Fabrication of TiO_2-Cu_2O Nanowire Photoelectrode for Dye-Sensitized Solar Cells Based on Natural Chlorophyll Dyes

Zaw Htet Aung[1], Than Than Win[2], Yin Maung Maung[3], Win Win Thein[4]

Abstract

Titanium dioxide (TiO_2) was deposited to ITO coated glass substrate by spin coating technique and it served as a core layer. Cuprous oxide (Cu_2O) shell layer was coated onto TiO_2/ITO/glass substrate structure by electrochemical deposition method. Structural, microstructure and optical properties of TiO_2-Cu_2O thin film were examined by X-ray diffraction (XRD), scanning electron microscope (SEM) and UV-Vis spectroscopy. The optical energy band gap E_g=2.81 eV was deduced for the TiO_2-Cu_2O thin film. Chlorophyll-based natural dyes such as bottle gourd leaves, spinach leaves and ivy gourd leaves were extracted and used as dyes sensitizer. UV-Vis spectroscopy was used to measure the energy band-gap of colorant. TiO_2-Cu_2O thin film was immersed in pigment and formed the core-shell electrode. For counter electrode, C (Carbon) layer was prepared on ITO/glass substrate TiO_2-Cu_2O thin film and counter electrodes were sandwiched together for DSSC design. Current density and voltage (J-V) characteristics were measured under illumination. From J-V curves, fill factor was calculated to be 0.62 % for bottle gourd leaves, 0.79% for spinach leaves and 0.82 % for ivy gourd leaves. The maximum output power was found to be 0.0032 mW/cm^2 for bottle gourd leaves dye, 0.0022 mW/cm^2 for ivy gourd leaves dye and 0.0018 mW/cm^2 for spinach leaves dye. The power conversion efficiencies (η) of the DSSCs were found to be 2.88 % for bottle gourd leaves dye, 1.93% for ivy gourd leaves dye and 1.59 % for spinach leaves dye. The best performance was obtained for DSSC sensitized with bottle gourd leaves dye in which the efficiency of the cell reached 2.88%.

Keywords: TiO_2-Cu_2O, Dye, Chlorophyll, DSSC, J-V

Introduction

The use of solar energy allows all parts of the world to exploit this energy. Solar energy is not environmentally friendly and cheap only, but also used as power that will exist for billions of years. Dye sensitized solar cell (DSSC) is one of the most promising devices for the conversion of visible light into electrical energy based on the sensitization of the wide band gap semiconductors (Al-Alwani *et al*., 2014). The dye-sensitized solar cells (DSSCs) are third generation solar cells developed by Grätzel and co-workers in 1991 (O'Regan & Grätzel, 1991), and already the best solar cells achieve 11.1% efficiency which is sufficient for practical implementation (Smith *et al.*, 2006 & Kimpa *et al.*, 201)). It is a low-cost solar cell belonging to the group of thin film solar cells and also based a photo electrochemical system which formed between a photo-sensitized anode and an electrolyte on a semiconductor.

Organic dyes used in the DSSC do resemble dyes found in plants, fruits and other natural products and several of these have been used in the production of dye-sensitized solar cells. Among the advantages of natural dyes are easy availability, environmentally friendly, ease of fabrication, low temperature process and low cost of sensitization material production. Many natural dyes such as anthocyanin, carotenoid, flavonoid, chlorophyll, tannin and cyanin found in leaves, fruits, flowers, seeds, and bark that can be extracted by simple methods that have been studied and tested as available and low cost materials (Al-Alwani, *et al*.,2014).

[1]Lecturer, Dr, Department of Physics, Hinthada University
[2]Associate Professor, Dr, Department of Physics, Mandalay University of Distance Education
[3]Associate Professor, Dr, Department of Physics, University of Yangon
[4]Professor and Head, Dr, Department of Physics, Hinthada University

The core-shell geometry of nanowires is thought to be able to enhance the efficiency of charge collection by shortening the paths travelled by minority carriers. An ideal core-shell configuration is highly desirable for its low recombination rate and high collection efficiency. Core-shell heterostructures formed by the growth of crystalline overlayers on nanocrystals offer enhanced emission efficiency, important for various applications. In recent years, the development of core/shell structured materials on a nanometer scale has been received extensive attention. The shell can alter the charge, functionality and reactivity of the surface, or improve the stability and dispersive ability of the core material (Vaizogullar *et al*., 2014 and Agbo *et al.*, 2011).

Transparent conducting oxides (TCOs) have long been an interesting area of research. This is largely due to its unique properties and diverse applications. Some of these TCOs include titanium oxide, tin oxides, cadmium oxides, ferrous oxide, cuprous oxides etc (Caglar, *et al*., 2006). Titanium oxide (TiO_2) has been one of the most studied oxides because of its role in various applications, namely photo induced water splitting, dye synthesized solar cells, solar cells environmental purifications, gas sensors, display devices batteries etc. (Agbo P.E , 2012). TiO_2 is a nontoxic naturally n-type semiconductor material which has a high-temperature stability and low production costs. A p-type semiconductor, cuprous oxide (Cu_2O) has the advantages of low consumption, nontoxic, and higher conversion efficiency. Therefore, it is widely used in solar cells, lithium ion batteries, biological sensors, gas sensors, magnetic storage, microdevices, and negative electrodes (Chem *et al*., 2010).

The crystal structure of the samples was examined by X-ray diffraction (XRD). The morphology of the nanostructure of the thin film was investigated by scanning electron microscopy (SEM). The UV-visible absorption or transmission spectra were obtained using SHIMADZU UV-1800 spectrophotometer. The fabricated solar cells were characterized by the current density-voltage (J-V) characteristics.

Experimental Procedures

Preparation of TiO_2-Cu_2O thin film

2 g of TiO_2 powder and 20 ml of methanol were mixed in the beaker. Then, it was annealed 110º C for 1 h with water bath. Next, this solution was continuously stirred by a magnetic stirrer for 1.5 h with 600 rpm to be homogeneous. After stirring, TiO_2 sol-solution was formed. Indium tin oxide (ITO) coated glass substrate was cleaned with acetone and deionized water about 10 min. The ITO coated glass substrate was subsequently baked at 80º C for 10 min to evacuate moisture. TiO_2 sol-solution was then deposited onto the glass substrates by spin coating at 1000 rpm for 5 min. This sample was annealed at 500º C for 1 h. Thus TiO_2 thin film was formed.

0.2 g of Copper (II) sulphate (Cu_2SO_4) and 25 ml of deionized (DI) water were mixed and aged with pH-3 for 10 min. Next, 6 ml of Lactic acid ($C_3H_6O_3$) and 25 ml of DI water were mixed and aged with pH -1 for 10 min. 4 g of sodium hydroxide (NaOH) and 25 ml of DI water were mixed and aged with pH-14 for 10 min. The above three samples were mixed and stirred by magnetic stirrer at 700 rpm for 1 h to get pH-10 solution. The sample prepared by electrochemical deposition method was made to dissolve in DI water. Then, this solution was deposited onto glass substrate by electrochemical deposition method. This mixture solution was treated as bath temperature at 100° C for 1 h. TiO_2 thin film substrate was placed into plating solution and connected it to the cathode of power supply. The copper plate was placed into plating solution and connected it to the anode. Parameter that affects the electroplating process was used at 5 volts in 1 h. After depositing, TiO_2-Cu_2O thin layer was annealed at 150° C for 30 min in air atmosphere. Finally, TiO_2-Cu_2O thin film was formed.

Preparation of Natural Dyes Extraction

The natural dyes were extracted with methanol by the following procedure. Fresh spinach leaves, fresh ivy gourd leaves and fresh bottle gourd leaves were washed with water and dried at room temperature. After drying, they were crushed into powder with agate motor. Each powder (1 g) was dissolved with 25 ml of methanol in the beaker. These solutions were kept at room temperature about one week. They were stirred with magnetic stirrer at 700 rpm for 1 h and were heated at 100° C with water bath for 1 h. And then, the residual parts were filter out and the resulting filtrates were used as dye solution. Glass substrates were kept in each solution for 15 h. These films were kept to be dried with room temperature. Optical properties of dye in UV and visible regions were analyzed by using SHIMADZU UV-1800 photospectrometer.

Preparation of Dye Sensitized Solar Cell Assembly

The dye sensitized solar cell device fabrication starts with cleaning of the indium tin oxide (ITO) coated glass substrates in distilled water and acetone. ITO, electrically conductive oxide-coated glass, is used as transparent electrode. Deposition area on the conductive side of the glass was defined by using masking tape. The size of the final open area was 1 cm × 1cm. TiO_2 sol-solution was deposited onto ITO glass substrates by spin coating with 1000 rpm for 5 min. Cuprous oxide (Cu_2O) shell layer was then coated onto TiO_2/ITO/glass substrate structure by electrochemical deposition method. After the tape was removed, these samples were annealed at 150º C for 30 min. Bottle gourd leaves dye, spinach leaves dye and ivy gourd leaves dye were used as the sensitizing dye molecules, while C (Carbon) was used as the counter electrode material. This electrode was immersed 12 h into bottle gourd leaves dye, spinach leaves dye and ivy gourd leaves dye solutions. The C (Carbon) counter electrode was prepared from carbon and carbon black powders onto an ITO glass and then followed by heating at 180º C for 1 h. DSSCs were assembled using sandwich structure by combining the two substrates (electrodes) that were ready. Substrates were combined together using binder clips. The fabricated solar cells were characterized by the current-voltage (J-V) characteristics.

Results and Discussion

XRD analysis of TiO_2 - Cu_2O thin film

Figure (1) showed the XRD patterns of TiO_2 - Cu_2O thin film. From XRD plot, almost reflections were well-matched with the diffracted peaks of standard anatase TiO_2 and Cu_2O. XRD analysis showed that the films were crystallized in the cubical phase of TiO_2-Cu_2O thin film. The TiO_2 peaks were found to be (1 0 1), (1 0 3), (0 0 4), (2 0 0), (2 0 2), (2 0 2), (1 0 5) and (2 1 1) planes. The Cu_2O peaks were found to be (1 1 1), (2 0 0), (2 1 1), (2 2 0) and (3 1 0) planes. The average lattice parameter of a-axis for TiO_2-Cu_2O thin film was observed as 5.1664 Aº. The average crystallite size was found to 69.3568 nm for TiO_2 and 75.2775 nm for Cu_2O. The diameter of spherical shaped crystallite again could be identified as crystallite size, which was calculated by Debye-Scherrer equation.

$$G = \frac{k \times \lambda}{B \times \cos\theta_B} \qquad (1)$$

where G is Crystallite size (Å), λ is wavelength of X-rays, B is FWHM of reflection and θ_B is Bragg angle.

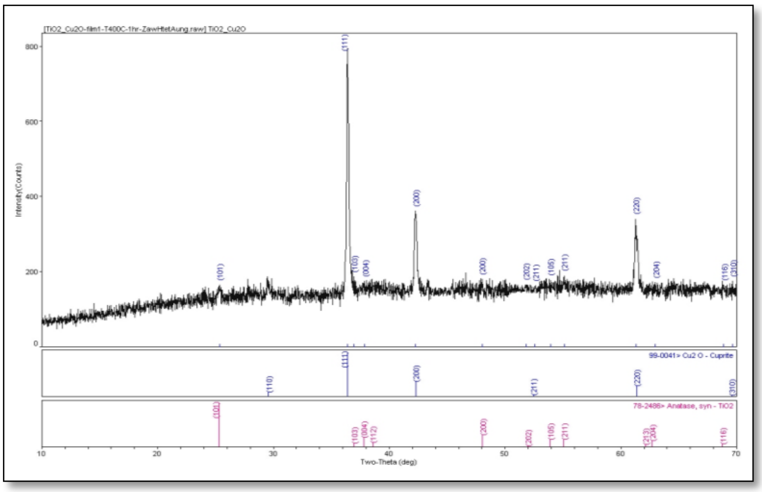


Figure (1) XRD pattern of TiO_2 - Cu_2O thin film.

Table (1) Crystallite size of Cu_2O of TiO_2-Cu_2O thin film.

No	Peaks	FWHM (deg)	Crystallite size (nm)
1	(111)	0.205	40.3626
2	(200)	0.229	36.79883
3	(211)	0.105	83.43205
4	(220)	0.221	41.33983
5	(116)	0.126	75.6480
6	(310)	0.055	174.0838
Average Crystallite size			75.27752

Table (2) Crystallite size of TiO_2 of TiO_2-Cu_2O thin film.

No	Peaks	FWHM (deg)	Crystallite size (nm)
1	(101)	0.260	30.9860
2	(103)	0.055	150.6805
3	(004)	0.263	31.59776
4	(200)	0.088	97.78400
5	(202)	0.115	76.06687
6	(211)	0.105	83.43205
7	(105)	0.217	40.6375
8	(211)	0.203	43.6704
Average Crystallite size			69.35689

SEM Investigation of TiO_2-Cu_2O thin film

The SEM image in figure (2) shows that the nanowires have a core–shell structure of TiO_2-Cu_2O thin film. The TiO_2-Cu_2O array consisting of cylinder shaped nanowires which have small feature sizes (an average diameter of ~ 90 nm and a typical length of ~ 2 µm). The position of nanowires were horizontally and vertically aligned and uniform distribution in this SEM image. The wires are in direct contact with the substrate, with no intervention TiO_2 particles layer.

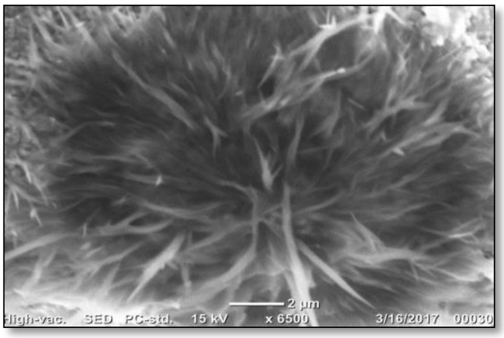


Figure (2) SEM image of TiO_2-Cu_2O thin film.

UV-Vis Analysis of TiO_2 -Cu_2O thin film

UV-Vis absorption values of TiO_2-Cu_2O thin film was measured in (SHIMADZU UV-1800) spectrophotometer The absorption peaks of TiO_2-Cu_2O thin film are 325.00 nm, 345.00 nm, 373.00 nm, 392 nm 407.00 nm 433.00 nm and 569.00nm. All absorption peaks of TiO_2-Cu_2O thin film are observed in the visible region. The transmission peaks of TiO_2-Cu_2O thin film are 421.00 nm, 453.00 nm, 482.00 nm, 507 nm, 547.00 nm and 576.00nm. The energy gap (E_g) was estimated by assuming a direct transition between valence and conduction bands from the expression ((Reddy *et al*., 1991) and (Vijay *et al.*, 2011) :

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

where K is a constant. The band gap (E_g) was determined from each film by plotting $(\alpha h\nu)^2$ versus hν and then extrapolating the straight line portion to the energy axis at $\alpha h\nu = 0$. From the graph, the optical energy band gap E_g= 2.81 eV for the TiO_2-Cu_2O thin film obtained in figure (3).

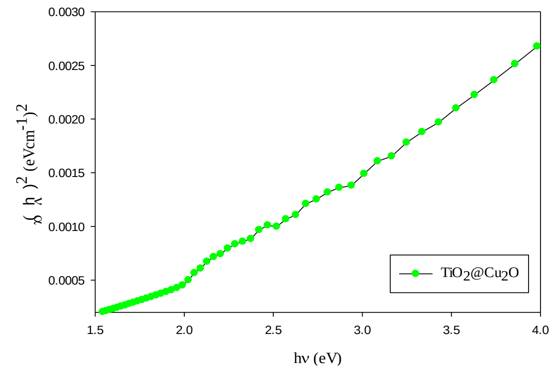


Figure (3) Plot of $(\alpha h\nu)^2$ versus hν for TiO_2-Cu_2O thin film.

UV-Vis Analysis of Natural Dyes

UV-Vis absorption values of dye films were measured in (SHIMADZU UV-1800) spectrophotometer. The UV-Vis photospectra of spinach leaves, ivy gourd leaves and bottle gourd leaves were recorded with respect to bare the substrate placed in the reference beam using beam spectrophotometer.

The absorption peaks of chlorophyll dye extracted from spinach leaves at room temperature are 536.00 nm, 616.00 nm and 663.00 nm. The cut off wavelength of spinach dye film absorption spectrum was 520.00 nm. The absorption peaks of chlorophyll dye extracted from ivy gourd leaves at room temperature are 534.00 nm, 616.00 nm and 664.00 nm. The cut off wavelength of ivy gourd dye film absorption spectrum was 515.00 nm. The absorption peaks of chlorophyll dye extracted from bottle gourd leaves at room temperature are 504.00 nm, 538.00 nm, 608.00 nm and 665.00 nm. The cut off wavelength of bottle gourd dye film absorption spectrum was 495.00 nm. All absorption peaks lie between the ranges of 504.00 to 665.00 nm. The optical band gap of spinach dye film from absorption spectrum was calculated to be 2.52 eV shown in figure (4). The optical band gap of ivy gourd dye film from absorption spectrum was calculated to be 2.54 eV shown in figure (5). The optical band gap of bottle gourd dye film from absorption spectrum was calculated to be 2.78 eV shown in figure (6). The absorption abilities of dye solutions are closely that of chlorophyll at room temperature.

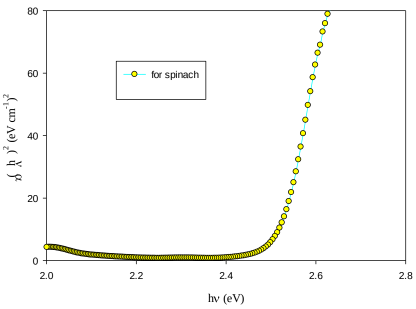


Figure (4) Optical energy band gap of spinach dye thin film.

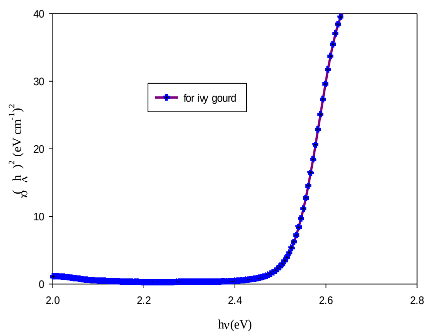


Figure (5) Optical energy band gap of ivy gourd dye thin film.

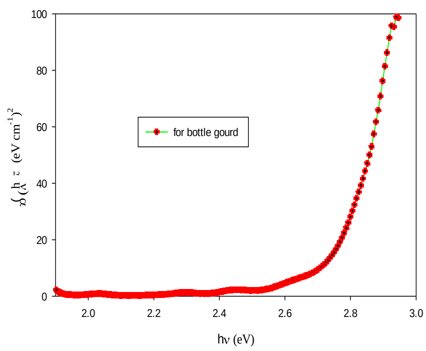


Figure (6) Optical energy band gap of bottle gourd dye thin film.

J-V Characteristics under Illumination

The performance of natural dyes as DSSC sensitizers was defined by several parameters such as short-circuit current J_{sc} and open-circuit voltage V_{oc} obtained under illumination conditions. The DSSC output power was calculated as P=JV using the J-V data. The maximum power (P_m) of each cell was obtained. The current density (J_m) and the voltage (V_m) corresponding to the maximum power point were then obtained. All of the photovoltaic performance parameters of DSSCs sensitized with different natural dyes are listed in table (3). Fill factor (FF) under illumination condition is a measure of a diode behavior of the cell. The J-V characteristic was obtained fill factor of 0.79% for spinach leaves dye according figure (7), 0.62 % for bottle gourd leaves dye according figure (8) and 0.82 % for ivy gourd leaves dye according figure (9). It was obtained using a current-voltage characterization as follows (Otakwa *et al*., 2012);

$$FF = \frac{V_m \times J_m}{V_{oc} \times J_{sc}} = \frac{P_m}{V_{oc} \times J_{sc}} \quad (3)$$

The efficiency η describes the overall performance of the DSSC. It is defined as the ratio of P_m to the power of incident radiation (P_{in}). The maximum output power was found to be 0.0018 mW/cm^2 for spinach leaves dye in figure (10), 0.0032 mW/cm^2 for bottle gourd leaves dye in figure (11) and 0.0022 mW/cm^2 for ivy gourd leaves dye in figure (12). The power conversion efficiency of energy to electricity conversion efficiency (η) of the cell with P_{out} electrical power under illumination condition is given by:

$$\eta = \frac{P_{out}}{P_{in}} \times 100\% = J_{sc} V_{oc} \frac{FF}{P_{in}} \times 100\% \quad (4)$$

where η is the efficiency, P_m is the maximum output power, J_m is the current density at maximum power point, V_m is the voltage at maximum power point, V_{oc} is the open circuit voltage, J_{sc} is the short circuit current density, FF is the fill factor and P_{in} is the incident optical power.

The power conversion efficiencies (η) of the DSSCs were observed to be 2.88 % for bottle gourd leaves dye, 1.93% for ivy gourd leaves dye and 1.59 % for spinach leaves dye. table (4) described efficiencies and Fill Factors of the fabricated DSSCs. The best performance was obtained for DSSC sensitized with bottle gourd leaves dye, where the efficiency of the cell reached 2.88%.

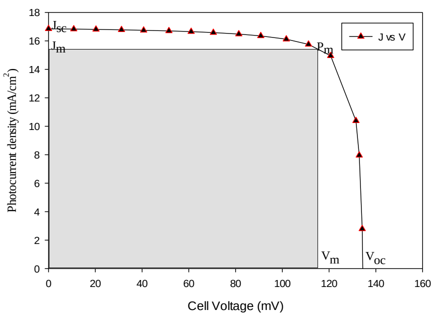


Figure (7) Photocurrent density versus Cell voltage curve for DSSC using spinach dye.

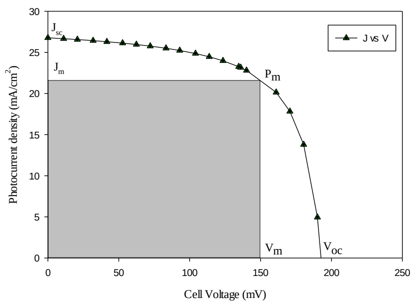


Figure (8) Photocurrent density versus Cell voltage curve for DSSC using bottle gourd dye.

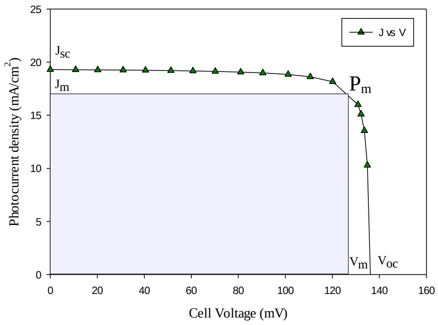
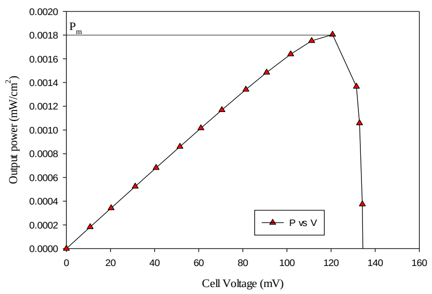


Figure (9) Photocurrent density versus Cell voltage curve for DSSC using ivy gourd dye.



Figurer (10) Output power versus Cell voltage curve for DSSC using spinach dye.

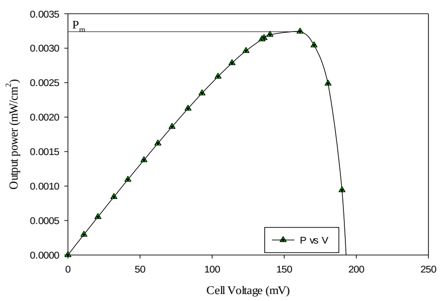


Figure (11) Output power versus Cell voltage curve for DSSC using bottle gourd dye.

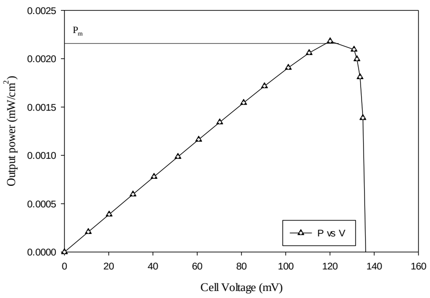


Figure (12) Output power versus Cell voltage curve for DSSC using ivy gourd dye.

Table (3) Photovoltaic Performance Parameters of the fabricated DSSCs.

Types of Dyes	J_{sc} (mA/cm^2)	V_{oc} (mV)	J_m (mA/cm^2)	V_m (mV)
Bottle gourd leaves	26.98	192.55	22.36	144.32
Ivy gourd leaves	19.32	135.90	17.92	121.02
Spinach leaves	16.94	134.14	15.55	114.81

Table (4) Efficiencies and Fill Factors of the fabricated DSSCs.

Types of Dyes	FF	P_m (mW/cm^2)	η (%)
Bottle gourd leaves	0.62	0.0032	2.88
Ivy gourd leaves	0.82	0.0022	1.93
Spinach leaves	0.79	0.0018	1.59

Conclusion

Titanium dioxide (TiO_2) thin films were deposited by the spin coating method onto ITO coated glass substrates. Cuprous oxide (Cu_2O) thin layers were deposited onto TiO_2/ITO thin layers by electrochemical deposition method. XRD analysis showed that in the cubical phase of TiO_2-Cu_2O thin film. The crystallite size of the thin films were found to be 72.316 nm for TiO_2-Cu_2O thin film. From SEM investigation, the TiO_2-Cu_2O array consisting of cylinder shaped nanowires which have small feature sizes (an average diameter of ~ 90 nm and a typical length of ~ 2 μm). UV-Vis absorption and transmission values of TiO_2-Cu_2O thin films were measured by (SHIMADZU UV-1800) spectrophotometer. The optical energy band is obtained 2.81 eV for the TiO_2-Cu_2O thin film. According to UV-Vis results, absorption peaks of the three dye samples of spinach, ivy gourd and bottle gourd leaves were found to be between 665.00 nm and 466.00 nm. In fact, all absorption peaks in the visible region indicated that the three dye samples exhibited the chlorophyll members. The band gap of the three dye samples calculated from absorption spectra and transmission spectra was about 2 eV. As the results obtained, it concluded that these dyes are quite credible and application for dye sensitizer in DSSC. Bottle gourd leaves dye, spinach leaves dye and ivy gourd leaves dye were used as the sensitizing dye molecules, while C (Carbon) was used as the counter electrode material. The fill factor was obtained from J-V characteristic 0.62 % for bottle gourd leaves dye, 0.79% for spinach leaves dye and 0.82 % for ivy gourd leaves dye. The maximum output power was to be found 0.0032 mW/cm^2 for bottle gourd leaves dye, 0.0022 mW/cm^2 for ivy gourd leaves dye and 0.0018 mW/cm^2 for spinach leaves dye.. The power conversion efficiencies (η) of the DSSCs were observed to be 2.88 % for bottle gourd leaves dye, 1.93% for ivy gourd leaves dye and 1.59 % for spinach leaves dye. The best performance was obtained for DSSC sensitized with bottle gourd leaves dye, where the efficiency of the cell reached 2.88%. It is expected that TiO_2-Cu_2O core-shell with natural colorant is cost-effective and eco-friendly DSSC.

Acknowledgements

We would like to thank Rector Dr. Tin Htwe and Pro-Rector Dr. Mar Lar, Hinthada University, for their kind permission to carry out this research work. This research was supported by Department of Physics, University of Yangon and Universities' Research Centre (URC), Yangon.

References

Agbo P. E, M. N. Nanbuchi, D. U. Onah, (2011). TiO_2/Fe_2O_3 core shell thin film for Photovolatic application, J of Ovonic Research, 7(2), 29-35.

Agbo P. E, (2012). "Temperature effect on the thickness and optical properties of core-shell TiO_2/ZnO crystalline thin films", Advances in Applied Science Research, 3(1), 599-604.

Al-Alwani M. A. M., Mohamad A. B, Kadhum A. A. H, Ludin N. A, Ba-Abbad M. M, (2014). Effect of Solvents on Natural Dyes Adsorption on the Surface of TiO_2 Film for Dye- Sensitized Solar Cell" , Australian Journal of Basic and Applied Sciences, 8(9), 34-37.

Chem L, S. Shet, Tang H,.Wang H, Yan Y, Turner J and.Al-Jassim M, (2010). "Electrochemical deposition of copper oxide nanowires photoelectrical applications", J. Mater. Chem, 20, 6962-6967.

Otakwa R. V. M, Simiyu, J, Waita, S. M., Mwabora J. M, (2012). "Application of Dye-Sensitized Solar Cell Technology in the Tropics: Effects of Air Mass on Device Performance", International Journal of Renewable Energy Research, 2 (3), 369-375.

O'Regan B & Grätzel M., (1991). "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films," Nature, 353 737–740.

Reddy P. S., Chetty G. R., Uthanna S., Naidu B. S., & Reddy P. J. (1991). Optical properties of spray deposited ZnO films. *Solid state communications*, 77, 899-901.

Smith H. M and Ekins-Daukes N. J., (2006). "Blueberry Electricity: An Experimental Introduction and Analysis of Fruit and Chlorophyll based Dye-Sensitised Solar Cells NSW A28" - School of Physics.

Vijay, B. S., & Pawar, B. H., (2011). Fabrication & Characterization of Nanostructured Zinc Oxide Thin Films, *Journal of Ovonic Research* , 7(4), 67 – 77.

Vaizogullar A. I & Balci A., (2014). "Snynthesis and Characterization of ZnO/SiO_2 core-shell Microprticles and Photolytic Studies in Methylene Blue", International J of Research in Chemistry and Environment, 4, 2248-2252.