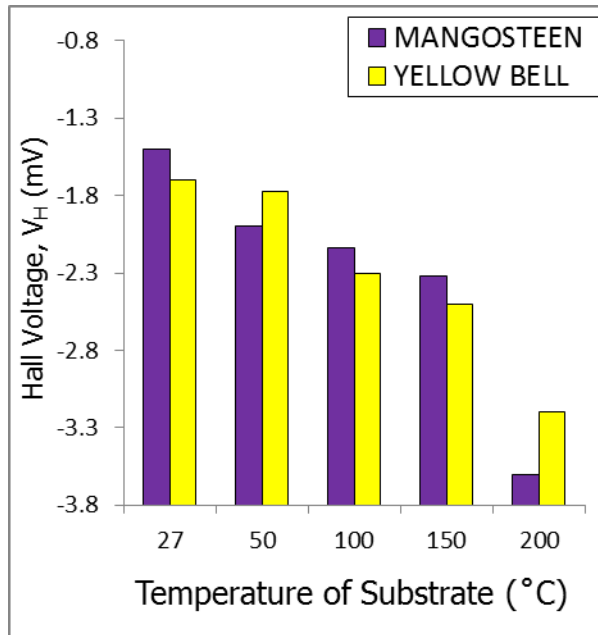


Figure 9: The Hall voltage for bilayer heterojunction organic solar cell

From Figure 8, the carrier concentration increases with increasing temperature of substrate for both samples. This can be explained by the lack of Oxygen to compensate possible divacancies and so, to an enhancement on the bulk defects [34]. Furthermore, Oxygen vacancies induce free electrons as conduction carriers [35]. The carrier concentration for heated ITO substrate was higher for all samples compared to samples

deposited on unheated ITO substrate. Figure 9, clearly shows that the Hall voltage is decreasing with the temperature of substrate. The unheated substrate (27°C) deposited exhibited the maximum point. The lowest Hall voltage detected for ITO/P3DT/MA was -3.6 mV (at 200°C). The range of Hall voltage obtained for these samples was between -1.50 mV to -3.6 mV. Figure 10 and Figure 11 shows the Hall Mobility and Hall coefficient respectively.

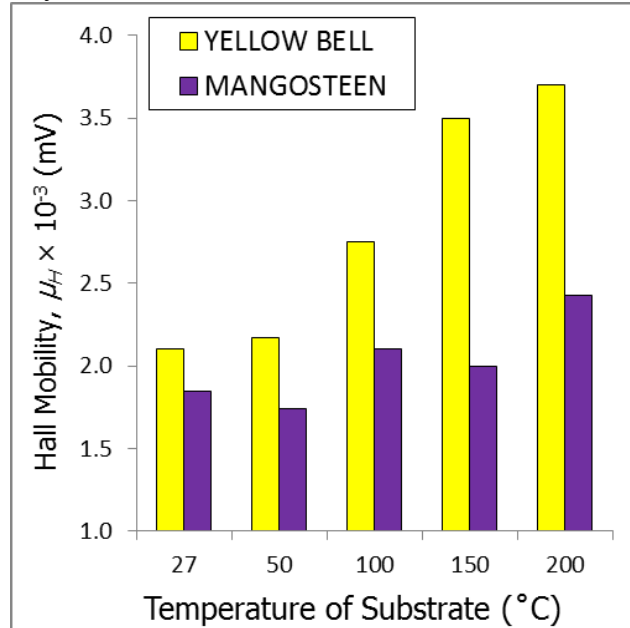


Figure 10: Hall Mobility for bilayer heterojunction organic solar cell

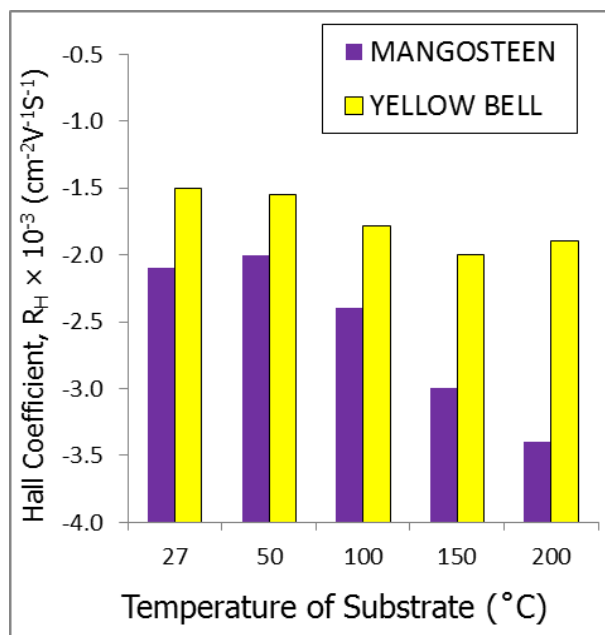


Figure 11: The Hall coefficient for bilayer heterojunction organic solar cell

Figure 10 clearly shows an increase as substrate temperature increases. For unheated substrate, ITO/P3DT/MA exhibited the lowest Hall mobility with 1.85 mV and an upward tendency shows as substrate temperature increase (heated substrate). For ITO/P3DT/YB were increasing as substrate temperature increasing. The Hall mobility and carrier concentration (Figure 8) is increasing with increasing temperature [36]. Free charge carriers are easily activated at relatively high temperature. This relationship is found to be in good agreement reported by [37, 38]. Referring Figure 11, for unheated substrate, the maximum Hall coefficient value observed was $-1.50 \times 10^{-3} \text{ cm}^{-2} \text{ V}^{-1} \text{ s}^{-1}$ and $-2.00 \times 10^{-3} \text{ cm}^{-2} \text{ V}^{-1} \text{ s}^{-1}$ for ITO/P3DT/YB and ITO/P3DT/MA respectively. In contrast, for heated substrate, the Hall coefficient was decline as substrate temperature incline for both samples. The observation agrees with the theory experimental that the Hall coefficient decreases with the charge density, n . This is revealed that, the heat treatment of substrate was affecting the Hall coefficient. In this case, light was used more effectively because the charge separation site increased by layer by layer the materials.

Types of Charge Carrier

The charge carrier type can be determined by the polarity of the Hall voltage and Hall coefficient. If negative, the charge carriers are electrons and the material is of the N-type. In this work, it was found that, the Hall coefficient is negative for all samples. This finding indicates that the majority carriers are electrons, according to the concept of semiconductors.

Thickness measurement

The thickness for ITO/P3DT/YB was thicker than ITO/P3DT/MA samples with 167.98 nm and 180.37 nm respectively. The thickness measurement was recorded using Profilometer and listed in Table 1.

Table 1: Thickness of the bilayer thin film sample

Bilayer samples	Thickness (nm)
ITO/P3DT/YB	180.37
ITO/P3DT/MA	167.98

In thicker samples, the mobile charge carrier density, n increases [39]. Therefore, the electrical properties of ITO/P3DT/YB was higher compared to ITO/P3DT/MA.

Efficiency

Figure 12 shows the efficiency of the samples at different intensity of light the sample. The efficiency of ITO/P3DT/YB was 0.092% to 0.211% while ITO/P3DT/MA detected was 0.013% to 0.172%. The highest efficiency for both natural dyes detected at 200°C substrate temperature.

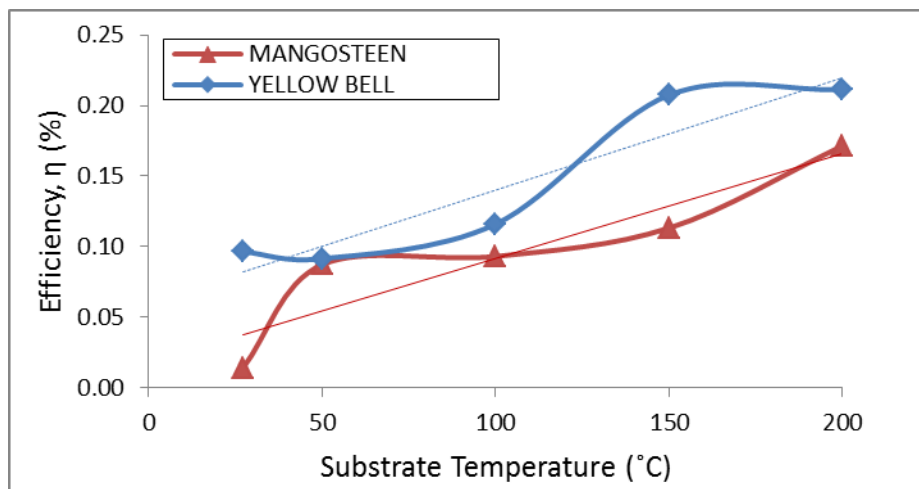


Figure 12: Efficiency of Organic solar cell

The interaction between conducting polymer (P3DT) and natural pigment such as xanthenes and anthocyanins plays an important role toward the efficiency of bilayer heterojunction organic solar cell, this might be due to possible inefficient electron/dye cation recombination pathway. The substrate temperature is also a factor affecting the efficiency of solar cell.

CONCLUSION

The ITO/P3DT/YB and ITO/P3DT/MA dye as bilayer heterojunction organic solar cell deposited on the heated ITO substrate were successfully prepared by spin coated technique and electrochemistry method. In this work, we found that the highest electrical conductivity at 200°C of temperature substrate was $2.36 \times 10^{-1} \text{ Sm}^{-1}$ for ITO/P3DT/YB. The polarity sign of Hall coefficient and polarity of Hall Voltage obtained were negative for all samples. This finding indicates that the majority carriers are electron. The ITO/P3DT/YB thin film shows higher electrical properties compared to ITO/P3DT/MA thin film samples. The presence of carbonyl and hydroxyl groups in the anthocyanin and xanthenes molecules bound to the surface of ITO, is in favor to facilitate the photoelectric conversion effect. The samples deposited on ITO substrate are successfully investigated and improve the electrical properties of the commercial ITO substrate. The efficiency detected in range of 0.013% to 0.211%. From the results we may conclude that the substrate temperature play major role in controlling the electrical properties of the bilayer heterojunction organic solar cell thin film. Furthermore, *Allamanda Cathartica Linn* (yellow bell flower) and *Garcinia mangostana Linn* (mangosteen fruit) are cost effective, renewable, eco-friendly. Hence, the study of these dyes is promising and can promote additional studies oriented to educate people on renewable energy sources, and disseminate knowledge for the optimization of solar cell components compatible with such dyes.

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