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Decay Nature of Efficiency over Time in Unsealed Aging Dye-Sensitized Solar Cell.

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Abstract: *Dye sensitized solar cell (DSSC), a third generation photovoltaic cell that mimics photosynthesis process were fabricated in this study using natural and synthetic dyes. The cells were operated under the same solar irradiance condition in an open field in the peak of dry season in Ado-Ekiti for a period of 20 consecutive days during which there is no rain/snow but sunshine with a fairly constant solar radiation of about 5.75kwh. Laboratory investigation carried-out under simulated (AM1.5, 100 mW/cm^{-2}) spectrumusing appropriated filters revealed that DSSCssensitized with synthetic and natural dyes exhibited efficiencies of 6.90 and 1.60 respectively. However, under open field operations, the natural dye prototype exhibits highest power output while the synthetic dye prototype exhibits great resistance to degradation and aging.*

Keywords; *photovoltaic, photosynthesis, solar irradiance, efficiency, prototype, aging.*

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I. Introduction

Dye-sensitized solar cell (DSSC) has become one of the most promising alternatives for the photovoltaic conversion of solar energy as compared to the conventional solid p-n junction photovoltaic devices[1] and are currently undergoing rapid development in an effort to obtain robust, efficient, and cheap devices that could cater for the rapid increase in the world energy demand. Beside, most solar cells available commercially that are based on inorganic silicon semiconductors are made of p-n junctions-which are relatively expensive to manufacture,apart from this, the manufacturing process releases harmful emissions to the environment thereby causing pollution[2] . Another advantages of DSSC are that; it can be engineered into flexible sheets, low cost of sensitization material production, ease of fabrication and low process temperature.
Due to the low cost of the overall production of DSSC, it has been expected that the DSSC type of solar cell will give a higher return of investment when compared to Silicon based solar cell.

Consequently, concerted effort has been divertedto the development of DSSCs based on nanoporous films of highband gap semiconductorsin recent years [3,4,5] although the energy conversion efficiencies are reasonable,the practical application requires resolution offabrication problems and improvement of the long-termstability. One of the main problem is encapsulation of the cellwith a liquid electrolyte. Completely foolproof sealingis a bit difficult, and the loss of volatile components in theelectrolyte cannot be totally ensured. The problem is aggravatedby a build up of pressure inside the cell dueto gaseous degradation products of the electrolyte. The performance of DSSC is mostly determined by the type of dye used as sensitizer. The efficiency of DSSC depends on the absorption spectra of the dye and its anchorage to the TiO_2 surface [7]. Synthetic inorganic compounds (ruthenium polypyridyl complexes) are one of the most effective sensitizers commonly engaged in DSSCs because of their high conversion efficiency, excellent chemical stability, and intense charge-transfer absorption in the entire visible light spectrum [8]. However, these complexes contain metals, which are relatively expensive and hazardous to the environment [9, 10], as such many types of natural organic dyes extracted from both root and shoot systems of various species of plants have been actively studied and tested as low cost alternative materials to replace rare and expensive ruthenium dyes [11,12,13,14,15].

Natural plant dyes can be extracted through simple procedures. These type of dyes have been a subject of various studies because of their cost efficiency, environment friendliness, non-toxicity and availability. However, natural dyes as sensitizers in DSSCs perform poorly because of weak binding capabilities to the surface of the wide –bandgap semiconductor oxide film; this in no small measure reduces excited electron transfer from the sensitizer to the conduction band of the porous film [16]. In this study, DSSCs of effective light exposure window of 1cm^2 were prepared using both synthetic and natural dyes and subjected to the same condition of solar energy conversion . Investigation on their open- field- performances was carried out over a period of twenty dayswithin the dry season during which Other parameters of DSSC necessary to facilitate the determination of efficiency were measured.

1.1 Experiment site location;

Ado –Ekiti where this investigations were carried-out is located within the southern Nigeria. It is on latitude 7.62° and longitude 5.22°E on the globe. Like the entire region within west Africa, there are two seasons; the wet and dry seasons, which differ by the level of precipitation, temperature, and humidity, with wet season recording higher precipitation, humidity, and lower temperature than the dry season. The wet season usually spans from April to September while the dry season lasts from October to March of the succeeding year[19]. The investigation reported in this paper was carried-out in the month February when the chosen location was favoured with abundant daily sunshine.

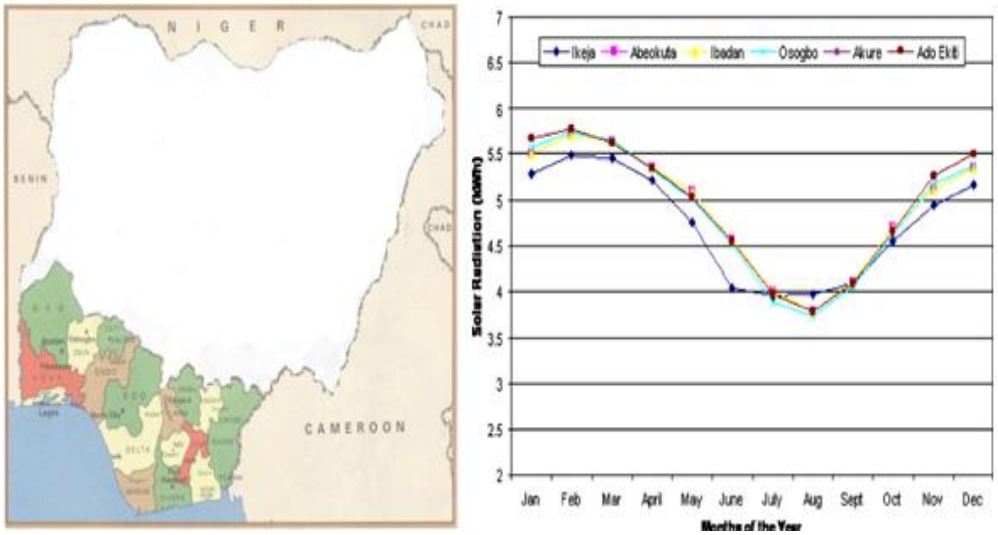


Figure 1. (a) Map of Nigeria showing the station locations. (b)NASA horizontal surface solar radiation in south western Nigeria[19].

II. Dye Preparation: This was done in two folds

2.1 Preparation of natural dye.

The efficiency of a cell depends largely on the homogeneity of the natural dye extract, in addition the desirable dye molecule should meet certain criteria such as matching with the solar spectrum and equally have a long-term operational stability. In order to achieve this desired homogeneity, vegetable samples of *Hibiscus sabdariffa*was extracted through a very rigorous process. First, the samples were washed with distilled water, cut into smaller pieces and finely blended. The blended samples were then filtered and the filtrate centrifuged to obtain a homogeneous dye extract.Few drops of the hydrochloric acid were added to the extract, this treatment which induces a pH=1.70 has been reported to cause a red shift in the absorption of the anthocyanins on the order of tens or nanometers (17). The dye was used as prepared.

2.2 Preparation of synthetic dye.

To prepare a synthetic dye that matches the experimental thresholds (i.e; strong light absorbsion , high solubility in organic solvent, sufficiently high LUMO, sufficiently low HOMO, high thermal and chemical stability) .One of the mostly widely used candidate that fit these threshold is N719 or cis-di(thiocyanato)-bis(2,2′-bipyridyl-4,4′-dicarboxylate) ruthenium(II)dye(Solaronix SA) .This was used as received.

2.3 Electrode Preparation:

2.3.1TiO_2 Photoanode

Fluorine doped indium tin-oxide (FTO) conductive glass sheets of dimensions 1.2 cm × 1.2 cm with sheet resistance of 15 Ω/cm^2 and transmittance>80% (Xinyan Tech. Ltd, Hong Kong) were first cleaned using an ultrasonic bath for 20 min, rinsed with distilled water, ethanol, and then dried.Thereafter, Strips of scotch tape (♯810, thickness 50μm) was fixed on the four sides of the hazing side of the conductive glass to restrict the thickness and area of TiO_2 paste to be deposited such that area of about 1x1cm^2 is made available for the spreading of TiO_2 paste .

The main property that makes TiO_2 a very useful material in this investigation is that it is highly hydrophilic that is, it has the particularity of dissociating the water it absorbs. The TiO_2 paste was prepared by blending commercial TiO_2 powder (0.2 g) , nitric solution (0.1M) of 0.4 ml, polyethylene glycol (0.08 g) and one drop of a non-ionic surfactant, Triton X-100. The mixture was well mixed in an ultrasonic bath for 50 minutes to ensure complete dispersion of TiO_2 nanoparticles.

Droplets of the paste were placed onto the prepared FTO glass arranged on the turn-table of a spin coater. The spin coater was operated for about 10 seconds to facilitate uniform spreading of the colloid on the FTO glass. Thickness of the TiO_2 film was controlled by multiple coating processes in which the coated substrates were subjected repeatedly to spin-coating and drying steps.

The prepared TiO_2 film was sintered at 450^0C for 30 minutes in open ends-cylindrical furnace to enhance the film/ TiO_2. particles compactness and crystallinity as the vehicle of the paste burns away. After sintering, the films were allowed to cool in-step naturally to avoid glass cracking and then kept in a desiccator for a later use.

2.3.2 PtCounter anode

Platinum (Pt) counter electrodes were fabricated by spreading a drop of 5 mM chloroplatinic acid hexahydrate ($H_2PtCl_6.6H_2O$) in isopropyl alcohol onto the FTO hazing surface followed by heating at 450^0C for 30 minutes. Pt- electrode is preferred because it has resistant to corrosive attacks by the redox couple (I^-/I^{-3}) beside,it facilitates a reversible redox reaction to occur in the cell during operation. Since only very small quantity of Pt is been used in making the counter electrode, this still reduces its cost at the same time maintaining its transparency for photon entry during field operation.

2.4 redoxElectrolyte

This was prepared from a combination of 0.6M butylmethylimidazolium iodide (BMII), 0.05 M I_2, 0.1 M LiI, and 0.5 M tert-butylpyridinein 1:1 acetonitrile/valeronitrile .

2.5 Open configuration assembly

Two TiO_2 – photoanodes were used as prepared; one was soaked in the natural dye and the other in the synthetic dye and both left to chemo- adsorbed dye for thirty minutes. Afterdye-impregnation, they were removed and the excessive dye wash with ethanol and then dried with hot air from hair-drier machine .

Two DSSCs were assembled by putting each dye sensitized photoanode against the Pt-counter electrodes such that the stained Titania/photoanode faced the platinum / counter-electrode forming the inside of the cell. However, care was taken to slightly shift the two glass plates in order to leave room for electrical contacts. then two similar binding clips were used to hold the electrodes together in each case. Immediately, the DSSCs cell formed were filled with a couple of electrolyte drops in between the edges of the plates before getting damaged by ambient air.

The iodide solution on the free edges of the slides was Cleaned and copper tape was applied to exposed edges of the positive and negative cell walls this in-turn helped to facilitate electrical contact.

Application of multimeter for the measurements of output power of the DSSCs is made possible by placing the alligator clips from the multimeter to each end of the exposed copper tape i.e; The negative electrode is the TiO_2 coated glass (the black wire is attached to this side), and the red wire to the Pt- coated glass slide which is the positive electrode. The solar cells were operated under solar radiation inopen field for the twenty consecutive days measurements.

II. Measurements

The total efficiency of dye sensitized solar cells depends on optimization and compatibility of each of its constituents especially between TiO_2 semiconductor and Dye molecules, the high surface area as well as the thickness of the TiO_2 semiconductor film usually facilitate an increased dye loading which consequently Improves electron transport in the DSSCs.

The spectral response of DSSC i.e, the relative efficiency of the DSSC's in detecting the light and absorbing the photons depends on the absorption properties the dye used. Therefore, the DSSC's efficiency is measured through the quantum yield for the overall charge injection process and is referred to as the Incident Photon to Electrical Conversion Efficiency (*IPCE*) . This quantity can be measured experimentally, in the laboratory using monochromatic light excitation.

$Isc = \int_0^{\infty} \mathrm{IPCE}(\lambda).Isum\lambda \ \mathrm{d}\lambda$ 1.1

Where; $IPCE = 1240(Isc/\lambda\varphi)$

I_{sum} : is the incident irradiance as a function of the wavelength λ.
Isc: is the current at short circuit (mA/cm²).
Φ: is the incident radiant flux (W/m^2).

In this investigation , the photocurrent under closed circuit I_{SC} is measured over the entire solar spectrum .The overall sunlight to electric power conversion efficiency of a DSSC is expressed in terms of the key performance parameters (*Isc*, *Voc*, *FF*) of the solar cell as;

$$\eta = \frac{P_{max}}{P_{in}} = \frac{I_{sc}.V_{oc}.FF}{P_{in}} \quad 1.2$$

Where;
FF: is the Fill Factor is the defined ratio $I_{max}.V_{max}/I_{sc}.V_{oc}$
P_{in}: Solar Power Input into the solar cell.
V_{oc}: The voltage across the open circuit.
Alternatively, the power output(P_{out}) and efficiency of the DSSCs could be derived from ;

$$P_{out} = V_{max}.\ I_{max} \quad \mathbf{1.3}$$

Where; V_{max}= Maximum potential difference / Voltage (daily maximum recorded Voltage).
I_{max}= Maximum Current (daily maximum recorded current in mA).
and the Overall Efficiency (η) $\eta = \frac{P_{max}}{P_{in}}$ 1.4
Where; *P_{max}= Maximum Power Output(P_{out}) obtainable and*
P_{in} = Power Input from the Sun
Also, **Power Difference(%) =** $\frac{\text{maximum } P_{out} - \text{minimum} P_{out}}{\text{maximum} P_{out}} x100$ 1.5

The direct radiation on the field was measured daily by pyrheliometerbetween 11:00am and 2:00pm on daily basis (i.e; within the daily 3 hours peak sunshine hours as determined by the sunshine hour recorder).

V. Results And Discussions

The photoelectrochemical parameters determinedunder simulated (AM1.5, 1000W/cm^{-2}) / direct solar spectrum with the aid of Newport/Oriel solar simulator, model 91160 (using appropriated filters) revealed *Efficiencies of* 1.60 and11.38 for DSSCs sensitized with *hibiscus sabdariffa dye and* Synthetic dye (N17) respectively.

This shows a significant dye adsorption resulting in enhanced *J*sc, and retarded charge recombination efficiently, leading to enhanced *V*oc in the synthetic dye sensitized DSSC more than the natural dye sensitized cell. This yielded a significantly improved power conversion efficiency.

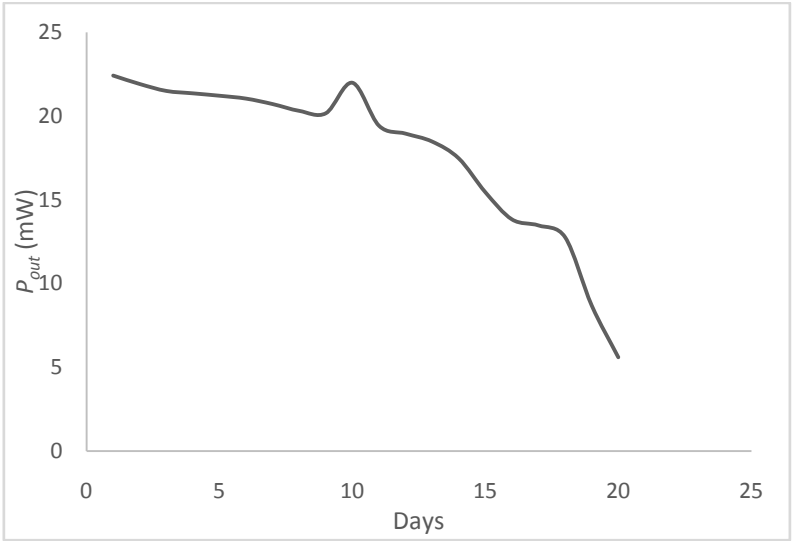
However , in open field operation the results obtained for the twenty consecutive days are displayed below;

Table 1.1. Outdoor Photochemical Data For DSSC Sensitized With Synthetic Dye

Day	Current Measured (mA)	Voltage Measured (V)	P_{out} (mW)
1	4.212	5.320	22.408
2	4.204	5.210	21.903
3	4.125	5.210	21.491
4	4.113	5.190	21.348
5	4.102	5.170	21.204
6	4.100	5.130	21.033
7	4.052	5.110	20.706
8	4.012	5.060	20.301
9	4.008	5.030	20.160

10	3.952	5.560	21.978
11	3.912	4.962	19.411
12	3.842	4.930	18.941
13	3.752	4.922	18.467
14	3.622	4.821	17.462
15	3.321	4.650	15.443
16	3,120	4.430	13.823
17	3.104	4.337	13.462
18	3.066	4.160	12.755
19	2.600	3.340	8.684
20	2.421	2.310	5.593

For DSSC Sensitized WithSynthetic Dye,the current goes from 4.212 mA on the first day to 2.421 mA on the twentieth day .Similarly, the Voltage drops from 5.320 V in the first day to 2.210 V in the twentieth day. The decay nature of these parameters give a power difference of 75.04% .The Net Power Output with respect to time /20 day duration is as depicted in ‘‘fig 1’’



The average net power output for this sample is 17.8285mW from which the Overall Efficiency is obtained as $\boldsymbol{\eta}$=**7**.43%

4.1 For naturally sensitized DSSC;

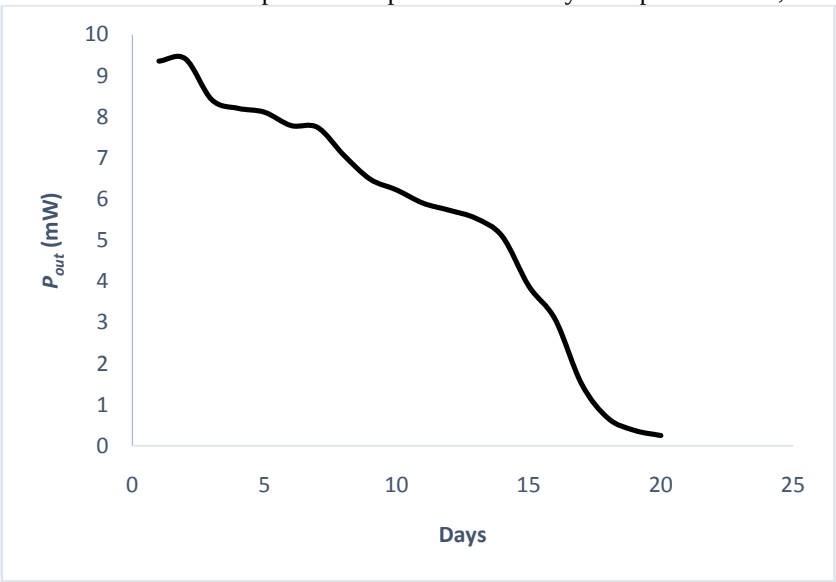
Hibiscus sabdariffa extracts corresponding to anthocyanins, becausethe chemical adsorption of these dyes occurs dueto the condensation of alcoholic-bound protonswith the hydroxyl groups on the surface ofnanostructured TiO_2 [18].

Table 1.2 Outdoor Photochemical Data For DSSC Sensitized With Natural dye Dye

Day	Current measured (mA)	Voltage measured (V)	Power Output (mW)
1	2.515	3.720	9.356
2	2.510	3.750	9.413
3	2.325	3.620	8.417
4	2.312	3.550	8.208
5	2.305	3.520	8.114
6	2.271	3.430	7.790
7	2.252	3.440	7.747
8	2.129	3.320	7.068
9	2.012	3.223	6.485
10	2.000	3.112	6.224
11	1.954	3.021	5.903
12	1.910	3.000	5.730
13	1.852	2.988	5.534
14	1.786	2.852	5.094
15	1.542	2.522	3.889
16	1.320	2.332	3.078
17	0.750	2.012	1.509
18	0.735	0.920	0.676
19	0.422	0.900	0.380
20	0.030	0.850	0.255

For the DSSC sensitized with *Hibiscus sabdariffa extract*the performance is depicted on table2, the current goes from 2.515 mA on the first day to 0.030 mA on the twentieth day. The Voltage drops from 3.720 V in the first day to 0.850 V in the twentieth day. This gives a power difference of 97.27**%**

The Net Power Output with respect to the 20 days is represented as ;



From table 2, the average net power output for this sample is 5.6658mW from which the Overall Efficiency is obtained as $\boldsymbol{\eta}$=2.36%

In conclusion, from the results displayed above one can clearly conclude that the N17 dye sensitized DSSC exhibits the highest Net Power Output values and the highest efficiency

One can also conclude that using synthetic dye significantly slows down the aging of the solar cells as revealed in the power difference of the cell sample. However, it does decreases the efficiency, compared to natural dye. Also, the overall efficiency of the Natural Dye sensitized DSSC is 2.36% and that of the Synthetic Dye prototype is 7.43% , this gives a significant difference of 5.07%. Therefore, in terms of efficiency , this attested to the fact that the N17 dye in DSSC has better ; intense charge – transfer absorption in the whole visible range, long excited lifetime, highly efficient metal – to – ligand charge transfer (MLCT) and conversion efficiency compared with natural dye sensitized DSSC. The results also shows that sealing or encapsulation of DSSC is significant .This greatly ensures the confinement of electrolyte in the cell and prevents air and moisture from entering as this could easily damage the electrodes. Although sealing is a bit difficult but the loss of volatile components in the electrolyte would be totally ensured ,a sealed DSSC can operate for an undetermined period of time when assembled correctly.

III. Conclusion

The synthetic dye DSSC exhibits a slower degradation to aging factor compared to the natural-dye DSSC. This gives an opening to further research to produce a dye that can resist degradation and aging while performing in the high end of the overall efficiency spectrum.Moreover, solvent evaporation and degradation under unsealed-cell condition may limit the long-term durability of the cell, so also high operating temperatures may enhanced the volatility of the solvent within the cell, and sometimes diffusion may limit the kinetics under high light intensities. All these could be eye-opener for further research in this discipline as well.

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References

[1]. Gra¨tzel, M. Nature, 414, 2001, 338-344.
[2]. Chen1. Y. S., Lee J. N., Tsai S. Y. and Ting C. C., Mater. Sci. Forum594, 2008, 324 - 330 .
[3]. Wongcharee, K., Meeyoo, V., Chavadej, S.: Dye-sensitized solarcell using natural dyes extracted from rosella and blue peaflowers. Sol. Energy Mater. Sol. Cells, 91(7), 2007, 566–571 .

[4]. Gra¨tzel, M.: Dye-sensitized solar cells. J. Photochem. Photobiol.C 4, 2003,145 .
[5]. Aduloju KelvinAlaba .Utilizing Dye Sensitization Potency OfBixaOrellana.Lseed and PlumeriaRubra.Lflower In Dye Sensitized Solar Cell. IOSR Journal of Engineering , Vol. 7, Issue 11 ,November 2017), 37-42.
[6]. WongchareeK., Meeyoo V. and ChavadejS., Sol. Energy Mater. Sol. Cells, 91 , 2007, 566.
[7]. ShahidM., Islam S. and MohammadF., J. Cleaner Prod.,53 , 2013, 310.
[8]. S. Hao, J. Wu, Y. Huang and J. Lin, Sol. Energy, 80 ,2006, 209.
[9]. H. Chang, H.M. Wu, T.L. Chen, K.D. Huang, C.S. Jwoand and Y.J. Lo, J. Alloys Compd., 495 (2010) 606.
[10]. ParkK.H., YoungK.T., Young P.J.,. Mei J.E, HoY.S., Young C.D. and WookL.T., Dyes Pigm., 96 , 2013, 595.
[11]. Aduloju K.A, Shitta M. B.O and Simiyu J . Effect of extracting solvents on the stability and performances of dye-sensitized solar cell prepared using extract from lawsonia inermis. Fundamental J. Modern Physics, 1(2), 2011,261-268.
[12]. KayA., Gra¨ tzelM., PhysJ.,Chem. 97 , 1993, 6272.
[13]. CherepyN.J, SmestadG.P, GratzelM., ZhangJ.Z, Ultrafast electron injection: implications for a photoelectrochemical cell utilizing an anthocyanin dyesensitized TiO_2 nanocrystalline electrode, J. Phys. Chem. B 101 , 1997, 9342.
[14]. SmestadG.P., Gra¨ tzelM., J. Chem. Educ. 75 , 1998, 752.
[15]. Aduloju K.A. khaya senegalensis and solanum melongena linn. As natural sensitizers for dye-sensitized solar cells. Scholars Research Library ; Archives of Applied Science Research, 3 (6), 2011,61-67 .
[16]. LudinN.A., Al-AlwaniM.A.M., MohamadA.B., KadhumA.A.H., Sopian K. and Abdul-KarimN.S., Renewable Sustainable Energy Rev. 31 , 2014, 386.
[17]. Calogero, G., Yum, J., Sinopoli, A., DiMarco, G., Gratzel, M., and Nazeeruddin, M. Anthocyannins and betalains as light-harvesting pigments for dye-sensitized solar cells. SciVerse Science Direct: Solar Energy86 ,2012, 1563-1575.
[18]. MengS., RenJ., KaxirasE., Nano Lett. 8 , 2008, 3266–3272.
[19]. Guardian Newspaper, Nigeria. November 4, 2010.
[20]. Guardian Newspaper, Nigeria. November 4, 2010.
[21]. Guardian Newspaper, Nigeria. November 4, 2010.
[22]. Guardian Newspaper, Nigeria. November 4, 2010.
[23]. Guardian Newspaper, Nigeria. November 4, 2010.
[24]. Guardian Newspaper, Nigeria. November 4,2010.
[25]. Victor Nnamdi Dike , Theo Chidiezie Chineke. Okey Nwofor, Ugo Okoro . Evaluation of horizontal surface solar radiationlevels in southern Nigeria .J. Renewable Sustainable Energy,3, 2011, 023101
[26]. David Martineau , Dye Solar Cells For Real-The Assembly Guide for Making Your Own Solar Cells. Solaronix SA, Rue de l'Ouriette 129, 2012, CH-1170 Aubonne. Switzerland

Aduloju KelvinAlaba. “Decay Nature of Efficiency over Time in Unsealed Aging Dye-Sensitized Solar Cell .” IOSR Journal of Applied Physics (IOSR-JAP) , vol. 10, no. 1, 2018, pp. 23-29.