ROSELLE PLANT PIGMENTS AS NATURAL PHOTOSENSITIZERS FOR DYE SENSITIZED SOLAR CELLS: THE EFFECT OF TIN OXIDE BLOCKING LAYER ON THE PHOTOELECTRIC PROPERTIES.

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Abstract

Dye sensitized solar cells (DSSCs) assembled on titanium dioxide (TiO_2) synthesized with plant dye extracted from dried Roselle plant pigments were fabricated. The dye extract and active layers were characterized using a (UV 752) ultraviolet-visible-Near Infra-Red (UV-VIS-NI) spectrophotometer, at the wavelength interval of 250 nm to 1100 nm, while the Tauc model was used to obtain the optical band gap. The absorption coefficient and behaviour of the extinction coefficient was investigated. The current and voltage features of the dye sensitized solar cell fabricated with the synthesized TiO_2 Photo-anode were analysed. The optical band gap of the dye sensitized solar cells fabricated were 2.6eV, 2.8eV and 3.0 eV respectively, while the conversion efficiency of the dye sensitized solar cells was 1.34%, 1.32% and 2.9%.

Keywords: *Titanium dioxide, optical properties, dye sensitized solar cell, band gap, Hibiscus sabdariffa, absorption coefficient, extinction coefficient.*

1. INTRODUCTION

The issues on energy crisis and its sustainability is one global topic seeking great attention and potentials for research. Solar energy is anticipated to be a major player as a sustainable energy source, there is need of coming up with pragmatic techniques for conversion, storage and distribution of the energy from the sun towards the issue on energy predicament and sustainable use. Dye-sensitized Solar cells are photo-voltaic gadgets capable of transforming evident light from the sun into electricity, and in addition are centered on a permeable tinny film of an extensive band-gap semiconductor oxide altered by colorant (Chergui *et al*, 2015). The manufacturing cost of Dye-sensitized Solar cells, which are third-generation solar cells is much less than that of silicon solar cells which have succeeded in electricity renovation proficiencies extending from 15% to 20%; nevertheless, applicable extraordinary assembling budget plus the habit of using harmful substances in the production of extremely refined silicon associated with the industrial procedure has stirred the exploration aimed at having alternative in the dye-sensitized solar cell which is a naturally friendly and a very cheap budget solar cell. Dye-sensitized solar cells have expanded weighty consideration since (Nazerruddin *et al*, 2001; O'Regan and Gratzel, 1991) reported an extraordinarily high conversion efficiency of nearly 10% using nanocrystalline mesoporous Titanium dioxide (TiO_2) film (O'Regan and Gratzel, 1991). Yet, these biological solar cells are still limited in low power conversion, proficiencies, and charge recombination is one of the principle explanations behind low current in dye-sensitized solar cells, so the performance of (DSSCs) is seriously decreased. A compact layer has been corroborated hypothetically and practically operational to wedge the electron recombination through the ancillary path. A compacted hindering deposit amongst the accompanying electron and the nano-crystalline Titanium dioxide (TiO_2) layer can viably forestall recombination at the cathode/electrolyte interface.

1.1 Solar Cell

To exploit the power of sunlight based energy and convert it to useful structures like power stays a vast task. Photovoltaic gadgets are the principle sunlight based verve change frameworks to gather sun based energy. These photovoltaic gadgets are known as sunlight based cells, they convert the striking beams of light from sun oriented emission toward electricity by means of the age plus ensuing assortment of elementary particle gap sets. Sun powered cells are arranged into three ages subject to their introduction and cost-sufficiency. The original of sun powered cells has generally higher effectiveness with costly creation costs. They are the old style instances of sun oriented cells and incorporate Silicon and Germanium. The business showcase is commanded by this age. Flimsy film sunlight based cells dependent on Cadmium Telluride (CdTe), Nanocrystalline Silicon, Amorphous silicon, and Copper indium gallium Selenide (CIGS) etc. mark the second age group cell. They have lower proficiency yet are a lot less expensive to create and utilize a less outer manufacture process. Third age group sun oriented devices comprise the categories of cells which weren't assembled during the first as well as second ages. A color sharpened (dye) sunlight based cell is a natural sun based cell of the third era.

Most third-age advances are not yet economically executed; however a lot of inquiry and a great deal regarding exploration is ongoing which are showing favourable prospect (Imran, 2013).

2. MATERIALS AND METHODS

2.1 Preparation of natural dye solution

Dried calyxes of Roselle plant were used as sensitizers of the dye sensitized solar cell fabricated. They were washed with distilled water, and the dye solution was prepared by boiling the roselle plant calyxes in 40cl of water to boiling temperature as seen in plate 2a and 2b respectively. The dye solution was allowed to cool down for 3hours and the cell was soaked overnight at room temperature in the dye extract, to allow the dye molecules to form covalent bond to the surface of the TiO_2. It was then stored away from light (in the dark); after 12 hours, the cell was brought out and rinsed with water and dried at 60^0C.

Fig 1. Hibiscus sabdariffa calyxes in water at boiling temperature.

Fig 2. Hibiscus sabdariffa dye extract

2.2 DSSC Assembling

The photoanode was prepared first by etching the fluorine doped tin oxide (FTO) glass (Solaronics) using electro-etching method, followed with a deposition of a blocking layer. The blocking layer was deposited to FTO glass substrate from a precursor of total volume of 40ml, which has a concentration of 0.1m of titanium isopropoxide, 0.4m of acetylacetone and methanol using the spin coating method, and subsequently annealed to 450^0C for 30 minutes. The Titanium dioxide (TiO_2) (usually a paste) was deposited onto the fluorine doped tin oxide

(FTO) glass substrate by ‘screen printing method’. On top of the glass substrates, a layer of (solaronix Ti-Nanoxide D/SP) screen printable paste was applied, outlining it on the active area. The sample was annealed gradually from 150^0C to 300^0C and then finally 450^0C. Once it is annealed to 150^0C, the samples were left to dwell for 10minutes and then annealed to 300^0C and left to dwell for another 10minutes and finally annealed to 450^0C. After annealing, the samples were allowed to cool down for 30minutes. On top of the fluorine doped tin oxide (FTO) glass substrates, a layer of Zirconium dioxide (Solaronix Zr-nanoxide Z/SP) screen printable paste was deposited using the screen printing method. This layer insulates the titanium dioxide mesoporous layer from the counter electrode. The sample was annealed to 400^0C for 30minutes and allowed to cool down for 30minutes. Propanol and cotton wool was used to clean the screen printing machine to rid it off any particle of the previous layer deposited. This layer becomes the negative terminal of the monolithic dye sensitized solar cells.

The counter electrode was prepared by screen printing a platinum (Pt) catalyst gel coating on the FTO glass substrate. A thin layer of platinum (Pt) was deposited on the glass substrates by screen printing (Solaronics platisol T/SP paste), which acts as a catalyst and annealed to 400^0C for 30 minutes. A layer of (Solaronix Elcocarb G/SP) screen printable paste was deposited using screen printing method on the active area. The elcocarb is just a conducting material and was printed to bridge the two conductive layers as it helps to transfer voltage to the back layer, and it becomes the positive terminal of the monolithic dye sensitized solar cells. The samples were then annealed to 400^0C for 30minutes, activating the elcocarb layer for working and then allowed to cool down to 100^0C.

The cell was soaked overnight at room temperature in the dye extract, for it to absorb into all the layers. It was then stored away from light (in the dark); after 12 hours, the cells were brought out and rinsed with water and dried at 60^0C.

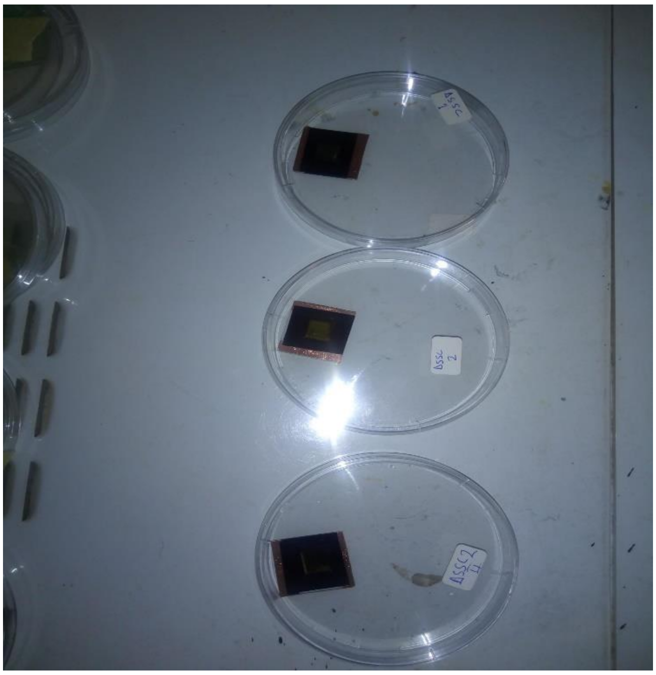

Fig 3. The Three samples of fabricated DSSCs

2.3 Optical Characterization

A (UV 752) ultraviolet-visible-Near Infra-Red (UV-VIS-NI) spectrophotometer U.K was used to carry out the optical study of the cells at the wavelength interval of 250 nm to 1100 nm. Absorbance values were obtained using the spectrophotometer and other optical properties like transmittance, reflectance, refractive index, absorption coefficient, extinction coefficient and energy band gap were evaluated using the following equations;

The transmittance (T) of the cells was evaluated using Equation (2.1) given by Lokhande *et al.* (2002).

$$T = 10^{-A} \tag{2.1}$$

Reflectance was obtained using equation (2.2) given by Lokhande *et al.* (2002).

$$R = 1 - (A + T) \tag{2.2}$$

Refractive index of the cells was calculated using Equation (2.3) as given by Ilenikhena, (2008) and Ohwofosirai *et al*. (2014).

$$\eta = \frac{(1+\sqrt{R})}{(1-\sqrt{R})} \tag{2.3}$$

The absorption coefficient was calculated from absorbance spectra using the Equation (2.4) given by Suresh and Isha (2016) and Mursal (2018). Where *d* is the thickness and measured in micrometer (μm), and *A* is the absorbance.

$$\alpha = \frac{2.303A}{d} \tag{2.4}$$

The extinction coefficient was obtained using Equation (2.5) (Tezel *et al*., 2017).

$$k = \frac{\alpha\lambda}{4\pi} \tag{2.5}$$

Optical conductivity was estimated using Equation (2.6) as given by (Ohwofosirai *et al.*, 2014).

$$\sigma_o = \frac{\alpha\eta c}{4\pi} \tag{2.6}$$

Where c is the speed of light.

The energy band gap was estimated using Tauc's model given in Equation (2.7) as given by (Tezel *et al*., 2017)

$$(\alpha hv)^n = \beta\left(hv - E_g\right) \tag{2.7}$$

Where α is the absorption coefficient, *h* is the Planck constant, ν is the photon's frequency, *E*g is the band gap energy and β is a constant. The *n* factor depends on the nature of the electron transition and is equal to ½ or 2 for the direct and indirect transition band gaps respectively.

2.4 Solar Simulation Characterization

The IV characteristics curves of the fabricated DSSCs were measured under an illumination of 100 mW/cm^2 using a Newport solar simulator (model 94043A), and I.V acquired by a Keithley 2400 source meter. Cell surface area is 1cm x 1cm.

3. RESULTS AND DISCUSSION

3.1 Optical characterization

The three layers in the DSSC are dye (roselle plant), TiO_2 layer and synthesized TiO_2 layer having absorption peak at 475, 335, and 320 nm respectively as shown in fig 4. The roselle plant (hibiscus sabdariffa) is a natural dye with wider absorption peak at lower wavelength range of solar spectrum. The spectrum of the synthesized TiO_2 shows even a wider absorption band and is expected to harvest more solar energy. The absorption coefficient revealed to what extent into the layers of the DSSC, light of a particular wavelength can enter before absorption. Fig 4 shows that the absorption coefficient is not constant but strongly depends on wavelength.

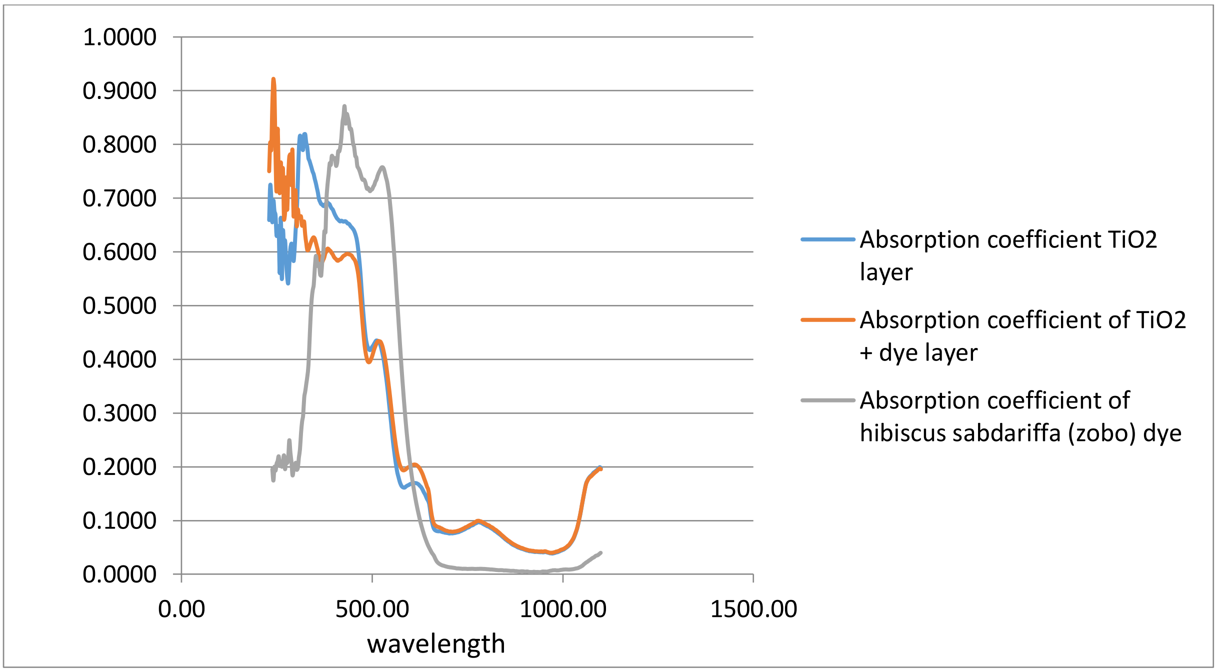

Fig. 4 Absorption coefficient of the different layers of the DSSC

The extinction coefficient of the dye, TiO2 layer and Synthesized TiO2 layer of the fabricated DSSC was investigated. The natural dye showed strong absorption in the visible and near infrared radiation wavelength. The synthesized TiO2 layer showed strong absorption in the infrared radiation spectrum as shown in Fig 5.

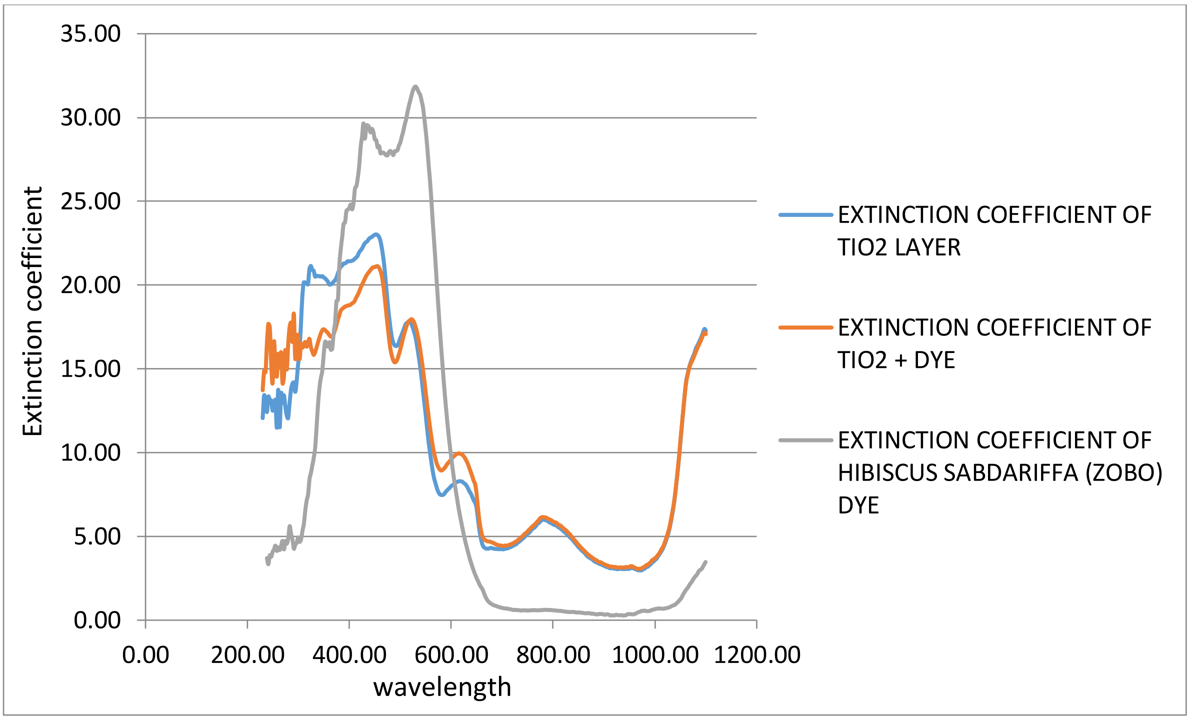

Fig. 5 Extinction coefficient of the different layers of the DSSC

3.2 Photovoltaic properties

Fig 6, Fig 7, and Fig 8 respectively shows the current voltage curves of the various DSSCs fabricated. Cell sample 1, 2, and 3 showed similar value of open circuit voltage, however cell 2 showed the highest value of short circuit current whereas cell 1 and 3 showed lower values in their short circuit current.

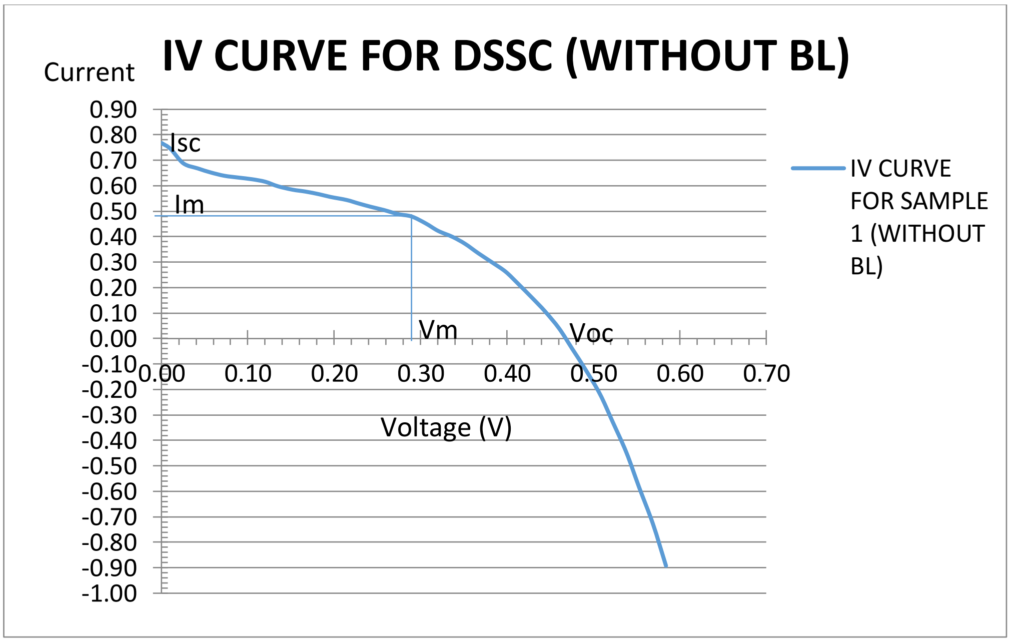

Fig 6. I/V curve for Sample 1 (DSSC without blocking layer)

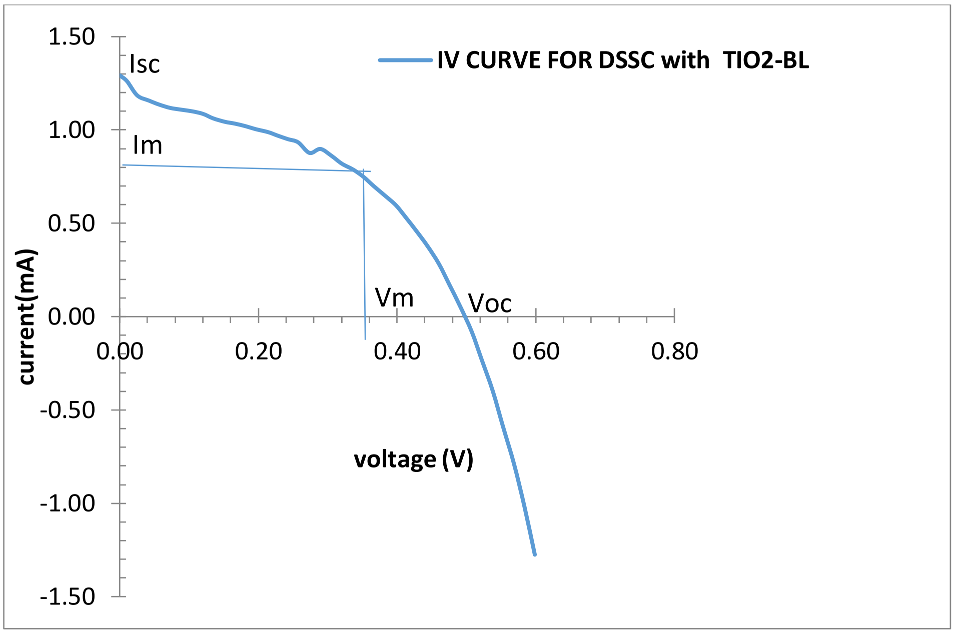

Fig 7. I/V curve for Sample 2 (DSSC with TIO_2 blocking layer)

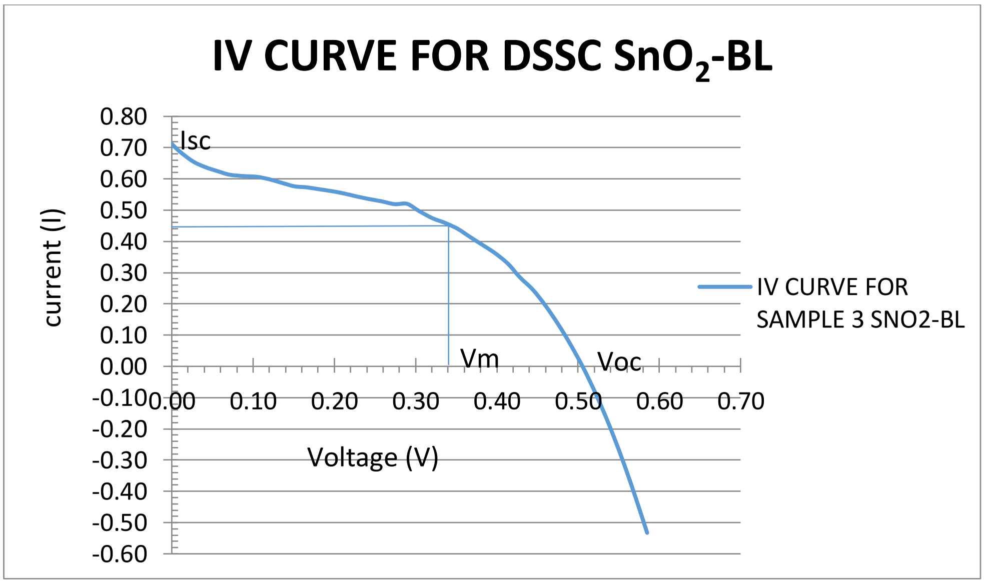

Fig 8. I/V curve for sample 3 (DSSC with SNO_2 blocking layer)

These values were measured under the illumination of 100 mW/cm^2. To investigate the DSSC performance, short circuit current (Isc), open-circuit voltage (Voc), maximum power point, fill factor (FF), and conversion efficiency (ŋ) were determined. Short circuit current (Isc) and open-circuit voltage, Im and Vm were determined from the IV curve interception with y- and x-axes respectively. Using these parameters, fill factor (FF) and conversion efficiency (ή) were calculated. All cell parameters of the fabricated DSSCs are presented in Table 1.

Table 1: Photovoltaic parameters of the Dye-sensitized solar cells (DSSCs) sensitized by Hibiscus sabdariffa.

TiO_2 DSSC samples (cell)	Voc (V)	Isc (mA/cm^2)	Vm (V)	Im (mA/cm^2)	FF	ή %
1.(without blocking layer)	0.47	0.78	0.29	0.48	0.38	1.34
2.(TiO_2 blocking layer)	0.50	1.3	0.36	0.8	0.44	2.9
3.(SNO_2 blocking layer)	0.50	0.70	0.35	0.45	0.37	1.32

CONCLUSION

Finally, three samples of dye-sensitized solar cells were fabricated and their optical properties such as absorption coefficient and extinction coefficient were determined using a (UV 752) ultraviolet-visible near infra-red (UV-VIS-NI) spectrophotometer. The photovoltaic properties of the fabricated DSSCs were ascertained using a Newpot solar simulator (Model 94043A) and I.V acquired by a Keithley 2400 source meter. Cell surface area was 1cm X 1cm, and short circuit current (Isc) and open-circuit voltage (Voc) values were obtained using Keithley 2400 source meter and other solar cell properties like fill factor (FF) and efficiency were also evaluated. The results presented showed an improved power conversion on cell 2 fabricated with a TiO2 sensitized with dye and having titanium dioxide as blocking layer with an efficiency of about 2.9%.

REFERENCES:

1. Chergui, M., Santomauro, F. G., Lübcke, A., Rittmann, J., Baldini, E., Ferrer, A., & Silatani, M. (2015). Femtosecond X-ray absorption study of electron localization in photoexcited anatase TiO_2. *Scientific Reports, 5*. https://doi.org/10.1038/srep14834

2. Grant, C. D., Adam, M. S., Greg, P. S., Janusz, K., Laren, M. T., & Jin, Z. Z. (2002).

Characteriztion of nanocrystalline and thin film TiO_2 Solar cell with Poly (3-undecyl 2, 2-bithiophene) as a sensitizer and hole conductor. *Journal of Electroanalytical Chemistry*, 522 (1), 40-48, https://doi.org/10.1016/S0022-0728(01)00715-x

3. Grätzel, M. (2004). Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells, *Journal of Photochemistry and Photobiology A: Chemistry*, 164 (1–3), 3-14.

4. Imran, K., Andrew, H., & Christos, F. (2013). A study on the optimization of dye-Sensitized solar cells. *Graduate theses and dissertations*. http://scholarcommons.usf.edu/etd/4519

5. Ito, S. T. N., Murakami, P., Comte, P., Liska, C., Grätzel, M. K., & Nazeeruddin, M. (2008).Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10%, *Thin Solid Films*, 516 (14), 4613–4619.

6. Lokhande, P., Patil, S., & Uplane, M. D. (2002). Deposition of highly oriented ZnO films by spray pyrolysis and their structural, optical and electrical characterization. *International Journal of Materials Engineering*, 2 (1), 12-17. https://doi.org/10.1016/S0167-577X(02)00832-7

7. Nazeeruddin .M.K, P. Péchy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi, & M. Grätzel, (2001). Engineering of Efficient Panchromatic Sensitizers for Nanocrystalline TiO_2-Based Solar Cells, *J. Am. Chem. Soc.*,123 (8), 1613-1624.

8. O'Regan, B., & Grätzel, M. (1991). A low-cost, high-efficiency solar cell based on dye-

Sensitized colloidal TiO2 films. *Nature*, 353, 737- 40.

9. Ozuomba, J. O., Ugwu, J. E., Azubuike, P., & Ekwo, I. (2015). The Optical properties of anthocyan doped nanocrystalline TiO_2 and the photovoltaic efficiency on DSSC. *Der Chemic Sinica*, 6 (11), 42 – 48.

10. Usami, A., & Ozaki, H. (2001). Computer simulations of charge transport in dye-sensitized nanocrystalline photovoltaic cells. *The Journal of Physical Chemistry B*; 105 (45), 77- 83.

11. Wali, Q., Fakharuddin A., & Jose. R., (2015). Tin oxide as a photoanode for dye-sensitised solar cells: current progress and future challenges. *Journal of Power Sources*, 293 (10)39 - 52.

12. Wang, L., Kang, B., Wang, P., & Qiu, Y. (2006). Review of recent progress in solid-state

dye-sensitized solar cells. *Solar Energy Materials and Solar Cells*, 90 (5), 49