

## Influence of Manganese doping on the Optical Absorbance of Solution-Processed Hybrid P3HT/TiO<sub>2</sub> Thin Film Solar cell

S. Malik<sup>1</sup>, Azyuni Aziz<sup>2</sup>, Fatin Hana Naning<sup>3</sup>

<sup>1</sup>(Assoc. Prof., Department of Physics, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjong Malim, Perak, Malaysia)

<sup>2</sup>(MSc Student, Department of Physics, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjong Malim, Perak, Malaysia)

<sup>3</sup>(PhD Student, Department of Physics, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjong Malim, Perak, Malaysia)

**Abstract:** Organic-inorganic hybrid nanocomposite thin film has drawn increasing attention in the development of photovoltaic (PV) cells due to their unique combined electrical and optical properties. A blend of organic and inorganic materials as the active layer in solar cell has been shown to hold significant potential in creating low cost and scalable power conversion. In this study, two types of inorganic materials, titanium dioxide (TiO<sub>2</sub>) and manganese (Mn) were blended with semiconducting polymer poly(3-hexylthiophene) (P3HT) solution and then spin coated on a quartz substrate. Field emission scanning electron microscope (FESEM) was employed to define the morphology of both samples. Energy-dispersive x-ray emission (EDX) spectroscopy has proven the existence of elements in the film. A new absorption peak at 608 nm was observed when Mn nanoparticles were doped inside the P3HT/TiO<sub>2</sub> thin films as shown by the ultraviolet-visible (UV-Vis) spectrophotometer. Substitution of Ti lattice sites with Mn atoms causes red-shift to the optical absorption spectra, allowing the doped photoactive layer to absorb longer wavelengths of the solar radiation. The transition metals such as Mn is expected to open a land of promising applications in the solution-processed hybrid organic-inorganic nanocomposite solar cell applications.

**Keywords:** Mn, P3HT, photoactive layer, solar cell, solution-processed thin film, TiO<sub>2</sub>

### I. INTRODUCTION

The ideal solar cell is achieved when the cell is simple to fabricate, low processing cost, consist of abundant materials, high power conversion efficiency, and long lifetime. Until now, most solar cells in the market are monopolized by silicon and semiconductor thin-film technologies. These manufacturing technologies produce solar cells with high power conversion efficiency (PCE), e.g. crystalline solar cells with its PCE in the range of 18 to 25% and thin film solar cell (based on amorphous silicon) has 20 % of PCE [1]. Although both technologies used abundant materials, have long lifetime cells and produce high PCE, the technology itself is complicated and expensive since it involves state-of-the-art equipments. Hence, researches are intensively carried out to find the alternative technology which is a simple fabrication process, e.g. solution-based, low cost and high PCE [2]. One of the promising novel technique is by utilizing organic and inorganic materials as a composite photoactive layer in solar cell devices.

Hybrid organic-inorganic nanocomposite materials have demonstrated as a potential candidate for future solar cells since its combine both their unique electrical and optical properties in the same device. This hybrid device shows advantages of tunability of photophysical properties of the inorganic nanoparticles while retaining the organic properties like solution processing, fabrication of devices on large and flexible substrates [3]. This type of solar cell takes advantages of optical properties optimization in inorganic and organic materials. Inorganic material such as perovskite offer high PCE [4] and carrier mobility. On the other hand, organic semiconducting polymer materials reduce manufacturing cost, since organic materials can be processed by a simple deposition method such as coating and printing technique at room temperature [5]. Hybrid organic-inorganic nanocomposite thin film solar cells can be easily fabricated by blending inorganic nanoparticles with organic materials which serves as photoactive layer of solar cells. The highest PCE for hybrid halide perovskites thin film solar cells as reported is ~20 % [4].

In this study, poly(3-hexylthiophene) (P3HT) was employed as organic material and titanium dioxide (TiO<sub>2</sub>) and manganese (Mn), which is a transition metal, as inorganic nanoparticles. Semiconducting polymer P3HT acts as an electron donor and poses a spectral range of photon absorption [6], has good light absorption and high charge carrier mobilities [7]. In contrast, TiO<sub>2</sub> which serves as electron acceptor is chosen because this inorganic nanocrystals is tunability and its absorption coefficients is high [1,8]. Mn nanoparticles were doped to

the P3HT/TiO<sub>2</sub> solution to investigate its effect on the optical absorbance spectra. Both samples, P3HT/TiO<sub>2</sub> and P3HT/TiO<sub>2</sub>/Mn were compared based on their surface morphology using field emission scanning electron microscopy (FESEM) with energy-dispersive x-ray emission (EDX) spectroscopy and optical properties using ultraviolet visible (UV-Vis) absorption spectrophotometer.

## II. METHODOLOGY

Substrates (quartz) were first, cleaned by immersing them in a piranha solution overnight, following by ultrasonication for three minutes, then scrubbed with detergent, rinse with deionized (DI) water and finally left to dry by the flow of nitrogen gas. The regio-regular P3HT in powder form was purchased from Sigma Aldrich and used as it is. The P3HT solution was prepared by dissolving the powder into its solvent, i.e. chloroform. Two types of solutions P3HT/TiO<sub>2</sub> and P3HT/TiO<sub>2</sub>/Mn with a concentration of 10 mg/ml were prepared. Deposition of photoactive layer was done by the spin coating technique. Figure 1 shows the structure of the film on a quartz substrate. Solutions were dropped on the quartz substrate and spun at a rotation speed of 3000 rpm. The complete spin coating procedures can be found elsewhere [9].

The photoactive layer was characterized by FESEM model SU 8020 UHRdel Hitachi with EDX to determine their surface morphology and to investigate the existence of TiO<sub>2</sub> and Mn elements in the photoactive layer. Optical characteristics were observed by ultraviolet-visible spectrophotometer model Jasco 570 UV-Vis-NIR to determine their absorption peaks.



Figure 1: Photoactive layer deposited on a quartz substrate

## III. RESULTS AND DISCUSSION

Optical and morphological characterizations were performed using UV-Vis absorption spectrophotometer and FESEM with EDX respectively. As can be seen from Fig. 2, UV-Vis absorption spectra show three different curves for pristine P3HT, P3HT/TiO<sub>2</sub> and P3HT/TiO<sub>2</sub>/Mn thin films. Thin film of P3HT exhibits strong absorption spectra at the visible wavelength range of 450nm to 650nm. The absorption peak was observed to shift to higher wavelength which is from 519nm (P3HT) to 551nm (P3HT/TiO<sub>2</sub>) and 560nm (P3HT/TiO<sub>2</sub>/Mn). The red-shift in the optical absorption peak suggest the lost of long-chain stacking of the polymer, hence causing conformation disorder when the nanoparticles were added into P3HT matrix [10]. When Mn is doped into the P3HT/TiO<sub>2</sub>, the shoulder curves of P3HT (602 nm) and P3HT/TiO<sub>2</sub> (605 nm) were disappeared. However, a new absorption peak at 608 nm was observed. This result revealed that Mn-doped TiO<sub>2</sub> in semiconducting polymer such as P3HT allows the photoactive thin film to absorb longer wavelengths of the solar radiation.

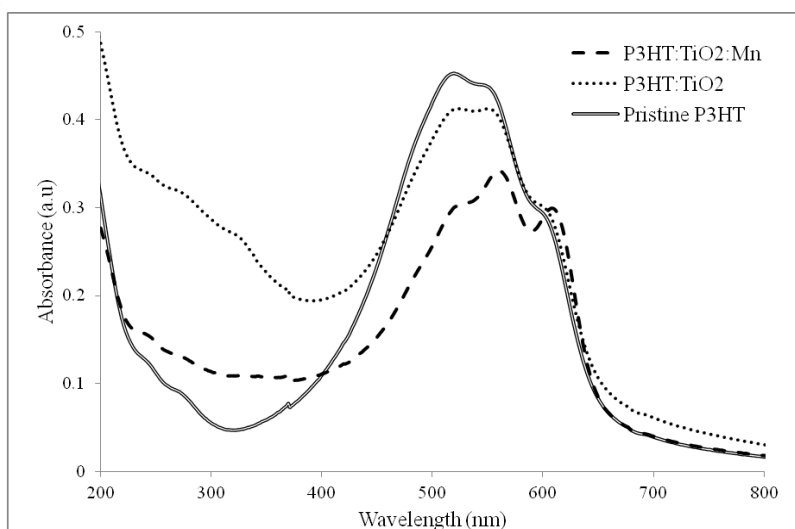


Figure 2: UV-Vis-NIR absorption spectra for pristine P3HT, P3HT/TiO<sub>2</sub> and P3HT/TiO<sub>2</sub>:Mn

Figure 3 shows morphology and element analysis for photoactive layer of (a) and (b) P3HT/TiO<sub>2</sub> and (c) and (d) P3HT/TiO<sub>2</sub>/Mn. As shown in Fig. 3(a) and (c), the shape of TiO<sub>2</sub> and Mn nanoparticles are almost spherical. The size of TiO<sub>2</sub> is in the range of 10 nm to 300 nm while size of Mn is smaller, 10 nm until 50 nm. As can be seen, before Mn nanoparticles were doped, TiO<sub>2</sub> nanoparticles are distributed uniformly. However, after doping (see fig. 3(c)), the distribution become non-uniform. This is because smaller sizes of Mn caused them to patched on the TiO<sub>2</sub> nanoparticles and filled the space between them. The EDX analysis (Fig. 3(b) and (d) ) shown Ti peaks at 0.45, 4.51 and 5.1 keV and Mn peaks at 0.60, 5.89 and 6.60 keV. Whilst, peak for carbon and oxygen is at 0.26 keV and 0.60 keV respectively.

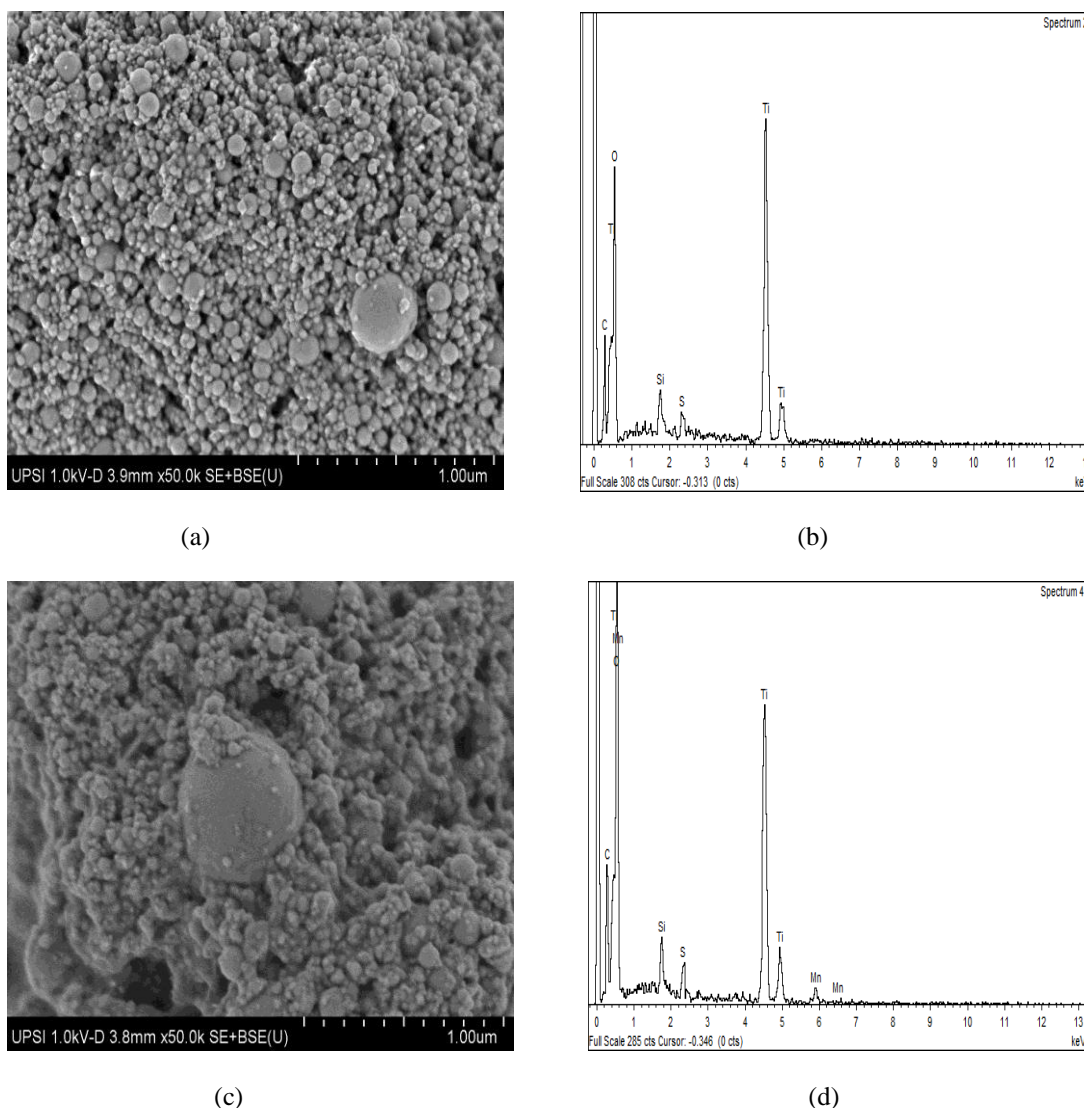


Figure 3: FESEM and EDX result for (a,b) P3HT/TiO<sub>2</sub> and (c,d) P3HT/TiO<sub>2</sub>/Mn

#### IV. CONCLUSION

Hybrid organic-inorganic solar cell was fabricated by spin coated a blended solution of semiconducting polymer (P3HT) with TiO<sub>2</sub> and Mn nanoparticles. UV-Vis absorption spectra shown three different curves for pristine P3HT, P3HT/TiO<sub>2</sub> and P3HT/TiO<sub>2</sub>/Mn thin films. A new absorption peak at 608 nm was observed. Substitution of Ti lattice sites with Mn atoms causes red-shift to the optical absorption spectra, allowing the doped photoactive layer to absorb longer wavelengths of the solar radiation. Similar result has been discovered by DFT (density functional theory) and DFT+U (DFT with Hubbard U correction for the on-site Coulomb repulsion) calculations to study the effects of Mn doping to the energy band structures and optical properties of rutile TiO<sub>2</sub> [11]. The transition metals such as Mn is expected to open a land of promising applications in hybrid organic-inorganic nanocomposite solar cell applications.

### **ACKNOWLEDGEMENTS**

Azyuni Aziz and Fatin Hana Naning are thankful to Universiti Pendidikan Sultan Idris, for the financial support through research grant 2011-0062-101-01, and MOSTI for eScience fund 03-01-11-SF0008. We would like to thanks Dr Reza Zamiri from Norwegian University of Science and Technology for providing the TiO<sub>2</sub> and Mn nanopowder.

### **REFERENCES**

- [1]. F. Xia, Z. Mingliang, W. Xiaodong, Y. Fuhua, and M. Xiangmin, Recent progress in organic–inorganic hybrid solar cells. *Journal of Materials Chemistry*, 1, 2013, 8694-8709.
- [2]. E. Morteza, Review:- Inorganic and Organic Solution-Processed Thin Film Devices. *Nano-Micro Lett.* 9(3), 2017, 23 pages.
- [3]. S. A. Malik, A. Aziz, and F. H. Naning, Morphology study of CdSe quantum dots in poly(3-hexylthiophene) (P3HT) prepared by Angle Lifting Deposition method, *International Journal of Science, Environment and Technology*, 6(2), 2017, 1476 – 1480.
- [4]. P. Seelam, and G. Lingamallu, Recent advances in perovskite-based solar cells, *Current Science*, 111(7), 2016, 1173-1181.
- [5]. A. Chilvery, S. Das, P. Guggilla, C. Brantley, and A. Sunda-Meya, A perspective on the recent progress in solution-processed methods for highly efficient perovskite solar cells, *Science And Technology Of Advanced Materials*, 17(1), 2016, 650-658.
- [6]. A. Facchetti, Polymer donor–polymer acceptor (all-polymer) solar cells, *Materialstoday*, 16(4), 2013, 123–132.
- [7]. F. H. Naning, S. Malik, R. Zamiri, Z. Ahmad, and A. Zakaria, Characterization of ZnO:P3HT Photoactive Layer, *Australian Journal of Basic and Applied Sciences*, 8(13), 2013, 115-12.
- [8]. E. S. Rosa, S. H. Munawaroh, and Pranoto, The influence of the composition of P3HT:TiO<sub>2</sub> on the characteristics of hybrid polymer solar cell. *IOP Conf. Series: Materials Science and Engineering*, 107, 2016, 012037.
- [9]. A. Aziz, F. H. Naning, S. A. Malik, and R. Zamiri, Determination of morphology of poly(3-hexylthiophene) with nanosphere and nanorod-shape of Zinc Oxide. *Advanced Materials Research*, 925, 2014, 304-307.
- [10]. J. E. Waldo, M. Beek, M. Wienk, and A. J. J. René, Hybrid Solar Cells from Regioregular Polythiophene and ZnO Nanoparticles. *Advance Functional Materials*, 16, 2006, 1112–1116.
- [11]. G. Shoa, Red shift in manganese- and iron-doped tio2: A dft+u analysis. *Journal of Physical Chemistry C*, 113(16), 2009, 6800-6808.