PHOTOCONDUCTIVITY OF HETEROJUNCTION MEH-PPV / TiO_2 NANOCOMPOSITE THIN FILMS

Fazlinashatul Suhaidah bte Zahid
Faculty of Electrical Engineering
Universiti Teknologi MARA
40450 Shah Alam
MALAYSIA
fazlinazahid@gmail.com

***Abstract*- This paper investigates the photoconductivity of the heterojunction of MEH-PPV/TiO_2 nanocomposite thin films by varying the weight ratio of TiO_2 and was deposited on the glass substrates by using spin coating technique. The influence of the amount of TiO_2 in the nanocomposite heterojunctions and photoconductivity as prepared blends compared to the single component of MEH-PPV was characterized by Voltage/Current (I-V) characterization in dark and under illumination, UV-VIS spectrophotometer and Field Emission Scanning Electron Microscopy (FESEM). The I-V measurements in dark and under illumination shows that the resistivity decreases and conductivity increases when the amount of TiO_2 increases. While UV-VIS spectrophotometer measurements show the optical band gap increases when the amount of TiO_2 increases. The FESEM images also show that the MEH-PPV/TiO_2 particles uniformly shaped but there are some large clusters were observed between the surface nanostructures.**

***Keywords* - MEH-PPV/TiO_2 nanocomposite, Current-Voltage measurement, Optical band gap.**

I. SCOPE OF WORK

The scopes of work in this research are:

i. The deposition of MEH-PPV/TiO_2 nanocomposite thin films using spin-coating technique.
ii. This study also investigated the effect of amount of TiO_2 on photoconductivity MEH-PPV/TiO_2 nanocomposite thin films.
iii. This study focused on the electrical properties of MEH-PPV/TiO_2 nanocomposite thin films for dye-sensitized solar cells applications and supported by optical properties and surface morphology.

II. OBJECTIVE

The objectives of this research are:

i. To deposite nanocomposite MEH-PPV/TiO_2 thin films.
ii. To study the electrical properties of MEH-PPV/TiO_2 nanocomposite thin films using I-V measurement when varying the weight ratio of TiO_2.
iii. To investigates optical properties of MEH-PPV/TiO_2 thin films using UV-VIS spechtrophotometer to determine the optical band gap.

III. INTRODUCTION

In recent years, an increasing interest has been devoted of the study of hybrid organic/inorganic nanocomposite due to the possibility of combining the electrical properties of semiconductor organic polymers with the optical peculiarities of inorganic nanoparticles like rods, particles and thin films. Soft solar cells based on such composite thin films are attractive for their technological potential to fabricate low cost photovoltaic devices [1].

In organic-inorganic hybrid solar cells with planar junctions, the power conversion efficiency is limited because the exciton diffusion length of the donor material is typically significantly shorter than its absorption length, resulting in recombing easily. In order to overcome this problem, a bulk heterojunction structure has been developed for organic-inorganic hybrid solar cells, in which inorganic nanocrystalline materials were usually used as alternative electron acceptors such as TiO_2 and ZnO [2, 3].

The organic composite that usually been used is conjugated polymers which are poly (*p*-phenylene vinylene) (PPV) and its derivatives have attracted a great deal of attention because of their particular structure and their highly interesting electroluminescent properties. However, this polymer is insoluble, intractable, and infusible and thus cannot be easily processed by conventional spin coating. One of the most recent study PPV derivatives is poly [2-methoxy, 5-(2'-ethyl-hexyloxy)-phenylenevinylene] (MEH-PPV) [4]. To enhance the performance of PPV-based devices several studies have been carried out on composites made with polymers and nano-oxide particles such as Titanium Dioxide (TiO_2) [5].

From the previous study it is found to have a good effect on the conductivity of the polymer host and it can influence its photovoltaic properties. The use of composites is believed to increase the electrical conduction [5] of the polymer and in addition to improve its stability [6]. In this study, TiO_2 nanopowder are blend into poly (2-methoxy, 5-(2'-ethyl-hexyloxy)-p-phenylenevinylene) (MEH-PPV) polymer in order to form a percolation geometry. In such blends, organic polymer acts as electron donor and the inorganic nanoparticles as electron acceptor [1].

Although MEH-PPV is not the most sufficient photovoltaic material, it has been chosen for this study because it well characterized and highly reproducible with low intrinsic traps density [7]. It is well-known that the MEH-PPV is a good exciton generator but the exciton diffusion length is very short at around 20 nm in the polymer film [8].The addition of TiO_2 nanopowder helps improving the device efficiency due to its n-type semiconducting nature and high surface areas. Inserting the TiO_2 helps charge separation and electron transport in devices. When the charges are separated at the MEH-PPV/TiO_2 interface, holes and electrons are transferred in MEH-PPV and TiO_2 films respectively because electron affinity of TiO_2 is higher than that of the MEH-PPV [9]. It is found that MEH-PPV blended with TiO_2 was found to have an improved conductivity as compared to polymer alone.

The results of this study are based on the electrical characteristics for MEH-PPV/TiO2 thin films with Au contacts and the morphology of the MEH-PPV/TiO_2. The results on non-blended MEH-PPV are comparable to results for electron-transporting polymers and nanopowder blended into MEH-PPV. It investigates the effect of the addition of this TiO2 nanopowder on the electrical and optical properties by I-V and UV-VIS spechtrophotometer measurement.

IV. EXPERIMENTAL

The experiment was done following the flow chart in Fig.1. A glass substrate was cut into square of 2cm by 2cm is used. Standard cleaning techniques is used for cleaning the glasses. The glasses substrates have been washed by acetone, methanol and de-ionized (DI) water by 15 minutes respectively and then dried by blow it with Nitrogen gas.

The MEH-PPV powder was dissolved in tetrahydrofuran (THF) solvent at concentration of 1g/1ml and was stirred for 48 hours. Four solutions of MEH-PPV were mixed with TiO_2 nanopowder that has been annealed at temperature of 450^{o}C in different weight ratios (5wt%, 10wt%, 15wt% and 20wt %). The mixtures were prepared by stirring for 1 hour and under ultarsonication for 1 hour. Spin coating method that setting at 3000rpm for 1 minute per layer was used to prepare MEH-PPV/ TiO_2 thin films.

After deposited by spin coating, the thin films were dried in oven at temperature of 60^{o}C for 10 minutes to evaporate the residual material. This spin coated process was continuous for 5 times to get the 5 layers of thin films. For current-voltage (I-V) measurement, an Au (gold) contact that acts as ohmic contact was sputtered on the hybrid film to complete the thin films.

The electrical properties were measured by using current-voltage (I-V) measurement in dark and under illumination while the optical properties were measured by UV-VIS spectrophotometer and the surface morphologies were characterized using the Field Emission Scanning Electron Microscopy (FESEM) equipment.

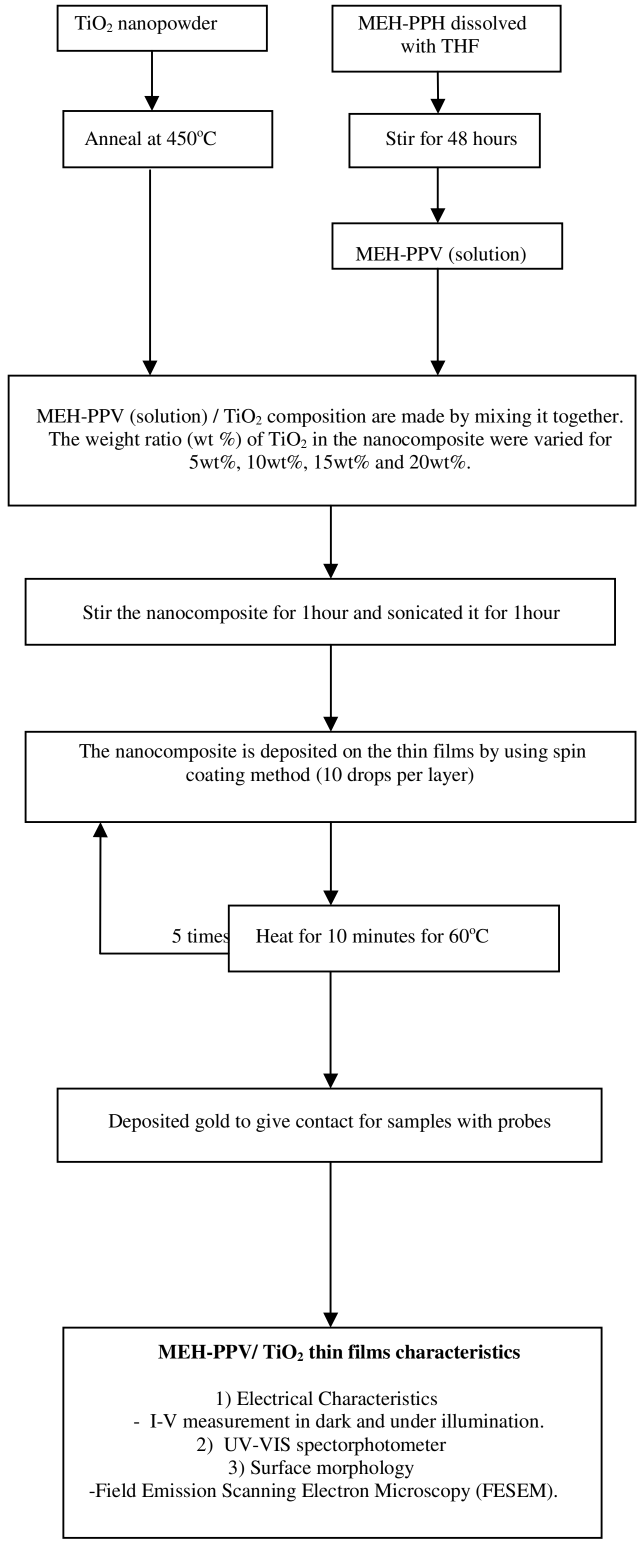

Fig. 1. Flow chart of the experimental procedure for the project.

V. RESULTS AND DISCUSSIONS

A. *I-V Measurement*

Current-Voltage was performed to the MEH-PPV/TiO_2 thin films structure in order to analyze the electrical properties. This information is most readily displayed in an I-V curve which is a graph of the resulting current flow versus applied potential difference.

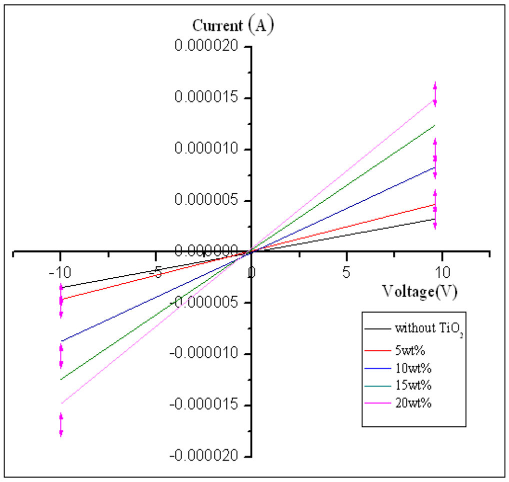

Fig. 2. The current-voltage (I-V) measurement of MEH-PPV/TiO_2 nanocomposite under illumination.

The slopes of the I-V curves increase significantly and turn-on voltage nanocomposite device decrease as the concentration of TiO_2 increases [8]. Fig. 2 shows current-voltage (I-V) graph of MEH-PPV/TiO_2 nanocomposite thin films by varying the weight ratio of TiO_2 under illumination. The graph inidicates that the slopes of I-V curves increases significantly as the weight ratio (wt %) of TiO_2 presence in the MEH-PPV/TiO_2 nanocomposite increases (5, 10, 15 and 20 wt% respectively). It also indicates that the current value at fixed voltage increase with weight ratio (wt %) of TiO_2 to indicate the enhancement of electron conductivity with weight ratio (wt %) of TiO_2 increase [9].

From the I-V curves, the resistivity,ρ and conductivity of MEH-PPV / TiO_2 nanocomposite thin films were calculated using following equation (1) and (2) :

$$\rho = \left(\frac{V}{I}\right)\frac{wt}{l} \qquad (1)$$

$$\sigma = \left(\frac{1}{\rho}\right) \qquad (2)$$

where V *i*s supplied voltage, I is measured current, t is the film thickness, w is the electrode width and l is the length between electrodes [10].

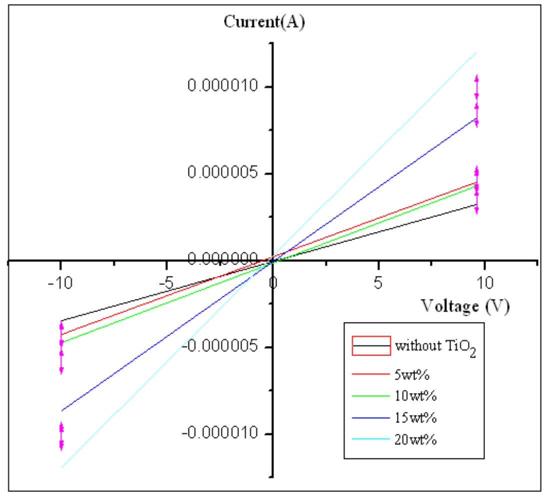

Fig. 3. The current-voltage (I-V) measurement of MEH-PPV/TiO_2 nanocomposite in dark.

Fig. 3 shows current-voltage (I-V) graph of MEH-PPV/TiO_2 nanocomposite thin films by varying the weight ratio of TiO_2 in dark. It can be observed from the graph that the slopes of I-V curves increases significantly as the weight ratio (wt %) of TiO_2 presence in the MEH-PPV/TiO_2 nanocomposite increases same as the I-V measurement of the thin films under illumination. The main reason is that the presence of semiconducting oxide particles covered with conducting polymer in the device produces more highly interpenetrated networks of TiO_2 at higher concentration. Thus, an enhanced charge transport route is desirable to achieve efficient electron conduction [9].

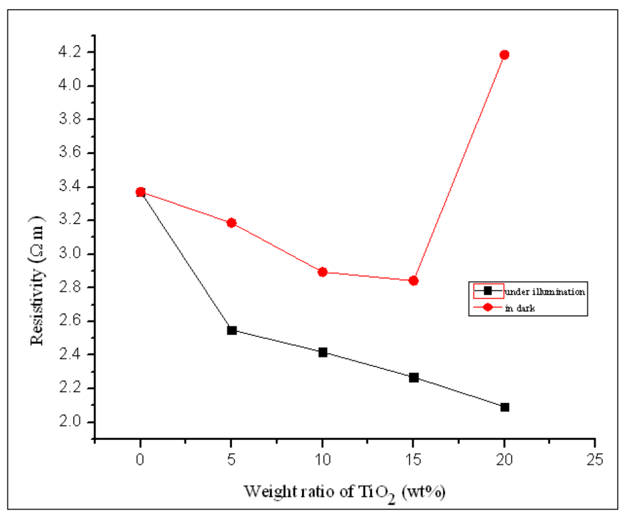

Fig. 4. Resistivity of MEH-PPV/ TiO2 nanocomposite thin films at various weight ratios (wt %) of TiO_2 under illumination and in dark.

From Fig. 4 above, it is shows that the resistivity of the MEH-PPV/TiO_2 nanocomposite is decreases as the weight ratio (wt %) of TiO_2 increases. This graph also indicates that the resistivity of thin films in dark is higher than under illumination. These results will be discussed further at the conductivity figure at Fig.5 since the resisitivity is reciprocal with the conductivity based on the equation (2). However, from these results, it also can be seen that resistivity at 20wt% of TiO_2 in the MEH-PPV/TiO_2 nanocomposite thin films in dark is increase. This occurs due to not-well dispersed of solutions that can be seen from FESEM.

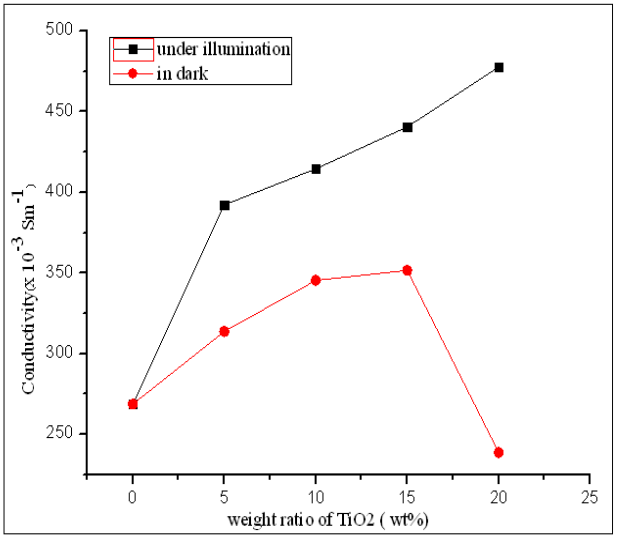

Fig. 5. Conductivity of MEH-PPV/ TiO2 nanocomposite thin films at various weight ratios (wt %) of TiO_2 under illumination and in dark.

From the Fig. 5 above, the results shows the improvement of conductivity properties as the weight ratio (wt %) of TiO_2 increases. Based on these results we take an explanation for the improved performance which supports the report by Le Ha Chi *et.al* [9]. The report states that I-V characteristics of the nanocomposite materials were significantly enhanced in comparison with the standard polymers [9]. The addition of the continuous TiO_2 thin films allows for the current to be conducted effectively and also prevents electrons from recombination back with holes in the MEH-PPV [11].

It is also found that typical photoconductivity behavior between in dark and under illumination has shown that the photocurrent generated under illumination is much higher. During illumination, the conductivity of MEH-PPV/TiO_2 nanocomposite thin films were increase higher than the thin films in dark showing that highest sensistivity over 10 V as shown in Fig. 2. The increment of the photocurrent under the influence of light intensity which is under illumination is due to the fact that increasing the light intensity leads, in turn, to an increase of the number of the excited carriers. Also it is evident Fig. 3 that at a certain value of light intensity, as the bias voltage increases the photocurrent increases too. This is regarded as a result of the increment of the carrier velocities [12].

B. UV-VIS Measurement

Fig. 6 shows the UV-VIS absorption spectra of MEH-PPV and its nanocomposite thin films in the wavelength range between 300 to 700 nm. For MEH-PPV thin films, the absorption band maximum was located around 480nm. For MEH-PPV/TiO_2 nanocomposite thin filmss it is found that the absorption band maximum was located around 500nm showing a slight shift as compared to sample without TiO_2 thin films.

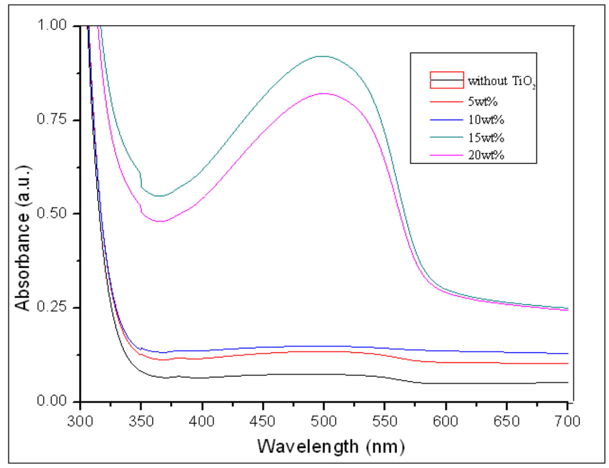

Fig. 6. UV-VIS absorption spectra of MEH-PPV/TiO_2 nanocomposite thin films at various weight ratios (wt %) of TiO_2.

This shift in absorption was found for all MEH-PPV/TiO_2 nanocomposites especially at 15wt% and 20wt% thin films and can be explained by the temperature effect induced by the use of ultrasonic bath for preparing the nanocomposite solutions. Indeed, in order to disperse the TiO_2 nanopowder homogeneously inside the polymer layer, an ultrasonic bath was applied to the polymer/nanopowder solutions for 1 hour before depositing thin films [14].

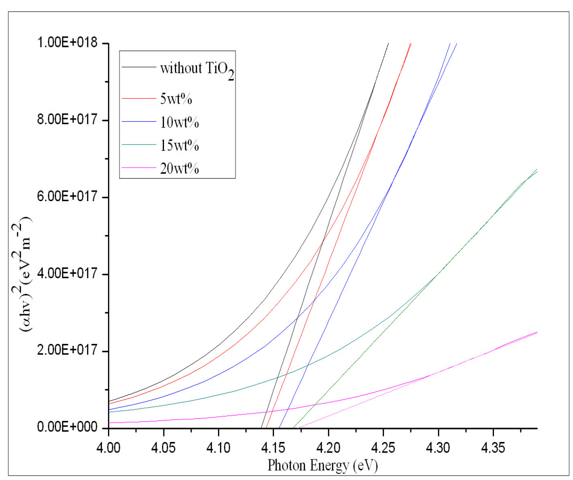

Fig. 7. Optical band gap estimation of MEH-PPV/TiO_2 nanocomposite by varying the weight ratio of TiO_2 using Tauc's plot.

The differences in absorption wavelength among the nanohybrids indicates the difference in band gap as affected by the varying the amount of the TiO_2 nanopowder in the nanocomposite. It is known that the relationship between the absorption coefficient α, and the optical band gap, Eg for fine particles obeys the following classical Tauc expression:

$$\alpha h\nu = A\,(h\nu - E_g)^{1/2} \qquad (3)$$

where A, α and hv are the edge-width parameter, linear absorption coefficient and incident photon energy, respectively. The band gap energy, Eg, thus can be determined from a Tauc plot of $(\alpha h\nu)^2$ versus hv [15]. Fig. 7 shows the extrapolation of the linear parts of the curves to the energy axis, estimating band gap energy of 4.13, 4.14, 4.16, 4.17 and 4.175 eV for sample of without TiO_2, 5wt%, 10wt%, 15wt% and 20wt% respectively.

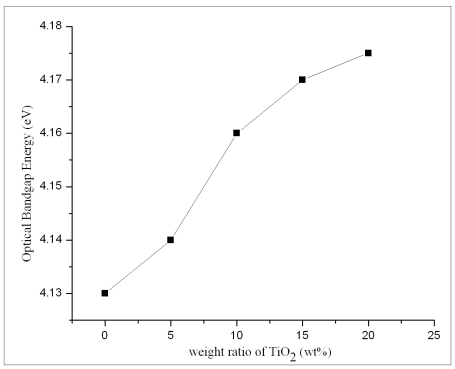

Fig. 8. Optical band gap energy of MEH-PPV/TiO_2 nanocomposite thin films by varying the weight ratio of TiO_2.

From the Fig. 8, the minimum photon energy that is needed to excite an electron into the conduction band is associated with the bandgap of a material. Optical band gap values are found to increases as the weight ratio of TiO_2 increases for direct transitions. From this result, it should be noted that the band gap value can be easily tuned by simply varying the concentrations of TiO_2 in the MEH-PPV/TiO_2 nanocomposite.

C. *Surface Morphology*

Field Emission Scanning Electron Microscopy (FESEM) has been used to investigate the structures and film surface morphology of these thin films. Fig. 9 shows that the surface morphology of the MEH-PPV/TiO_2 nanocomposite thin films at different weight ratio of TiO_2 (without TiO_2, 5wt%, 10wt%, 15wt% and 20wt% respectively). The resulted FESEM images showed the presence of TiO_2 nanopowder has been combined together with MEH-PPV and formed thin films.

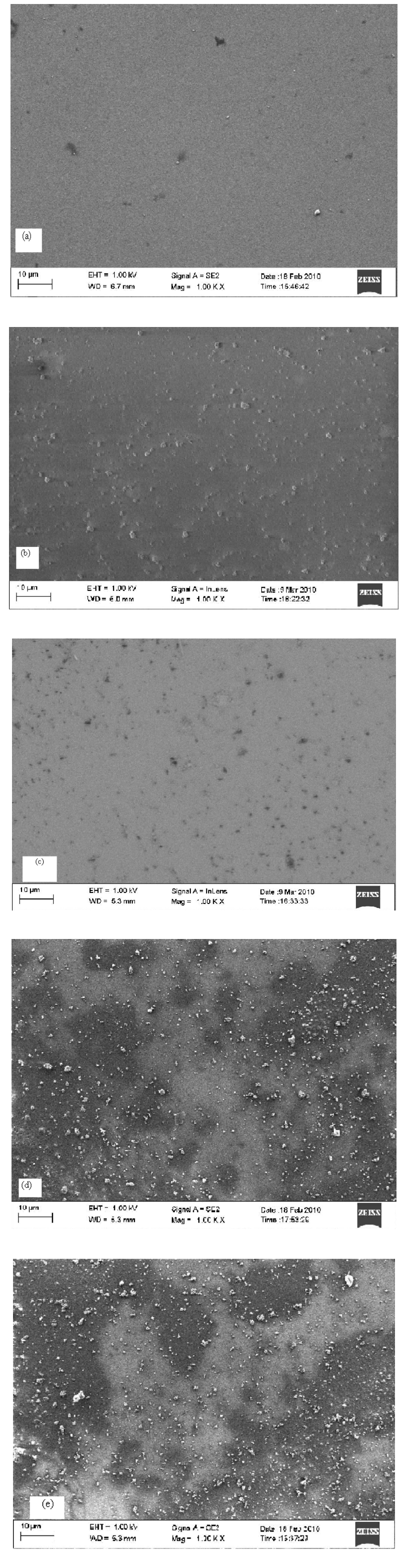

Fig. 9. FESEM image of MEH-PPV/ TiO_2 nanocomposite at 1K magnification: (a) without TiO_2, (b) 5wt% (c) 10wt%, (d) 15wt% and (e) 20wt%.

Fig. 9 (a), (b) and (c) shows the smooth morphology and better dispersion of MEH-PPV/TiO2 nanocomposite hybrid. The TiO_2 nanopowder was randomly distributed in the polymer matrix for the interconnecting work formation [11]. A homogenous distribution of TiO_2 nanopowder in polymer is also can be observed from these figures.

The MEH-PPV/TiO_2 nanocomposite particles uniformly shaped but there are some larger clusters were observed in the nanostructures as shown in Fig. 9 (d) and (e). In the observed samples, the distribution of TiO_2 nanoparticles is not uniform, there are big bright points indicating clusters of the TiO_2 nanoparticles. This proved that by using the ultrasonic stir the nanoparticles were not completely dispersed. This instability shape and morphology appeared maybe because there are few unrelated steps in the preparation of solutions or deposition steps that were not accurate has been taken along the process. It is worth mentioning that these MEH-PPV/TiO_2 thin films are deposited in air, which may cause the degrading of thin films performance dramatically since polymer is highly sensitive to Oxygen (O_2) and moisture [5].This thing must give an attention because it is very important as it will give an effect to the resisitivity and conductivity of thin films as shown in the Fig. 4 and 5.

The FESEM figures also indicated that the nanocomposite thin films prepared by spin-coating method are well distributed which is very important to develop continous transport pathway to enhance electron mobility.

VI. CONCLUSIONS

In this work, the electrical and optical properties of MEH-PPV/TiO_2 nanocomposite thin films have been investigated. It is shown that the conductivity increases from $270X10^{-3}$ to $475x10^{-3}$ Sm^{-1} as the weight ratio of TiO_2 presence in MEH-PPV/TiO_2 nanocomposite increases. The deposited nanocomposite film also showed a higher photoconductivity when compared to the single components of MEH-PPV due to the availability of numerous interfaces for enhanced charge transfer at the heterojunction. It is found that efficient conductivity properties have been found in MEH-PPV/TiO_2 nanocomposite due to the formation of large interconnecting network between TiO_2 nanopowder and MEH-PPV polymer matrix, which significantly improves electrical transport and enhance the performance of thin films in the optical properties as well.

The results suggest that by increasing the weight ratio of TiO_2 in the MEH-PPV/TiO_2 nanocomposite give a promising in enhance the performance of hybrid MEH-PPV/TiO_2 bulk heterojunction solar cells. The band gap of the MEH-PPV/TiO_2 nanocomposite is increase from 4.13 to 4.175 eV as the amount of TiO_2 increases. To clarify whether this change in the band gap is related to the energy shift of the conduction band minimum (Ec) or valence band maximum (Eb), further studies are needed.

VII. FUTURE DEVELOPMENTS

For future development of the MEH-PPV/TiO_2 nanocomposite thin films, the conductivity of this films need to be improved as its increase the conductivity and higher energy band gap. It also known that the ability of electrical transportation in films depends greatly on its thickness and the electrical conductivity would increase when the thickness of MEH-PPV/TiO_2 thin films increase as reported by *Erol Sancakter et.al* [16]. So the cycles of the deposition layers need to be repeats to get desired thickness. For recommendation another weight ratio of TiO_2 need to be done to know the further results and to know the properties of the MEH-PPV/TiO_2 nanocomposite thin films in the fabrication industry.

ACKNOWLEDGEMENT

The author wish to express heartily gratitude to Assoc.Prof.Dr.Mohamad Rusop and Puan Puteri Sarah for the advices, encouragement and guidance throughout the progress of this project. The author also would like to gratefully acknowledge NANO-Sci Tech Centre and Solar Cell Laboratory technicians, Mr.Azlan and Mr.Suhaimi for their assistance in the lab.

REFERENCES

[1] A.Petrella, M.Tamborra, P.D.Cozzoli, M.L.Curri, M.Striccoli, P.Cosma, G.M. Farinola, F.Babudri, F.Naso, A.Agostiano, "TiO_2 nanocrystals-MEH-PPV composite thin filmss as photoactive material", Science Direct, (2003).

[2] Kwong C.Y, Chong W.C.H, Djurisic A.B, Chui P.C, Cheng K.W, Chan W.K, "Poly(3-hexylthiophene):TiO_2 nanocomposite for solar cells applications", Nanotechnology Vol 15, No.9, pp 1156-1161, (2004).

[3] Zeng T.W., Lin Y.Y., Lo H.H., Chen C.W.,Chen C.H, Liou S.C., Huang H.Y., Su W.F. "A large interconnecting within hybrid MEH PPV/TiO_2 nanorod photovoltaic devies." Nanotechnology, vol.17, No21, pp.5387-5392,(2006).

[4] A.Ltaief, J.Davenas, A.Bouazizi, R.Ben Chaabane, P.Alcouffe, H.Ben Quada, "Film morphology effects on the electrical and optical properties of bulk heterojunction organic solar cells based on MEH-PPV/C_{60} composite." Science Direct, (2004).

[5] G.Kicklbick. "Prog.Polym.Sci", pp 83, (2003).

[6] H.Neugebauer, C.Brabec, J.C.Hummenen, and N.S. Sariciftci, "Sol. Ener. Mater.Sol. Cells", pp 35, (2000).

[7] A.J.Breeze, Z.Schlesinger, and S.A.Carter, "Charge transport in TiO_2/MEH-PPV polymer photovolataics", Physical Review, Vol.64, (2000).

[8] C.Thanachayanont, K.Inpor, S.Reabanko, P.Boonchan, N.Mahingsupan V.Meeyoo, S.Sahasitiwat, C.Sae-Kung and P. Sichanugrist, "An effect of TiO_2 morphology on performance of ITO/TiO_2/MEH-PPV/Au solar cell". IEEE Journal.

[9] Le Ha Chi, Nguyen Nang Dinh, Pham Duy Long, Dang Tran Chien and Tran Thi Chung Thuy, "Study on Electrical and Optical Properties of the Hybrid Nanocrystalline TiO_2 and Conjugated Polymer Thin filmss", Nano-Net 2009, pp84,(2009).

[10] B.L. Anderson, R.L. Anderson, "Fundamentals of Semiconductor Devices", McGraw-Hill, pp 113-114, (2005).

[11] Nguyen Nang Dinh, Le Ha Chi1, Nguyen Thang Long, Tran Thi Chung Thuy, Tran Quang Trung and Hyung-Kook Kim,"Preparation and characterization of Nanostructured composite films for organic Light Emitting Diodes", Journal of Physics:Conference Series 187, (2009).

[12] Tsung-Wei Zeng, Yun-Yue Lin1, Hsi-Hsing Lo,Chun-Wei Chen, Cheng-Hsuan Chen2, Sz Chian Liou, Hong-Yun Huang2 andWei-Fang Su, "A large interconnecting network within hybrid MEH-PPV/TiO2 nanorod photovoltaic devices", Institute of Physics Publishing Nanotechnology 17, (2006).
[13] G.A. Gamal, A. T. Nagat, M. M. Nassary and M.A. Abou Alwafa, "Effect of Oblique Illumination on PhotoconductivityPhenomena", Egypt. J. Sol., Vol. (26), No. (1), (2003).
[14] S.H Yang, P.Le Rendu, T.P Nguyen and C.S.hsu, " Fabrication of MEH-PPV/SiO_2 and MEH-PPV/TiO_2 nanocomposite with enhanced luminescent stabilities", Science Direct, (2007).
[15] Akhmad Herman Yuwono, Binghai Liu,Junmin Xue, John Wang, Hendry Izaac Elim, Wei Ji, Ying Li and Timothy John White, "Controlling the crystallinity and nonlinear optical properties of transparent TiO2–PMMA nanohybrids", Journal of Materials Chemistry, (2004).
[16] Erol Sancaktar, "Thickness Dependent Conduction of Various Particles for Conductive Adhesive Applications", IEEE Journal,(1998).