Electrical and Hall Effect Study of Hybrid Solar Cell

N. A. Nik Aziz, M. I. N. Isa, and S. Hasiah

***Abstract*—This work focuses on electrical and Hall Effect study of hybrid solar cell (HSCs). In particular, attention is given to investigations of HSCs with the architecture combining conjugated p-type polymer, poly (3-hexylthiophene) (P3HT), and inorganic ZnO heterojunctions with chlorophyll (CHLO) from marine microalgae as a dye. The films were prepared by spin coating technique and analyzed by using four point probes to calculate the conductivity. The results show that, the conductivity was increased by the increment of light intensity and concentration of CHLO. Lastly, the samples were analyzed using Hall Effect measurement to calculate the highest charge carrier in the sample of hybrid solar cell.**

***Index Terms*—Chloropyhll, hybrid solar cell, poly (3-hexylthiophene), zinc oxide.**

I. Introduction

Photovoltaics (PV), is a solar power technology that uses solar cells to convert incident sunlight directly into electricity with zero emissions. By now, PV technology has established itself as one of the best solutions to bring forth flexible and long-term solutions for rural electrification in the poorest areas of the world. Hybrid solar cell (HSC) is the combination of both organic and inorganic semiconductors. The HSC is also known as dye- sensitized solar cell which have an interesting low cost alternatives to conventional solar cell and their efficiencies is over 10 % percent has been achieved [1].HSC combine advantages of both organic and inorganic semiconductors. Hybrid photovoltaics have organic materials that consist of conjugated polymers that absorb light as the donor and transport holes [2].The term organic semiconductor is used to describe organic materials (conjugated oligomers or polymers) that possess the ability of transporting charge carriers and have been studied since the 1950s [3]. The electronic conductivity of these materials lies between that of metals and insulators spanning a broad range between 10^{-7} and 10^{3} Scm^{-1}. Holes and electrons in π orbitals are the typical charge carriers in organic semiconductors. Charge transport typically depends on the ability of the charge carriers to move from one molecule to another, which depends on the energy gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels. These materials are either based on oligomers such as pentacene, anthracene, rubrene, or oligothiophenes, or on polymers such as polypyrrole, polyacetylene, poly (3-hexylthiophene) (P3HT), or poly (p-phenylenevinylene) (PPV). Organic semiconductors have attracted much attention because of their fundamental scientific importance and impressive improvements in performance in a wide variety of photonic applications, such as organic light-emitting diodes (OLED), organic field-effect transistors (OFET), organic solar cells (OSC), liquid crystals, sensors, and many more[4]-[7]. Inorganic materials in hybrid cells are used as the acceptor and electron transporter in the structure. The hybrid photovoltaic devices have a potential for not only low-cost by roll-to-roll processing but also for scalable solar power conversion. In hybrid solar cells, an organic material is mixed with a high electron transport material to form the photoactive layer [8]. The two materials are assembled together in a heterojunction-type photoactive layer, which can have greater power conversion efficiency than a single material [9].

In this study, a hybrid solar cell were formed to find its conductivity, Hall Effect measurement and to elucidate its efficiency in the absorption of energy. Zinc oxide and a polymer, P3HT were used together with CHLO in producing this hybrid solar cell. ZnO, a wide band gap inorganic semiconductor has high crystalinity and conductivity in photoelectric properties, and it was prepared by hydrothermal method [10]. The nature dye was used as sensitizers because of sensitizers having a broad absorption band in conjunction with oxide films of nanocrstalline morphology permits to harvest a large fraction of sunlight [11].

II. Experimental Procedures

A. Materials

Poly (3-hexylthiophene) was synthesized before used. Zinc oxide (ZnO) was synthesized by using hydrothermal method and left to growth on the indium tine oxide (ITO) coated glass. The natural dye was synthesized from marine microalgae to get the chlorophyll. The others raw materials such as methanol, acetone, zinc acetate dehydrate,zinc nitrate and hexamethylenetetramine were purchased from Sigma Aldrich.

B. Sample Preparation

1) 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. Ultrasonic machine was used to clean the ITO coated glass. Firstly, ITO coated glass were immersed in the 20ml detergent solution for 10 minutes at 30 ℃. Secondly, the ITO coated glasses were put in distilled water for 5 minutes at the same temperature. This step was repeated three times in order to clean the detergent solution on the ITO glass. Then, the

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step was continued with acetone for 5 minutes at 30 ℃. Lastly, the ITO coated glasses were immersed with distilled water to remove stained of acetone for 5 minutes at 30 ℃ and left to dry completely at room temperature.

2) Fabrication of hybrid solar cell

The samples were coated by spin coating techniqueto ensure the thin film was applied uniformly on the ITO coated glass. The fabrication of hybrid solar cell is shown in Fig. 1.

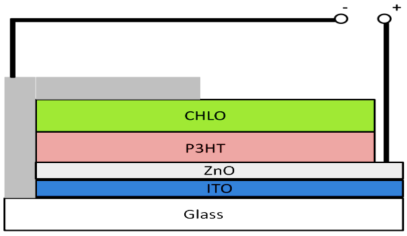

Fig. 1. The diagram of hybrid solar cell.

C. Characterization and Measurements

1) Electrical conductivity

Electrical conductivity is the capacity of any object or substance to conduct an electric current. When an electrical pottential difference is placed across a conductor its movable charges flow, giving rise to an electric current. The conductivity can be measured as follow [12]:

$$R_S = 4.532\frac{V}{I} \tag{1}$$

where,

R_S= sheet resistance (resistivity),

4.532 = correction factor,

V = voltage measured and

I = the current applied from the test unit.

Thus, electrical conductivity can be determined by;

$$\sigma = 1/R_S \tag{2}$$

where,

σ = electrical conductivity and

R_S = the sheet resistivity.

2) Efficiency of hybrid solar cell

The efficiency of hybrid solar cell can be calculated as follow,

$$\eta = \frac{P_{out}}{P_{in}} \times 100\% \tag{3}$$

$$P_{in}\text{=Intensity} \times \text{Effective Surface Area} \tag{4}$$

$$P_{out} = I_{max} \times V_{max} \tag{5}$$

where, $\eta$is the efficiency, I is current and V is voltage.

3) Hall effect measurement(HEM)

In HEM, the samples should have well-defined geometries and good ohmic contacts in order to obtain the accurate results. The samples must have vdP geometry. The ITO substrates were placed on the sample holder as shown in Fig. 2. The sample on the holder system is then connected to contacts 1, 2, 3 and 4, using the silver paint on four edges.

The connection is then tested using a multimeter to measure the resistance for each contact to ensure proper contact.

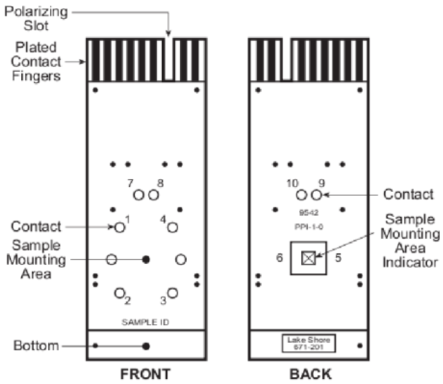

Fig. 2. The geometry of sample holder.

The measurements were performed using the Leois-JSF software which developed and tested through the corporation of Physical Sciences Department, Universiti Malaysia Terengganu, lead by Dr Salleh Harun and Nanorian Technology [13]. The Hardware system called Hall Effect Measurement (HEM) system model 7600 is supplied by Lakeshore Ltd. The important part of this HEM system is ensuring that the room temperature and set temperature was equivalent (20 ℃) in order to prevent the power supply from breakdown. The measurement consists of two parts. The first parts are called the IV curve traces measurement and the second part is variable magnetic field measurement. The purpose of IV curve traces measurement is to make sure that all the contacts are in good connections. In this work, the magnetic field fixed was 10 kG (1 Tesla) and the current was 0.1 A.

In addition, Fig. 3 shows the numbering of sample for Hall calculations which used in this work.

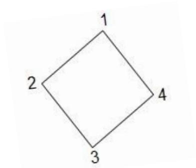

Fig. 3. The numbering of sample for Hall calculations

The explanations below are according to Fig. 3.

1) $V_{+31,42\,(+B)}$ = The current is passed from point 3 to 1, and the Hall voltage measured between 4 and 2.
2) $V_{-31,42\,(+B)}$ = The current is passed from point 1 to 3, and the Hall voltage measured between 4 and 2.
3) $V_{+42,13\,(+B)}$ = The current is passed from point 4 to 2, and the Hall voltage measured between 1 and 3.
4) $V_{-42,13\,(+B)}$ = The current is passed from point 2 to 4, and the Hall voltage measured between 1 and 3.
5) $V_{+31,42\,(-B)}$ = The current is passed from point 3 to 1, and the Hall voltage measured between 4 and 2 in negative field.
6) $V_{-31,42\,(-B)}$ = The current is passed from point 1 to 3, and the Hall voltage measured between 4 and 2 in negative field.
7) $V_{+42,13\,(-B)}$ = The current is passed from point 4 to 2, and the Hall voltage measured between 1 and 3 in negative field.
8) $V_{-42,13\,(-B)}$ = The current is passed from point 4 to 2, and the Hall voltage measured between 1 and 3 in negative field. According to [13], HEM can be callculted as follow,

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

$$= [V_{+31,42(+B)} - V_{+31,42(-B)} + V_{-31,42)-B)} - V_{-31,42(+B)} - V_{+42,13(-B)} + V_{-42,13(-B)} - V_{-42,13(+B)}]/8 \qquad (6)$$

For Hall coefficient (R_H) in unit cm^3.C^{-1}, two values of R_H are calculated using following equations;

$$R_{HC} = 10^8 \frac{t[cm]}{B[G]} \frac{+V_{-31,42(-B)} - V_{+31,42(-B)}}{+I_{-31(-B)} - I_{+31(-B)}} \qquad (7)$$

and

$$R_{HD} = 10^8 \frac{t[cm]}{B[G]} . \frac{V_{+42,13(+B)} - V_{-42,13(+B)}}{I_{+42(+B)} - I_{-42(+B)}} \frac{+V_{-42,13(-B)} - V_{+42,13(-B)}}{+I_{-4(-B)} - I_{+42(-B)}} \qquad (8)$$

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

$$R_{H\ avg} = \frac{R_{HC} + R_{HD}}{2} \qquad (9)$$

If the thickness is unknown, the layer or sheet carrier concentration, $n_s = n$, is used instead of the bulk density,

$$n_s = \frac{8\times10^{-8}\times IB}{q v_{H\ (total)}} cm^{-2} \qquad (10)$$

where, B in Gauss unit, I in ampere, and V_H in volt. Then the Hall mobility (μ_H) is given by

$$\mu_H = \frac{|V_{H\ avg}|}{\rho\ avg} [cm^2.V^{-1}.s^{-1}] \qquad (11)$$

Lastly, types of charge carrier. It is determined by the polarity sign of $V_{H\ avg}$ from (6) and polarity sign of $R_{H\ avg}$ in (9). 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.

III. Result and Discussion

A. Conductivity Study

The conductivity at different intensity of light is shown in the Fig. 4. The conductivity was proportional with the intensity of light for sample 5-CHLO and 10-CHLO with the regression value 0.99 and 0.98 respectively. The conductivity of the sample with and without CHLO shows the different because of CHLO are involved in photosystem assembly and contribute to light harvesting by absorbing light energy in a region of the visible spectrum. It also provides protection from excess light via energy dissipation and free radical detoxification. Thus, the conductivity of the sample with CHLO is more stable.

The temperature-dependent conductivity measurements are carried out to analyze the mechanism of ionic conduction in hybrid solar cell. Fig. 5 shows the variation ionic conductivity with the reciprocal temperature for hybrid solar cell. The linear variation of logs versus 1000/T plots for sample 5-CHLO and 10-CHLO suggests an Arrhenius type thermally activated process. This suggested that there is no phase transition of hybrid materials in the temperature range studied.

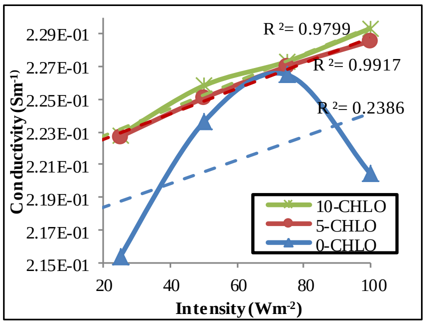

Fig. 4. The conductivity at different intensity of light.

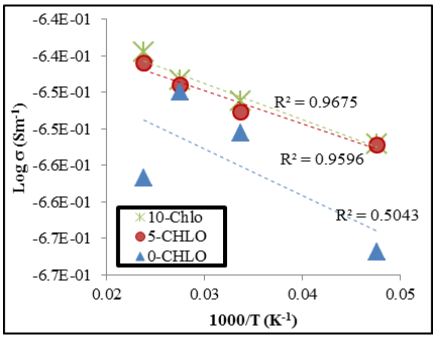

Fig. 5. Temperature dependent for the samples.

The conductivity can be expressed

$$\sigma = \sigma_o \exp\left(-\frac{E_a}{kT}\right) \qquad (12)$$

$$Intensity\ of\ light = kT^4 \qquad (13)$$

where the σ_o is the pre-exponential factor, E_a is activation energy, k is Boltzmann constant (5.678E-8 Wm^{-2}-K^4) and T is temperature.

Due to the black body radiation, the black body at a specific temperature is determines by the intensity of light at each frequency as shown in equation (13). Table I shows the activation energy of blended polymer films with different composition. E_a can be obtained from the slope and the pre-exponential factor can be obtained from the intercept at the vertical axis from the Fig. 5 [14]. The results reveal that E_a decreases effectively with the increasing of conductivity. From these results, interaction of polar molecules of the hybrid materials may help to dissociate the H^+ ions in the CHLO. As temperature increases, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion. This, in turn, favors hopping inter-chain and intra-chain ion movements and, accordingly, the conductivity of the polymer electrolyte becomes high [15].

TABLE I: Conductivity and Activation Energy of the Samples at 100Wm-2

Samples	Conductivity x 10^{-1} (Sm^{-1})	Activation Energy (eV)
0-CHLO	2.204	3.270
5-CHLO	2.286	4.216
10-CHLO	2.294	4.547

B. Efficiency of Hybrid Solar Cell

Fig. 6 shows the efficiency of the samples at different intensity of light. Again, the sample with CHLO shows the highest efficiency with 0.1% to 0.4 %. These results were significant as the results in the Fig. 4 and Fig. 5 respectively. The interaction between ZnO and the CHLO plays an important role towards the efficiency of HSC. According to [16], this might be due to possible inefficient electron/dye cation recombination pathways.

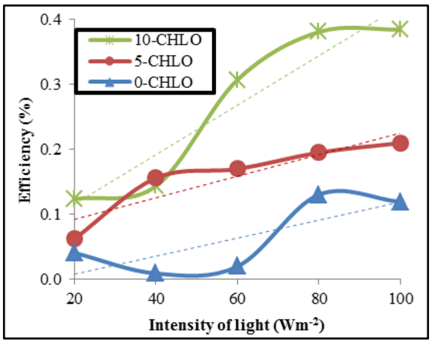

Fig. 6. Efficiency of hybrid solar cell.

In fact H^+ are the potential determining ions for ZnO and that proton adsorption causes a positive shift of the Fermi level of the ZnO, thus limiting the maximum photovoltage that could be delivered by the cells.

Thus, introducing a functional group, such as carboxyl group and optimizing the structure of CHLO are necessary to improve the efficiency HSC. Some complication such as dye aggregation on nanocrystalline film produces absorptivity that results in no electron injection. According [17], dye aggregation is a serious issue that occurs when compounds fill the free space between the dye molecules, partially blocking the physical contact between the P3HT and ZnO semiconductor film surface, reducing reaction and inhibiting dye aggregation.

C. Hall Effect Study

The mobile charges in conventional conducting materials are negatively charged (they are, in fact, electrons). Hall Effect can be used to determine whether the mobile charges in materials are positively or negatively charged.

1) Hall voltage and hall coefficient

Clearly, it is possible to determine the sign of the mobile charges in a current carrying conductor by measuring the Hall voltage.

TABLE II: HALL VOLTAGE OF MATERIALS IN HYBRID SOLAR CELL

Materials	Hall Voltage, $V_{Hall} \times 10^{-3}$ (mV)	Hall Coefficient, $R_H \times 10^{-3}$ ($cm^{-2}V^{-1}S^{-1}$)
ZnO	-2.132	-2.193
P3HT	-3.923	-1.690
CHLO	-1.552	-1.628
Hybrid	-2.120	-2.211

The results in the Table II show the value of hall voltage and hall coefficient for materials in the hybrid solar cell. The value is negative for all materials and it is show that the mobile charges are negative. This charge is the same with the metals (because they are electrons). However, in some types of semiconductor the mobile charges turn out to be positive. These positive charge carriers are called holes. Holes are actually missing electrons in the atomic lattice of the semiconductor, but they act essentially like positive charges.

2) Carrier concentration and hall mobility

The excitation of a carrier from the valence band to the conduction band creates free carriers in both bands. The concentration of these carriers is called the intrinsic carrier concentration, denoted by n_s. Semiconductor material which has not had impurities added to it in order to change the carrier concentrations is called intrinsic material. The intrinsic carrier concentration is the number of electrons in the conduction band or the number of holes in the valence band in intrinsic material. This number of carriers depends on the band gap and on the situation of the material such as temperature.

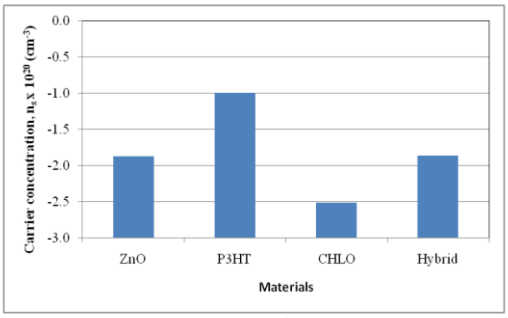

Fig. 7. Charge carrier concentration of materials in hybrid solar cell.

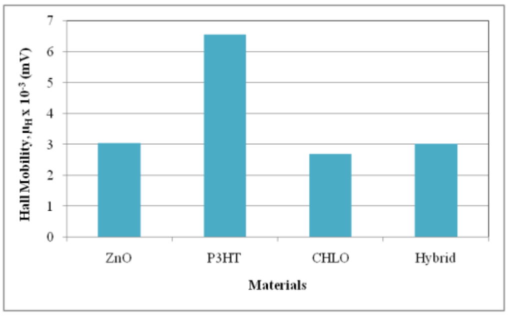

Fig. 8. Hall mobility of materials in hybrid solar cell.

Fig. 7 and Fig. 8 show the charge carrier concentration and hall mobility of materials in the hybrid solar cell. From both of Figure, P3HT show the highest value of charge carrier concentration and hall mobility followed by hybrid solar cell, ZnO and CHLO. The energy band gap for P3HT is 1.9eV, ZnO is 3.37 eV and for CHLO is 5.15eV. A large band gap is more difficult for a carrier to be excited across the band gap, and therefore the charge carrier concentration is lower in higher band gap materials. Alternatively, increasing the temperature makes it more likely that an electron was excited into the conduction band, which increased the charge carrier concentration. The larger free carrier density is due to the low resistivity [18], [19] and high conductivity of film [20].

IV. CONCLUSION

The organic/inorganic HSCs with the architecture combining conjugated p-type polymer, poly (3-hexylthiophene) (P3HT), and inorganic ZnO heterojunctions with chlorophyll (CHLO) from marine microalgae as a dye were successfully prepared by spin coating technique. The highest conductivity at 100 Wm^{-2} was 2.294 x 10^{-1} Sm^{-1} for sample 10-CHLO. The sample

10-CHLO also shows the highest efficiency with 0.1% to 0.4%. From the Hall Effect measurement it was found that, polarity sign of $V_{H\,avg}$ and polarity sign of $R_{H\,avg}$ obtained were negative for all samples. This finding indicates that the majority carriers are electron.

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