

Transmittance and Band Gap Analysis of Dye Sensitized Solar Cell

Oviri O.K. and Ekpunobi A.J.

Physics Department, Faculty of Physical Sciences, Nnamdi Azikiwe University, P.M.B 5024, Awka, Anambra State, NIGERIA

Available online at: www.isca.in

Received 28th September 2012, revised 3rd October 2012, accepted 20th November 2012

Abstract

Transmittance which is the fraction of incident light at a specified wavelength that passes through a sample and energy band gap which is the energy difference between the conduction band and valence band are essential characteristics for analyzing the performance of a dye sensitized solar cell in relation to the solar energy absorbed. Anacardium occidentale dye which was used as the sensitizer gave a transmittance which increased gradually from the ultraviolet region through the visible range to the infrared region; having its peak and least values at 1099.15m and 299.87m of wavelength respectively. With a band gap of 3.271eV, the dye gave a value of 1.48eV. The possible significance of these findings is discussed.

Keywords: Dye sensitized solar cell; transmittance, photon energy, Anacardium occidentale.

Introduction

Since the advent of dye sensitized solar cell (DSSC), several scientists have engaged themselves in researches notably after Grätzel et al breakthrough in 1991¹. As shown in figure 1, a DSSC is composed of a nanocrystalline mesoporous photoanode-absorbed dye, a counter electrode and an electrolyte containing iodide and triiodide ions. Its operation is based on the working principle of the orthodox solar cell in which sunlight enters the cell through the transparent fluorine-doped tin oxide (FTO), striking the dye on the surface of the TiO₂. Photons striking the dye with enough energy will be absorbed to create an excited state of the dye, from which an electron can be injected directly into the conduction band of the TiO₂, and from there it moves by diffusion (as a result of an electron concentration gradient) to the clear anode. Meanwhile, the dye molecule has lost an electron and the molecule will decompose if another electron is not provided therefore, the dye strips one from iodide in electrolyte below the TiO₂, oxidizing it into triiodide. This reaction occurs quite quickly compared to the time that it takes for the injected electron to recombine with the oxidized dye molecule, preventing this recombination reaction that would effectively short-circuit the solar cell. The triiodide then recovers its missing electron by mechanically diffusing to the bottom of the cell, where the counter electrode re-introduces

the electrons after flowing through the external circuit. In DSSCs, the dye as a sensitizer plays a key role in absorbing sunlight and transforming solar energy into electrical energy. Several dyes ranging from metal complexes and organic dyes have been used as sensitizers but the highest efficiency of DSSCs achieved has been DSSCs sensitized by Ruthenium compounds absorbed on nanocrystalline TiO₂ with an efficiency of about 11–12%^{2, 3}. Although such DSSCs have provided a relatively high efficiency, there are several disadvantages of using noble metals in them; noble metals are considered as resources that are limited in amount, hence their costly production. On the other hand, organic dyes (anthocyanin dyes) are not only cheaper but have also been reported to reach efficiency as high as 9.8%⁴. However, organic dyes have often presented problems as well, such as complicated synthetic routes, low yields^{5,6} and a high transmittance (this is the fraction of incident light at a specified wavelength that passes through a sample). Due to their cost efficiency, non-toxicity, and complete biodegradation, natural dyes have been a popular subject of research. In this research work, the characterized transmittance, transmittance-absorbance relation and also the determination of the band gap energy level of the anthocyanin dye notably Anacardium occidentale which is used as the sensitizer will be analysed.

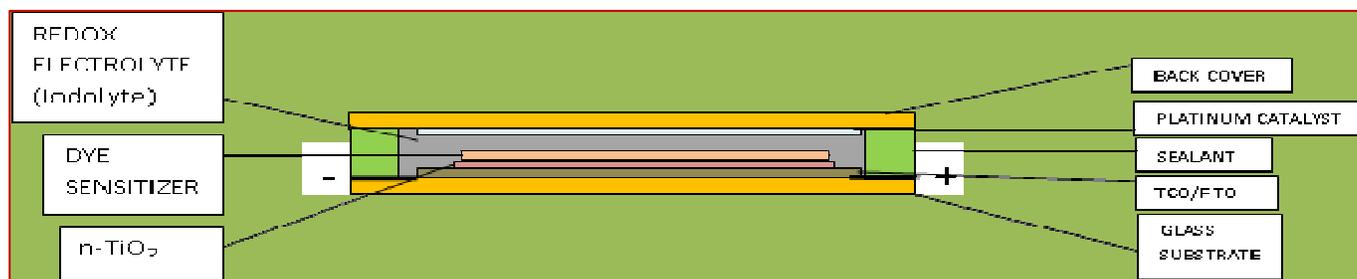


Figure-1

An assembled solar cell using anthocyanin dye sensitizer

Material and Methods

The conductive glass plates (FTO glass, fluorine-doped SnO₂, sheet resistance 15Ω/cm²) TCO22-15, the titanium oxide (TiO₂) nanopowder Ti-Nanoxide T37/SP (20 nm), Ti citrate complex (IV) solution and the electrolyte used is liquid electrolyte (Iodolyte PN-50). All reagents were of analytical grade and were used as received from Solaronix SA. Sensitizer which was chosen for this experiment is *Anacardium occidentale*.

Dimensioning of (TCO) Substrate: Dimensioning of (TCO) substrate transparent fluorine-doped tin oxide (FTO) coated glass substrates (Solaronix TCO22-15) with a sheet resistance 15Ω/sq, were used as substrates⁷. The conducting side of the glass was detected by the use of a multimeter as the non-conducting side does not give any reading. Alternatively, the side that feels hazy when passing gently with the finger is the conducting side of the glass. The TCO glasses were not handled with bare fingers rather with hand gloves to avoid contamination. The 5cm by 5cm substrate was cut into 2.5cm by 2.5cm by the use of glass cutter. Hence the cell active area of the substrate is 3mm by 14mm (0.42cm²).

Preparation of Electrodes: In the preparation of the photo anode which consists of several layers, the blocking layer is the first of such layers to be deposited. The blocking layer was prepared by spin coating⁸ the obtained Ti citrate complex (IV) solution deposited on the FTO firstly at 300rpm for 10sec to disperse it and then coated at 3000rpm for 60sec. In this manner, two layers were deposited with each of the layers being tested by a multimeter respectively to see if it reads. Each layer was followed by a heat treatment at 300°C for 10min after the final layer, the film is sintered at 450°C (15°C/min) in a carbolyte tubler furnace for 30min and thereafter, allowed to cool down uniformly. The blocking layer was introduced to block or reduce back recombination reactions. Subsequently, place the FTO (after the blocking layer application) unto the screen printer⁹ for the application of the nanocrystalline n-TiO₂. The deposition was done by screen printing from a 70 count polyester mesh. Two such layers were sufficient to give a film thickness of 7.6μm. The film was sintered in air for 30min at 450 °C. After the deposition of the nanocrystalline TiO₂, propan-2-ol (BPH-ANALAR) was used to clean the remnant of the n-TiO₂ on the screen printer in order to pave the way for the deposition of the scattering layer. The scattering layer is composed of the deposition of the n-TiO₂ (Solaronix D37/SC) using the screen printer on the n-TiO₂ layer (Solaronix T37/SP). After the screen printing, it was heated gently with an electric heater at 100°C for 10mins so as to get the layer dried. Thereafter, the screen printed FTO was loaded into the furnace and heated to 450°C for 30mins. The thickness was confirmed by a profilometer (DECTAC).

The counter electrode was prepared using doctor blade method¹⁰. A multimeter was used to test the surface of the FTO glass to determine the conductive surface. After then, I mapped

out an area equal to the active area on the photoanode with a celotape. A platinum catalyst gel (Solaronix Pt-Catalyst T/SP) unto the area mapped out on the conductive glass (Solaronix FTO), before drying at 100 °C for 10 min on an electric heater and firing at 450 °C for 30 min in the furnace. After heating, put off the furnace and let it cool down uniformly to prevent the cracks on the deposit.

Preparation of dye Sensitizer Solution: Fresh cashew-bark was crushed in a porcelain mortar with little quantity of distilled water added to increase the fluid content. The resulting extract was filtered, placed in a petridish and used immediately without further purification.

Sensitizer Impregnation Using *Anacardium occidentale*: The sintered photo anode, a little bit warm, was slowly immersed (its face-up) in the dye extracted; and kept at room temperature overnight in a petri-dish to complete the sensitizer uptake. It was subsequently rinsed with ethanol and dried.

Assembling of DSSC: The dye sensitized solar cell (DSSC) was assembled accordingly by the procedure outlined below: the photoanode was pressed against the platinum coated counter electrode in such a way that the conductive surfaces of both the photoanode and counter electrode were placed against each other to enable electrical connection. The cell was sealed by a 25μm thick surlyn polymer foil (Solaronix Meltonix 1170-25PF). Sealing was done by keeping the structure under a hot-press iron at 140°C for 15-30 seconds. The liquid electrolyte Iodolyte AN-50 (composed of ionic liquid, lithium salt, pyridine in acetonitrile solvent) was introduced by using a pipette into the cell gap through a slit cut into opposite ends during sealing of the cell with the hot melt foil. The gap was then covered with epoxide based glue.

Measurements: The transmittance spectrum of the dye and FTO glass were recorded on a Perkin-Elmer L20 spectrophotometer; cell active area was 0.42cm². Thickness measurement of 7.6μm were obtained with a Dectac Profilometer, sheet resistance of 13.4726Ω/sq was obtained with a four point probe. The cell was characterised for their electrical performance in the dark by a digital Keithley 236 multimeter connected to a computer and photocurrent measurement were carried out by using a class A solar simulator, (orieel 6) at air mass 1.5(AM1.5) and irradiance (100W/cm²).

Results and Discussion

In optics and spectroscopy, transmittance is the fraction of incident light (or other electromagnetic radiation) at a specified wavelength that passes through a sample^{11, 12}.

In equation form,

$$T_{\lambda} = \frac{I}{I_0} \quad A_{\lambda} = \frac{I_0 - I}{I_0} \quad (1)$$

where I_0 is the intensity of the incident radiation and I is the intensity of the radiation coming out of the sample and T_λ is the transmittance. The transmittance of a sample is sometimes given as a percentage. It is related to the absorbance A of same sample by the equation 2 below.

$$A = -\log_{10} T_\lambda = -\log_{10} \left(\frac{I}{I_0} \right) \quad (2)$$

Figure 2 and 3 shows the transmittance exhibited by the anthocyanin dye as well as the n-TiO₂. At a range of 300nm – 400nm within the ultraviolet region, the dye as well as the n-TiO₂ FTO exhibited a low value of transmittance but increased gradually through the visible region and obtained maximum values at the infrared region respectively¹³. This tells us that more of the incident radiation at the infrared region passed through the samples without being adequately absorbed as against that witnessed in the ultraviolet-visible range.

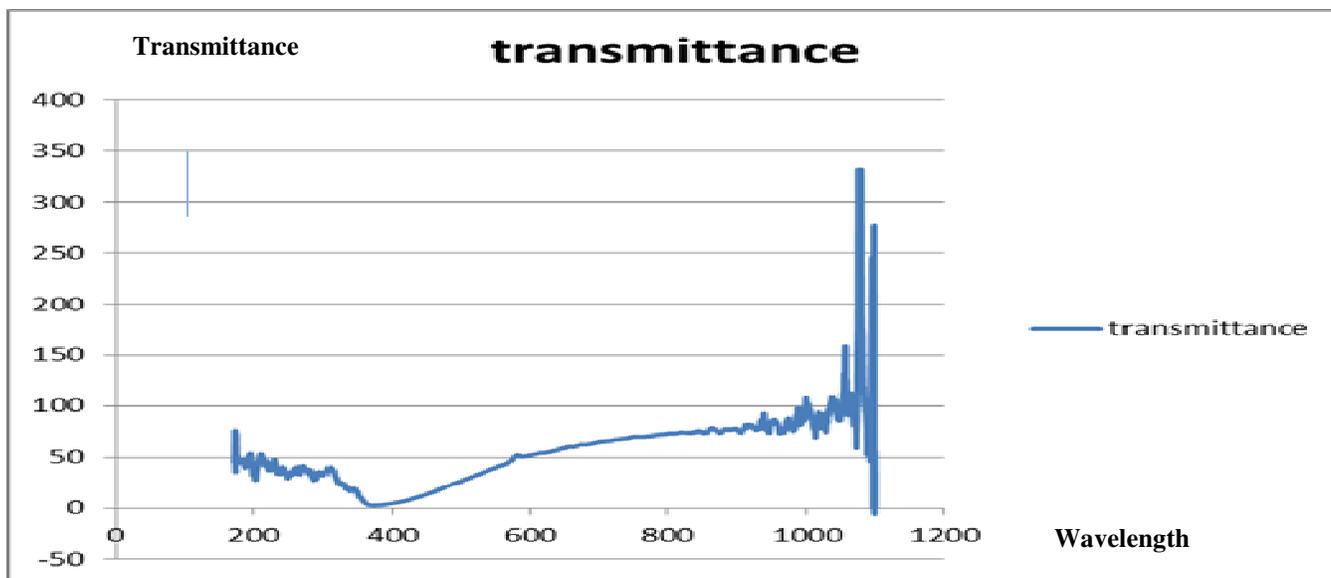


Figure-2
 Transmittance of the anthocyanin dye

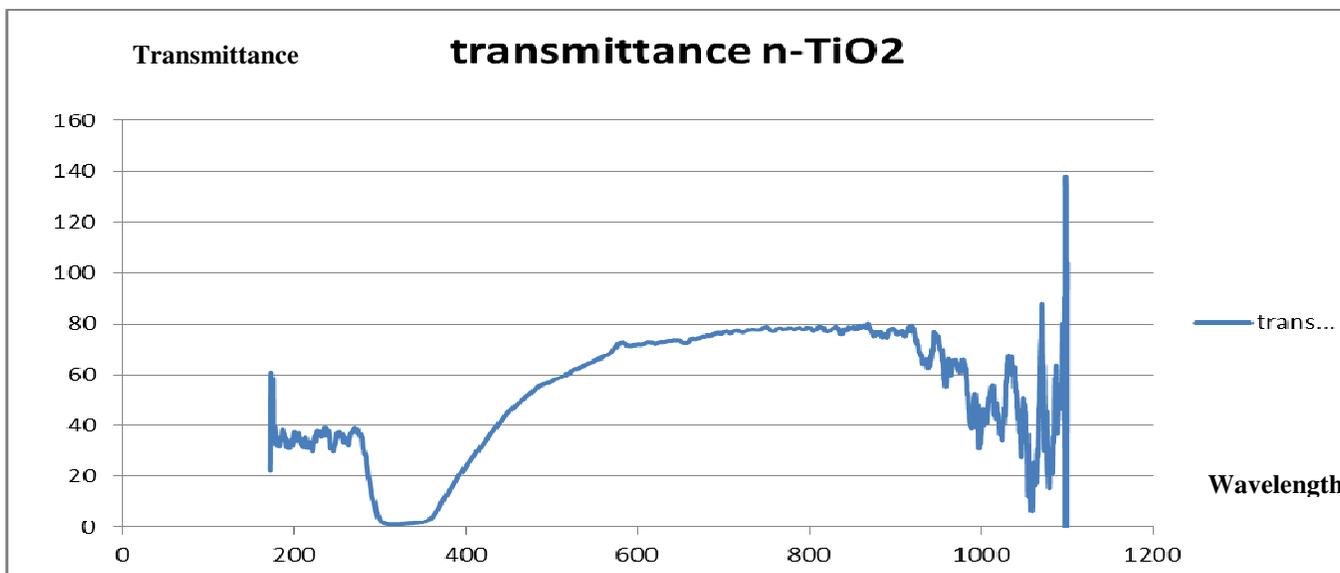


Figure-3
 Transmittance of n-TiO₂ FTO Glass

Determination of Band Gap of Dyed TiO₂

$$E = hv$$

$$= \frac{hc}{\lambda} \quad \text{-----} \rightarrow \quad \mathbf{3}$$

h is the planck's constant, v is the frequency, λ is the wavelength and c is the speed.

The numerical value of the symbols is: h = 6.63 x 10⁻³⁴J.s, c = 3.0 x 10⁸m/s, 1eV = 1.60 x 10⁻¹⁹J, E = photon energy

For example, taking the approximate values for the wavelength from a range of 200nm – 900nm we have the following values for the photon energies.

Firstly taking λ = 200nm = 200 x 10⁻⁹m and substituting it into equation 3 above consecutively, we obtain the respective energy.

$$E = \frac{6.63 \times 10^{-34} \times 3.0 \times 10^8}{200 \times 10^{-9} \times 1.6 \times 10^{-19}}$$

$$E = \frac{1.989 \times 10^{-25}}{3.2 \times 10^{-26}}$$

$$E = 6.22\text{eV.}$$

The corresponding photon energies for other wavelengths are shown in table 1 below.

Absorption Coefficient: The absorption coefficient determines how far into a material, light of a particular wavelength can penetrate before it is absorbed¹⁴. The absorption coefficient of the respective wavelengths is obtained by the division of the absorbance with the wavelength.

Taking λ = 200nm

$$\text{Absorption coefficient } (\alpha) = \frac{0.46558}{200 \times 10^{-9}}$$

$$= 2.3279 \times 10^6 \text{ m}^{-1}$$

$$\text{Absorption coefficient square } (\alpha^2)$$

$$\alpha^2 = 5.41912 \times 10^{12} \text{ m}^{-2}$$

Taking a look at the graph in figure 4, it can be seen that it has its peak at 3.271eV of photon energy which falls within the band gap range by Wunderlich et al (2005) that epitaxial anatase TiO₂ normally falls within the band gap range of 3.20-3.51eV¹⁵. With a deduction from the graph, the Anacardium occidentale dye has an energy band gap of 1.48eV which has aided in the reduction of the band gap of the n-TiO₂.

Figure 5 below shows relationship between the photo energy and wavelength. From the graph, it can be seen that as the photo energy decreases, the wavelength increases from the ultraviolet region to the infrared region.

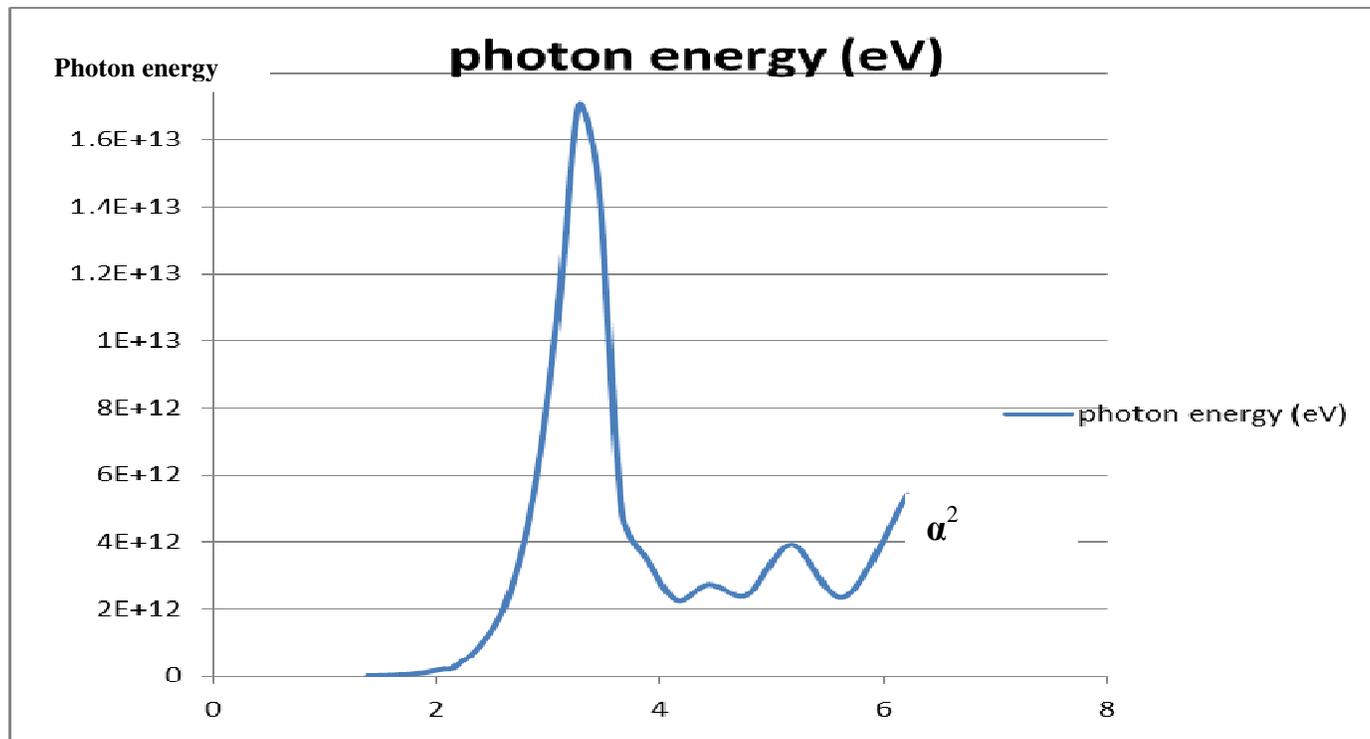


Figure-4
 A graph showing the relationship between photon energy and absorption coefficient squared α²

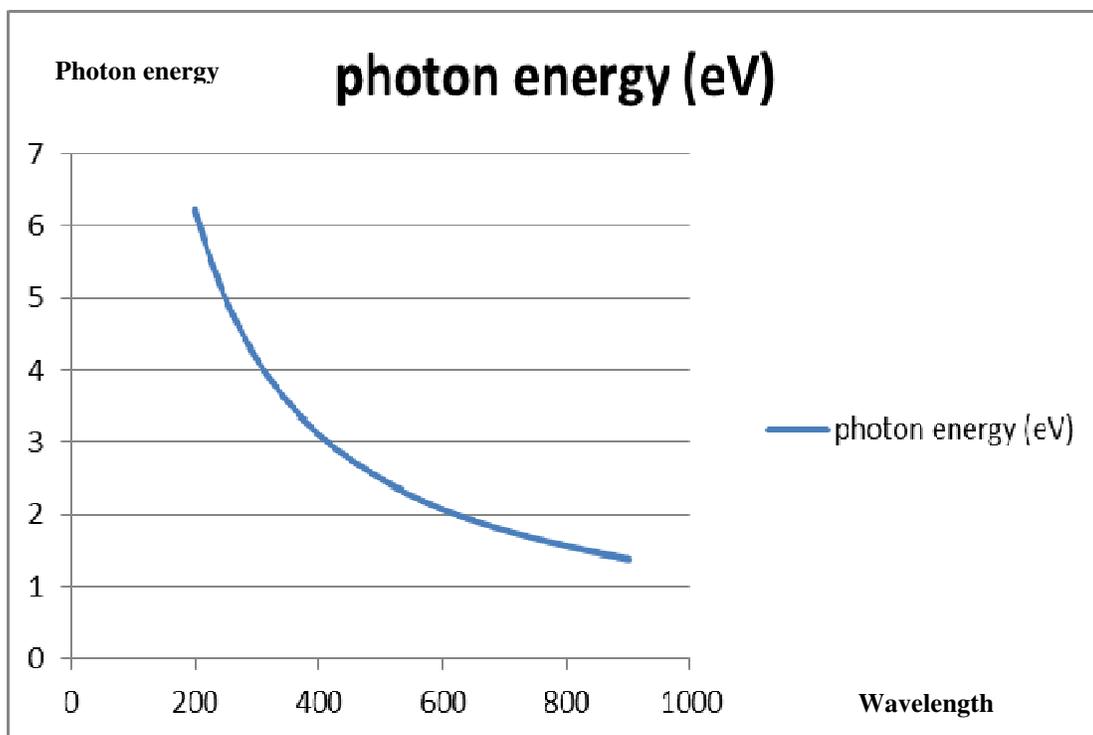


Figure-5
Photon energy against the wavelength

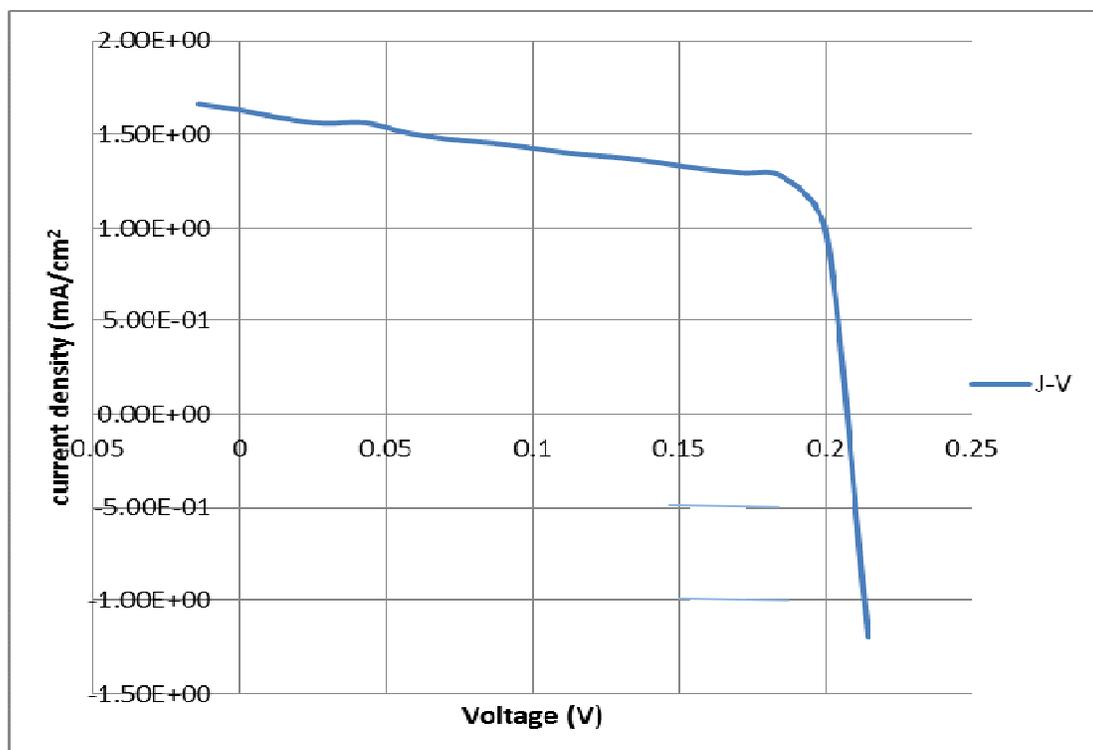


Figure-6
Photocurrent-voltage (I-V) curve of the DSSC

Table-1
The values of Photon energy of the respective wavelengths of the Anacardium occidentale dye

Wavelength (nm)	Absorbance	Absorption Coefficient $\alpha \times 10^6$ (m^{-1})	Absorption Coefficient $\alpha^2 \times 10^{12}(m^{-2})$	photon energy (eV)
200	0.465580414	2327902.068	5.41913E+12	6.216
220	0.338111627	1536871.032	2.36197E+12	5.651
240	0.475538966	1981412.357	3.92599E+12	5.18
260	0.404889744	1557268.247	2.42508E+12	4.781
280	0.463315327	1654697.598	2.73802E+12	4.44
300	0.45164744	1505491.467	2.2665E+12	4.144
320	0.598547761	1870461.752	3.49863E+12	3.885
340	0.74802129	2200062.617	4.84028E+12	3.656
360	1.380332861	3834257.948	1.47015E+13	3.453
380	1.567768514	4125706.617	1.70215E+13	3.271
400	1.356083666	3390209.164	1.14935E+13	3.108
420	1.138597032	2710945.315	7.34922E+12	2.96
440	0.950549382	2160339.504	4.66707E+12	2.825
460	0.798548251	1735974.458	3.01361E+12	2.702
480	0.66464241	1384671.687	1.91732E+12	2.59
500	0.573407418	1146814.835	1.31518E+12	2.486
520	0.495270948	952444.1315	9.0715E+11	2.391
540	0.421670292	780870.9114	6.09759E+11	2.302
560	0.370906552	662333.1283	4.38685E+11	2.22
580	0.284197146	489995.0797	2.40095E+11	2.143
600	0.282379419	470632.3646	2.21495E+11	2.072
620	0.264800452	427097.5025	1.82412E+11	2.005
640	0.242983765	379662.1332	1.44143E+11	1.942
660	0.217821305	330032.2801	1.08921E+11	1.884
680	0.207615315	305316.6402	93218250758	1.828
700	0.188652924	269504.1778	72632501877	1.776
720	0.177152233	246044.7674	60538027550	1.727
740	0.168405345	227574.7901	51790285102	1.68
760	0.155933081	205175.1071	42096824591	1.636
780	0.14838702	190239.7697	36191169961	1.594
800	0.140813651	176017.0633	30982006577	1.554
820	0.131238042	160046.3924	25614847728	1.516
840	0.127861216	152215.7333	23169629464	1.48
860	0.119735337	139227.136	19384195408	1.446
880	0.130826973	148667.0144	22101881173	1.413
900	0.12158162	135090.6892	18249494302	1.381

The cell gave an efficiency of 0.48% and a fill factor 0.56 and a short circuit current of 1.63mA/cm².

Conclusion

The Anacardium occidentale sensitized dye solar cell exhibited a high transmittance at the visible to infrared region which suggests that it absorbed lower photon energy at this range compared to the ultraviolet region. Semiconductor materials have a sharp edge in their absorption coefficient, since light which has energy below the band gap does not have sufficient energy to excite an electron into the conduction band from the valence band; consequently, this light is not absorbed. This

shows that if Anacardium occidentale dye is mixed with co-absorbents which will have low transmittances and low band gap energies in the visible to infrared region, a higher cell performance will be achieved in terms of efficiency of the cell. Further studies will be focused on identifying the effects of using co-absorbents on the sensitizer.

Acknowledgement

I give my gratitude parents Mr and Mrs E.A Oviri, Dr E.E Uduaghan (Governor of Delta State) for their financial support for my research work and Prof A.J. Ekpunobi for his supervisory role on my research work. I pray almighty God continue to bless them in all their endeavours.

References

1. O'Regan B. and Grätzel M., A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO₂ Films, *Nature*, **353 (6346)**, 737–740 (2011).
2. American Chemical Society., Ultrathin, Dye-Sensitized Solar Cells Called Most Efficient To Date, *ScienceDaily*, 20, 09, (2006)
3. Gao F. Wang Y., Zhang J., Shi D., Wang M., Humphry-Baker R., Wang P., Zakeeruddin, S.M. and Grätzel, M., A New Heteroleptic Ruthenium Sensitizer Enhances the Absorptivity of Mesoporous Titania Film for a High Efficiency Dye-Sensitized Solar Cell, *Chemical Communications*, (23), 2635–7 (2008)
4. Zhang G., Bala H., Cheng Y., Shi D., Lv X., Yu Q. and Wang P., High Efficiency and Stable Dye-Sensitized Solar Cells with an Organic Chromophore Featuring a Binary Conjugated Spacer, *Chem. Communication*, 2198–2200 (2009).
5. Tributsch H., Dye Sensitization Solar Cells. A Critical Assessment of the Learning Curve, *Coordination Chemistry Reviews*, **248**, 1511 (2004)
6. Haiying W., Dye Sensitized Solar Cells, University of Alabama Department of Chemistry (2002)
7. <http://www.solaronix.com/products/electrodes> retrieved 05, 08, (2012)
8. Dirk S. W. and Thomas D., Spin Coating From A Molecular Point of View, Its Concentration Regimes, Influence of Molar Mass and Distribution, *Materials Research Innovations*, **7**, 314 (2003)
9. http://en.wikipedia.org/w/index.php?Title=Screen_printing&oldid=495168421, Retrieved 08, 05, (2012)
10. Paul D. and Fleming L., The Gravure Doctor Blade. Gravure Printing, (2012)
11. IUPAC handbook definition, Retrieved, 10, 09, (2012).
12. CRC Dictionary of pure and applied physics, CRC Press, Editor: Dipak Basu (2001)
13. Michael B., Nanowires Could Lead to Improved Solar Cells , *NewsWireToday*, 03, 06, (2006)
14. <http://www.pveducation.org/pvcdrom/pn-junction/absorption-coefficient>, Retrieved 15, 09, (2012)
15. Wunderlich W., Ohta S., Ohta H., and Koumoto K., Effective Mass and Thermoelectric Properties of SrTiO₃-Based Natural Superlattices Evaluated by Ab-Initio Calculations, 252 (2005)