Influence of dye pH on photoelectric properties of dye sensitized solar cells using natural dye extracted from red bougainvillea glabra flower

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Abstract— Dye-sensitized solar cells were fabricated using *bougainvillea glabra* flower dye extracts as natural dye sensitizers at three dye pH values of 1.23, 3.0 and 5.7. Water was used as dye extracting solvent. Dye-sensitized solar cells (DSSCs) from dye extract of pH 3.0 had the highest photocurrent density J_{sc} of 18.61 mA/cm^2 and highest fill factor FF of 0.60. While the Dye-Sensitized solar cells (DSSCs) from dye sensitizer pHs of 1.23 and 5.7 had photocurrent densities J_{sc} of 5.79 mA/cm^2 and 11.34mA/cm^2, and fill factors of 0.42 and 0.57 respectively. The maximum powers P_{max} of the DSSCs were 1.07, 4.91 and 2.85 for dye sensitizer pH of 1.23, 3.0 and 5.7 respectively.

Keywords—Dye sensitizes solar cell; Dye sensitizer; Bougainvillea glabra; pH

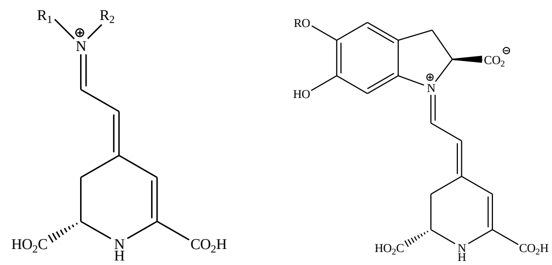
I. INTRODUCTION

Dye-sensitized solar cell (DSSC) was developed by Gratzel *et al.,* [1] and has attracted considerable attention due to its environmental friendliness and relative low cost of production [2]. Sensitizer dye in DSSC plays a key role in harvesting sunlight and transforming solar energy into electric energy and thus of paramount importance to photovoltaic cell performance and efficiency [3]. It attaches to the surface of a wide band-gap mesoporous semiconductor serving as electron transporter [4]. Ruthenium based dye sensitizers are very expensive and hard to prepare, which restricts their large-scale applications in solar cells, stimulating the search for alternatives such as natural dyes.

Anthocyanins from natural pigments and carotenoids have been used as natural dye sensitizers in DSSC and have shown low to modest solar energy conversion efficiencies [5-7]. These natural dyes are easy to prepare, cheap, non-toxic, environmentally friendly and easily biodegradable. Betalain is another interesting class of pigments, whose purified extracts from commercial sources have been subjected to photoelectrochemical study [8]. Betalains consisting of the yellow betaxanthins and red-violet betacyanins are a group of water-soluble nitrogen–containing alkaloid pigments characteristic of certain members of plant sub-order *chenopodineae* within *caryophyllales* and some higher fungi [9]. They absorb visible radiation over the range 476-600 nm, they are immonium derivatives of betalamic acid (the chromophore of all betalains) and divided into two structural groups: the red-violet betacyanins that has a maximum absorptivity at $\lambda \approx 535$ nm and the yellow-orange betaxanthins with maximum absorptivity at $\lambda \approx 480$ nm [10, 11].

Bougainvillea a source of betalain pigment, is a member of the *Nyctaginaceae* family comprising of 18 shrubby species which though indigenous of South America are distributed widely in the world, with flowers ranging from white, yellow, orange and various shades of red to purple and violet colour [12-14]. The Betalain pigment in *Bougainvillea* is different from that in other sources due to the presence of saccharide type present in the betanidin (an aglycone of most betacyanins) which is produced 90% from betacyanins, and the remaining 10% comes from indicaxanthin a common betaxanthin [15]. *Bougainvillea glabra* has been found to have eleven violet-red pigments having maximum absorbance in wavelength range of 522-551 nm and is known to have two epimeric betacyanins; bougainvillein-r-1 and isobougainvillein-r-1 [15].

The general structure of Betalain is shown in Fig. 1 [10], it contains carboxylic functions which facilitate TiO_2 surface binding.



(a) (b)

Fig. 1. General structures of the main betalain (a) Betaxanthin (R_1 = H and R_2 = amine or amino acid group), (b) Betacyanin (R = β-D-glucose)

Betalains are characterized by high molar extinction coefficients in the visible region and pH dependent redox properties [14]. They are relatively stable over pH range 3-7, however at pH less than 3.5 the absorption maximum shifts towards lower wavelength (Jack and Smith1996). Acidic conditions is known to induce recondensation of betalamic acid with amine group of the addition residue (Schwatz and von Elbe) and favours betalain sensitized photo-electrodes with high optical densities capable of complete absorption in the visible range of 400-600 nm [6]. Solar energy conversion efficiency being a function of photocurrent density J_{sc}, open circuit voltage V_{oc} and fill factor FF [sze], suggest their improvement is essential to raising the conversion efficiency. This work report the use of water extracts of red Bougainvillea glabra flower a source of betalain as dye sensitizer and the influence of sensitizer dye pH on the photoelectric parameters of the DSSCs.

II. EXPERIMENTAL

A. *Preparation of Dye*

The *Bougainvillea glabra* flower extracts were prepared by crushing 20 g of the flower in a porcelain mortar with a pestle and adding 50 ml of water to the crushed matter. This was filtered to get the raw extract of the flower and divided into three specimens and used as sensitizing dye at three different pH. The first specimen, the as-extracted dye had a pH of 5.70, the pH of the second specimen was adjusted to 3.0 by adding 4 drops of 20% HCl to it while the third specimen after adding 8 drop of HCl had a pH value 1.23.

B. *Electrodes Preparation and DSSC assembling*

The transparent conducting oxide was flourine doped tin oxide (FTO) with a sheet resistance of 15 Ω/cm^2 (SOLARONIX). The TiO_2 film was prepared by blending the commercial TiO_2 powder (Degussa, P25) of Ca. 0.2g, nitric solution (0.1M) of 0.4ml, polyethylene glycol (MW 10,0000) of ca. 0.08g and one drop of a non-ionic surfactant, Triton x – 100. The mixture was well mixed using an ultrasonic bath for 1 hour. Squeegee was used to screen-print the resulting TiO_2 paste on the conducting layer/FTO glass substrate. It was left for 30 minutes so that the paste could settle to reduce the irregularity of the surface. The substrates were then left to dry. This screen-printing procedure was repeated to obtain the TiO_2 working electrode of appropriate thickness of 9 µm.

Prior to sensitisation the TiO_2 photo-anodes were pre-heated at 150 ^{0}C for 30 minutes, allowed to cool and then sintered at 450 ^{0}C for 45 minutes to rid the film of water molecules. After cooling to 80 ^{0}C, the TiO_2 electrodes were immersed into the three dye solutions of pH 1.23, 3.0 and 5.7 for 16 hours. The photo-electrode were then rinsed with 99% ethanol solution, to remove excess dye and thereafter left to dry. The counter electrode was made from platinum catalyst T/SP product by SOLARONIX which was screen-printed using a polyester mesh of 90 and dried. The substrates were sintered for 1 hour at 45 ^{0}C. The DSSC was assembled from the various components following the procedure reported elsewhere [16].

III. CHARACTERIZATION

The absorption spectra of the dyes were determined using an AVASPEC 2048 UV-Visible spectrophotometer, while the morphology and composition characterisation of the nanoporous TiO_2 film was carried out using Carl Zeiss EVO MA-10 scanning electron microscope (SEM), with EDX model ISIS 300 Oxford. Simulated Solar irradiation was provided by a Solar Simulator, Model 4200-SCS Semiconductor Characterization System under the irradiation of AM 1.5 (100mWcm^{-2}) and the Current-Voltage curves were recorded by a digital Keithley multimeter Model 2400 coupled to a computer.

IV. RESULTS AND DISCUSSION

A. Results from the UV-Vis analysis

Fig. 2 shows the UV-Vis optical absorption spectra of the *bougainvillea* flower dye extracts at three different pHs. Absorption spectra of a dye reflect optical transition probability between the ground state, the excited state and the solar energy range absorbed by the dye. The three dyes extract show absorption peaks centered between 310 and 340 nm in the UV-range, with maximum peaks at 330 nm for pH 5.7 and 327 nm for pH 3.0 and 1.2. The dye extracts at pH 1.23 and 3.0 have about the same absorption intensity in short wavelength range, with dye extract at a pH of 5.7 having the highest intensity in this range. The lowest absorption intensity in the long wavelength is observed for dye pH of 1.23, indicating a highly suppressed absorbance as a result of degradation of batanin in very strong acidic environment [18]. Dye extract at a pH of 3 display broad absorption peak in the 480–560 nm range resulting from $\pi-\pi^*$ transitions due to the mixed contributions of the yellow-orange betaxanthins (480 nm) and of the red-purple betacyanin (540 nm) [6]. At a pH of 5.7 the extract has a highest but flattened absorption spectrum in the long range wavelength indicating a suppressed absorption peaks at this pH and a wider range of red, orange, yellow and blue light can be absorbed. Absorbance peaks around 300 and 535 nm are characteristic absorptions for red violet betalain group, betacyanin [14].

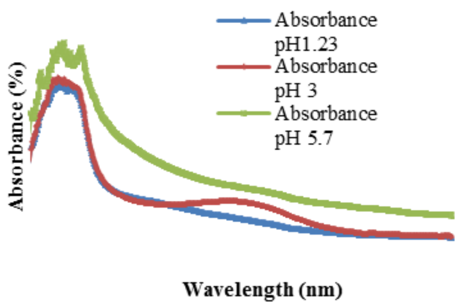


Fig. 2. Absorption spectrum of the dye extract from bougainvillea Red flower for $pH_{1.23}$, $pH_{3.0}$ and $pH_{5.7}$.

The betaxanthin and betanin concentration in the dye extracts in µM are estimated from the absorbance A at 482 and 536 nm from the absorbance spectra using [10],

$$[B_{betax}] = 23.8A_{482} - 7.7A_{536}$$

$$[B_{betan}] = 15.38A_{536}$$

$[B_{betax}]$ is the betaxanthin concentration and $[B_{betan}]$ the betanin concentration. The betaxanthin concentrations were 7.39, 8.79 and 15.17 µM for pH of 1.23, 3.0 and 5.7 respectively, while the betanin concentration at a pH of 1.23, 3.0 and 5.7 were 4.35, 8.15 and 11.26 µM respectively.

B. Scanning Electron Microscope (SEM)/ Energy Dispersive X-Ray EDX of TiO_2 film

Fig. 3 shows the scanning electron micrograph of the TiO_2 (anatase) film. The TiO_2 film has thickness of 9 µm and a mean particle size of 20 nm. It shows a mesoporous surface of the spherical nanoparticles of TiO_2 that forms nanopores across the surface. The nanoporous structure provides increase effective surface area for dye adsorption which allows electrons to travel and be collected at the conducting substrate, so as to have a greater chance for recombination.

The EDX analysis of the TiO_2 electrode in Fig. 4 shows the presence of Titanium, Oxygen, Nitrogen and Carbon. The presence of chlorine in the compound was due to $TiCl_4$ which was applied at a final treatment of the porous TiO_2 electrodes in the anatase TiO_2 compound contained.

C. Measurements of photoelectric characteristics

The current–voltage curve of a solar cell yields important photoelectric parameters such as short-circuit current density J_{sc}, the open-circuit voltage V_{oc}, the current I_{mp}, and voltage V_{mp} at the maximum power point P_{max}. The photoelectric characteristic of the DSSCs were inspected under the simulated sunlight source (AM1.5). With current-voltage (I-V) curve taken as the foundation, the maximum power point P_{max} is calculated as im equation (1),

$$P_{max} = V_{mp}.I_{mp} \qquad (1)$$

and the Fill Factor (FF) is determined from equation (2),

$$FF = P_{max}/V_{oc}.J_{sc} \qquad (2)$$

Though the physical principles behind the operation of different types of photovoltaic cells are generally different, the current-voltage curve of well of cells are similar, and can be characterized and compared with each other in terms of FF, V_{oc}, and J_{sc}.

The I-V and P-V curves of the DSSCs at different pH are shown in Fig. 5 and 6. Three aspects of the current density-voltage curve are considered and compared. These are the fill factor, FF, which is a measure of the efficiency of a solar cell, the short circuit current density, J_{sc}, and the open circuit voltage, V_{oc}. The curves of the DSSC using dye sensitizer with a pH of 1.23 are inferior to those at pH of 3.0 and 5.7.

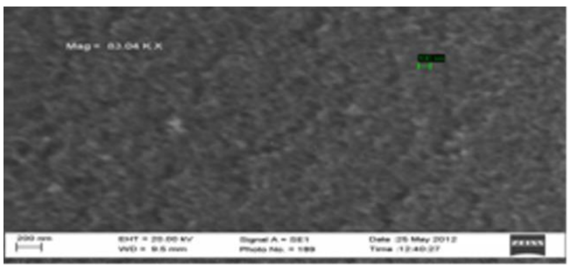


Fig. 3:.SEM micrograph of a nano porous TiO_2 (anatase) film

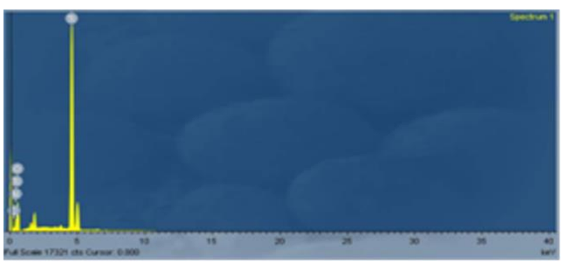


Fig. 4. Elemental composition of TiO_2 compound

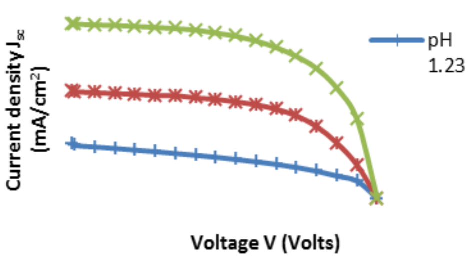


Fig. 5. I-V curves of the cells using dye sensitizers at pH of 1.23, 3.0 and 5.7

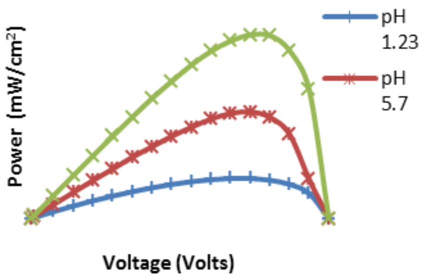


Fig. 6. The P-V characteristics of the DSSCs.

The open-circuit voltage V_{oc} of 0.44 V is obtained for the three DSSCs. The DSSC prepared from a dye pH of 3.0 have the highest photocurrent density J_{sc} and highest fill factor of 18.61mA/cm^2 and 0.60 respectively. At a dye sensitizer pH of 1.23 the DSSC has lowest Photocurrent density of 5.7 mA/cm^2 and lowest fill factor of 0.42 due to betanin degradation in very strong acidic environment with resultant inefficient light harvesting by the dye and inefficient charge injection into the TiO_2 nanoparticles; also possible cell deterioration by acid leaching is expected as the pH goes lower. For a dye pH of 5.7 the J_{sc} of the DSSC is 11.41 mA/cm^2, and FF of 0.57. The maximum power point values P_{max} of the DSSCs are 1.07, 4.91 and 2.85 for dye pH of 1.23, 3.0 and 5.7 respectively. The photoelectric parameters are listed in Table 1.

TABLE 1: PHOTOELECTROCHEMICAL PARAMETERS OF THE CELLS SENSITIZED WITH NATURAL EXTRACTS

Dye Sensitizer pH	*J_{sc} (mA/cm^2)*	*V_{oc} (V)*	*P_{max} (mW/cm^2)*	*FF*
1.23	5.79	0.44	1.07	0.42
3.0	18.61	0.44	4.91	0.60
5.7	11.41	0.44	2.85	0.57

The obtained photoelectric parameters using bougainvilla glabtra flower dye extract as sensitizer dye at pHs of 1.23, 3.0 and 5.7 are reasonably high compared to J_{sc} of 1.881-2.344 mA/cm^2 and V_{oc} between 0.23-0.26 V from betalain pigments extracted from bracts of bougainvilla glabtra and bougainvilla spectabilis at a pH of 5.7 [14]. Also alhough J_{sc} of up to 9.5 mA/cm^2 have been reported at a dye pH of 1.0 from other sources of betalain, corresponding V_{oc} was just between 0.23-0.3 V [6]. The obtained photoelectric parameters at dye pHs of 1.23 and 5.7 are much lower than that of black dye which is superior to all charge-transfer sensitizers on the basis of photovoltaic performance under AM 1.5 presently, with a certified J_{sc} of 20.5 mA/cm^2 and a V_{oc} of 0.72 V, the J_{sc} at dye sensitizer pH of 3.0 is encouragingly close to that of the black dye.

V. CONCLUSION

Betalain raw extracts of bougainvillea glabra were used as natural dye sensitizers for DSSCs at different dye sensitizer pH. The DSSC from a dye sensitizer pH of 3.0 showed the best performance parameters with J_{sc} of 18.61 mA/cm^2, and a good fill factor of 0.60. At a dye sensitizer pH of 5.7 the DSSC exhibited a reduction in photocurrent J_{sc} density to 11.41 mA/cm^2 and a fill factor of 0.57. At a pH of 1.23 the DSSc exhibited the least cell performance parameters with J_{sc} of 5.79 mA/cm^2 and a fill factor of 0.42, this is due to batanin degradation in very strong acidic environment and possible cell deterioration by acid leaching as the pH goes lower. The maximum power point values P_{max} of the DSSCs were 1.07, 4.91 and 2.85 for dye pH of 1.23, 3.0 and 5.7 respectively.

ACKNOWLEDGEMENT

This study was supported by grant from the University Board of Research (UBR) of the Federal University of Technology, Minna, Nigeria.

REFERENCES

[1] B. O'Regan and M. Grätzel, “A low cost high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films”, Nature, vol. 353, pp. 737-740, 1991.

[2] H. Zhou, L. Wu, Y. Gao, T. Ma, “Dye-sensitized solar cells using 20 natural dyes as sensitizers”, Journal of Photochemistry and Photobiology A: Chemistry vol. 219, pp. 188-194, 2011

[3] H. Chang, H. M. Wu, T. L. Chen, K. D. Huang, C. S. Jwo, Y. J. Lo, “Dye-sensitized solar cell using natural dyes extracted from spinach and ipomoea”, Journal of Alloys and Compounds, vol. 495, No. 2, pp. 606–610, 2010.

[4] S. Erten-Ela, “Photovoltaic effect of nanostructured TiO_2 layers in dye sensitized solar cells”, J. Optoelect. Adv. Mat., vol. 14, No. 9-10, pp. 758 – 762, 2012.

[5] Q. Dai, and J. Rabani, “Photosensitization of nanocrystalline TiO2 films by anthocyanin dyes”, J. Photochem. Photobiol. A: Chemistry, vol. 148, 17–24, 2002.

[6] G. Calogero , G. Di Marco, S. Cazzanti , S. Caramori , R. Argazzi, Al. Di Carlo and C. Alberto Bignozzi, “Efficient Dye-Sensitized Solar Cells Using Red Turnip and Purple Wild Sicilian Prickly Pear Fruits”, Int. J. Mol. Sci., vol. 11, pp. 254-267, 2010.

[7] F. G. Gao, A. J. Bard and L. D. Kispert, “Photocurrent generated on a carotenoid-sensitized TiO2 nanocrystalline mesoporous electrode”, J. Photochem. Photobiol. A: Chemistry, vol. 130, 49–56, 2000.

[8] D. Zhang, S. M. Lanier, J. A., J. L., Avent, J. Lum, and J. L. McHale, “Betalain, pigments for dye-sensitized solar cells”, J. Photochem. Photobiol. A: Chem., vol. 195, 72–80, 2008.

[9] N. Koboyashi, J. Schmidt, V. Wray and W. Schliemann, “Formation and Occurrence of Dopamine-derived Betacyanins” , Phytochemistry, vol.56, pp 429-436, 2001.

[10] D. Strack, T. Vogt, and W. Schliemann, “Recent advances in betalain research”, Phytochemistry, vol. 62, 247–269, 2003.

[11] H. M. C. Azeredo, “Betalains, properties, sources, applications, and stability – a review”, International Journal of Food Science and Technology, vol. 44, pp. 2365–2376, 2009.

[12] D. F. Mabberley, A Portable Dictionary of Vascular Plants, MJ. UK: Cambridge University Press ,1997.

[13] G. Impellizzeri, M, Piattelli and S. Sciuto, “Acylated betacyanins from *Drosanthemum floribundum*”, Phytochemistry, vol. 12, pp. 2295–2296, 1973.

[14] A. R. Hernández-Martínez, S. Vargas, M. Estevez and R. Rodríguez, “Dye-sensitized Solar Cells From Extracted Bracts *Bougainvillea* Betalain Pigments,” 1st International Congress on Instrumentation and Applied Sciences, Cancun, Q. R., Mexico, October 26-29, 2010.

[15] M. Piattelli and F. Imperato, “Pigments of *Bougainvillea glabra*” Phytochemistry, vol. 9, pp. 2557–2560, 1970.

[16] M. I. Kimpa, M. Momoh, K. U..Isah, H. Nawawi Yahya, and M. M. Ndamitso, “Photoelectric Characterization of Dye Sensitized Solar Cells Using Natural Dye from Pawpaw Leaf and Flame Tree Flower as Sensitizers”, Materials Sciences and Applications, vol. 3, pp. 281-286, 2012.