The Effect of Annealing Time on TiO₂–Based Dye Sensitized **Solar Cell: Natural Pigment**

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ABSTRACT--- In this analytical approach we fabricate and characterized a Titanium Dioxide Dye sensitized solar cell using Doctor-Blade Technique. Annealing study as a function of time of the samples at 20, 30 and 40 minutes respectively, constant annealing temperature of 450°C was maintained throughout the study. The J-V measurements was conducted using a Kiethley 2400, source meter under A.M 1.5 (1000W/m²) illuminations from a Newport class A solar simulator. The results shows that at the miscellaneous annealing time, V_{oc} (voltage at zero current) = 0.28V, 0.30V and 0.29V, the short circuit current density J_{sc} =95.5 μ Acm⁻², 104.1 μ Acm⁻²and 105 μ Acm⁻², the fill factor FF= 0.411, 0.448 and 0.525 and the performance efficiency, $\eta = 0.011$, 0.014 and 0.016 respectively. An outstanding result of $V_{oc}=0.30$, $J_{sc}=105 \text{mAcm}^{-2}$, FF=0.525 and $\eta=0.016$ was achieved. It was observed that the power density, Fill Factor and efficiency increases with increase with increase in annealing time.

Keywords---- TiO₂, DSSC, Annealing Time, Roselle

1. INTRODUCTION

By considering natural resources use up as related to surroundings demand, energy utilization is one most common issue of discussion todays. The needs for the development of a global sustainability in the scientific society open up a direct access for researchers daily looking for an alternative source of current fossil fuels [1]. The emergence of Dye-sensitized solar cells (DSSCs) as s source of energy, due to their potentialities such as low-cost, adjustability, production alleviation, progressive efficiency, and safety [2][3]. Significant progress was achieved for DSSC thereby presenting some unccustomed constituents such as sensitizer, electrolytes and surfactants, together with photo-anode with numerous morphologies for third generation solar cell substantial. Even though, they presented unlimited advantages, yet they have one major disadvantage of having liquid electrolyte: leading to temperature instability and suffered from degradation. [4]. DSSC are made up of p- and n-type materials. Both the two states of the semiconductor degenerate at the Fermi levels, responsible for drained region and a charge decoupling [5]. Photons absorption occurs at p-type zone, thereby creating an electron-hole twosome. Available electron is then forced into n-type zone and the hole move continuously to p-type zone [6]. It's so interesting device for its easy production and availability of its components [7]. This device (DSSC) work based on the principle of energy conversion, that convert solar energy into electricity made up of two conductive glasses and sandwiched between; nanoscale titanium dioxide, dye and electrolyte. Sun light absorption where made by sensitizer then accelerating the electrons to the conduction band of TiO₂. On the other hand, the sensitizer accommodates the electrons directly from electrolyte redox duo and it rejuvenates again. Congenital colors (sensitizers) where abundance and can be collected from plants, leaves and flowers, they also have more advantages ahead of metallic complexes and other organic dyes[8]. They are simply collected; do not necessitate sanctification and present low cost. Some common examples are crocetins, chlorophyll, carotenoids, and anthocyanins [1].

In DSSC, dye is responsible for visible light absorption (e.g., ruthenium complexes and Natural pigments as considered in this study). Having ruthenium complexes as the outstanding candidate so far. Despite the fact that it can present an efficiency greater than 11% [9][10]. Perhaps, purchasing cost of ruthenium-dyes (previously reported as greater than \$1,000/g) is becoming an issue, as there is a need of good and safer alternative with promising performance to partake all the necessary challenges for large-scale production of dye sensitized solar cell [11]. For a DSSC to produce a photocurrent density, the energy of the dye excited-state necessarily must be higher than the conduction band edge. High

quantum efficiency for injection is achieved when the dye LUMO is both energetically matched and reasonably strongly coupled to the underlying semiconductor. The dye should absorb strongly from the blue end of the visible spectrum to the near infrared[12].

Titanium dioxide (TiO_2) is an inexpensive, nontoxic and photo-stable material, which has good photosensitivity, optical and photocatalytic properties for various applications including optics, microelectronics, and photocatalysis. It is known that band gap of TiO_2 is about 3.2 eV and it has three phase structures in nature including anatase, rutile, and brookite[13]. TiO_2 absorbs only UV light, which comprises only a small fraction (\sim 5%) of solar spectrum. As a result, dye molecules are employed for visible light capture [14]. When photon shine onto the dye, electrons are excited gradually from the ground state (A) to the excited state (A*) Eqn (1) and then injected into the conduction band of the Titanium-Dioxide (TiO_2) electrode leading to the oxidation of the Electrons (A*) Eqn (2). The presence of injected electrons in the conduction band of Titanium-Dioxide (TiO_2) would be dispatched within TiO_2 nanoparticles and diffused toward the Transparent Conductive Oxide (TCO). Finally, the electrons circle and reach the counter electrode through the circuit Eqn (3). Then oxidation reaction of photosensitizer would occur (A*) and attracts electrons from the I* ion redox mediator leading to circulation/regeneration of the ground state (A), and the I* is oxidized to I*_3*. The oxidized redox mediator (electrolyte), I*_3*, diffuses toward the counter electrode and then it is reduced to I*_1* ions Eqn (4).

$$A + hv \rightarrow A^{*}$$
 (1)
 $A^{*} \rightarrow A^{+} + e^{-} (TiO_{2})$ (2)
 $A^{+} + e^{-} \rightarrow A$ (3)
 $I_{3}^{-} + 2e^{-} \rightarrow 3I^{-}$ (4)

So far, DSSC's photogenerated efficiency depends on its four energy levels of the: i. the excited state (LUMO) ii. The ground state (HOMO) of the photosensitizer, iii. The Fermi level of the TiO_2 electrode and iv. The redox potential of the mediator (I^-/I_3^-) in the electrolyte. DSSC's characteristics parameters are simply explored from J-V study. The power ratio (FF-fill factor) and efficiency (η) is evaluated according Eqn (5) and (6) respectively [15].

$$FF = \frac{P_{max}}{V_{oc} \times I_{sc}}$$

$$\eta = \frac{V_{oc} \times I_{sc}}{E}$$
(5)

This paper, presents the consequence of annealing behavior on the Titanium Dioxide - Roselle Dye Sensitized Solar Cells application and the advantages of hybridization at different annealing time to the performances of DSSC. The fabrication of the cell is in accordance with the procedure reported by Doctor-blading technique.

2. EXPERIMENTAL DETAILS

2.1 Materials

Titanium Dioxide TiO_2 (79.89Mw, 99%), isopropanol, ethanol were procured from Tofel Ltd, Kano-Nigeria,Indium tin oxide coated (ITO) glass slide (25mm x 25mm with surface resistivity $10\Omega/sq$)obtained from TechinstroLtd-India, silver paste from ENSON Japan Ltd. I⁻/I⁻³ was prepared as based on the Nanolab procedure.

2.2 Fabrication of DSSC

ITO glass plates were rinse with isopropanol, ethanol, and then deionized water and dried in air, sellotage was lay on as elbow room to regulate film viscidity purposely to maintain some portion for electrical contact. A measured amount of well commixes crushed set off carbon of soot was mixed with Anionic surfactant liquid was used as counter electrode material (carbon paste). The carbon paste which was prepared through Doctor-blading technique were serviced at one of the ends of the conducting glass and compartmentalized with a squeegee sneaking through the tape-covered edges. The deposition of our counter electrode on indium doped tin oxide (ITO) glass substrate was enabled through the doctorblading method. TiO₂ paste (Qualikems, Ltd.) was propagated across the targeted portion between the sellotape on the conducting glass substrate using the same Doctor-Blade technique. The TiO2 coating was then dried in air at room temperature for 10 min and sintered at various annealing time of 20, 30 and 40 min at constant annealing temperature of 450 °C. The thickness of the photoanode film was about 0.07 mm and its area was 2 x 2 cm². After cooling to 29 °C the TiO₂ electrodes were immersed into purified Roselle juice. After the dye adsorption the films were cleaned with pure ethanol to remove the excess Roselle-dye and dried for 20 min. The resulting nanoporous layer made from the sintered particles was stored in a sealed environment to avoid moisture absorption from ambient air [16]. The binder clips was cleaned with ethanol before it was rightly placed on the dyed working electrode. The conductive side of the transparent electrodes was gently placed on top of conducting carbonized side of the counter electrodes. We introduced 0.5 ml drops of the electrolyte (Iodide/triiodide) through one of the gap left between the two glass plates by capillary action[17]. Electrical contacts were made by applying the silver paste ((ENSON, Ltd.) on the uncoated areas along the conducting side of electrode.

2.3 Photovoltaic Performance of DSSC

The performance of the DSSCs were electrically analyzed thereby acquiring a current curve as a blowout of voltage, generated under the calibrated AM 1.5 solar simulator Controller (Newport, Oriel instruments, Model: 69922) with a light intensity of 100 mWcm⁻² and a computer controlled digital source meter (Keithley, Model: 2400). The DSSCs photoelectrochemical parameters, i.e., the fill factor (FF) and light to-electricity conversion efficiency (η), were calculated based on equation (5) and (6).

Cell	Annealing Time (min)	V _{oc} (v)	J _{sc} (mA/cm ²)	P _{max} (mW/cm ²)	FF	η (%)
1 st	20	0.28	95.5	11	0.411	0.011
2^{nd}	30	0.30	104.1	14	0.448	0.014
3^{rd}	40	0.29	105	16	0.525	0.016

3. RESULTS AND DISCUSSION

Table 1:- Summarized Results of Titanium Dioxide Dye Sensitized Solar Cells Output Parameters at various Annealing time.

The J-V characteristics of TiO₂-Roselle DSSCs are shown in Table 1. The performance of the TiO₂-Roselle DSSCs was investigated through electrical current and voltage outputs under different annealing time.

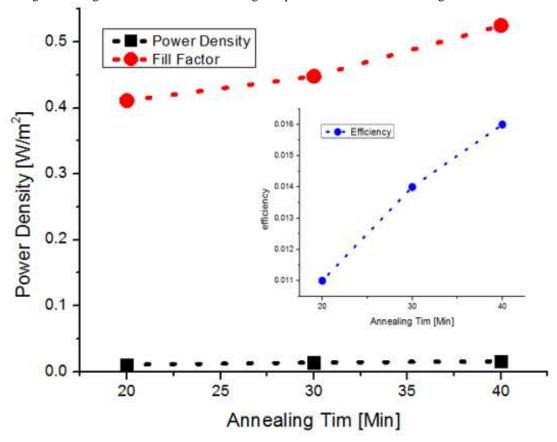


Fig. 1: Variation of Output Power Density, Fill Factor vs Annealing Time. Inset shows the Efficiency vs Annealing time.

Fig.1 shows the effect of annealing time on the maximum output power generated. It was observed that the power density increases with increase in annealing time which could be due to the complete burning of all the chemical contains in the TiO_2 paste (see black symbol). The effect of annealing time on the Fill factor by the fabricated DSSCs was studied and we observed that the increase in fill factor leads to the increases in annealing time (see red symbol). Fig.1 (Inset) shows the direct effect of annealing time on the energy conversion efficiency. Again it was observed that the increase in the in the efficiency causes an increases in the annealing time.

4. CONCLUSION

Titanium Dioxide-based DSSC was successfully fabricated at miscellaneous annealing time of 20, 30 and 40 min. It was observed that the power density, Fill Factor and efficiency increases with increase with increase in annealing time which could be due to the complete burning of all the chemical contains in the TiO₂ paste [3]. In this paper, we presents the effect of annealing treatment process on the Titanium Dioxide - Roselle DSSC application and the advantages of hybridization at different annealing time to the performances of DSSC. It was further evaluated that the efficiency of the fabricated solar cell could improve by increasing the annealing time from 40minutes above.

5. REFERENCES

- [1] R. Szostak *et al.*, "Anthocyanin from Vitis labrusca grape used as sensitizer in DSSC solar cells," *J. Mater. Sci. Mater. Electron.*, vol. 26, no. 4, pp. 2257–2262, 2015.
- [2] S. Pei, A. Pandikumar, H. Ngee, and N. Ming, "Essential role of N and Au on TiO 2 as photoanode for efficient dye-sensitized solar cells," *Sol. Energy*, vol. 125, pp. 135–145, 2016.
- [3] B. I. Adamu, H. Y. Hafeez, and I. I. Ibrahim, "Effect of Annealing Temperature on The Electrical Properties of Titanium Dioxide (TiO2) Roselle Dye Sensitized Solar Cell.," *Int. J. Adv. Res.*, vol. 4, no. 9, pp. 192–199, 2016.
- [4] M. H. Jusof Khadidi and E. A. Hamid, "Fabrication and Characterization of Titanium Dioxide-Based Sensitized Solar Cell Using Vinegar," *2nd Int. Conf. Environ. Energy Biotechnol.*, vol. 51, no. 26, pp. 139–142, 2013.
- [5] Q. Tang, J. Duan, Y. Duan, B. He, and L. Yu, "Recent advances in alloy counter electrodes for dye-sensitized solar cells. A critical review," *Electrochim. Acta*, vol. 178, pp. 886–899, 2015.
- [6] B. I. Adamu, G.Babaji, A. S. Gidado, I. M. Musa, & S. S. A., and H. Y. Hafeez, "Influence of Thickness on Titanium Dioxide Roselle (Zobo) Dye Sensitized Solar Cell Experimental Detail," *Int. J. Pure Appl. Sci.*, vol. 6, no. 2, pp. 71–78, 2016.
- [7] R. Faccio, L. Fernández-Werner, H. Pardo, and A. W. Mombré, "Current trends in materials for dye sensitized solar cells.," *Recent Pat. Nanotechnol.*, vol. 5, no. 1, pp. 46–61, 2011.
- [8] B. I. Adamu, "Fabrication and Characterization of Titanium Dioxide Roselle (Zobo) Dye Sensitized Solar Cell," (Masters, Diss. Bayero Univ. Kano), p. 80, 2015.
- [9] M. Grätzel, "Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells &," *J. Photochem. Photobiol. A Chem.*, vol. 164, pp. 3–14, 2004.
- [10] H. Chang and Y. Lo, "Pomegranate leaves and mulberry fruit as natural sensitizers for dye-sensitized solar cells," *Sol. Energy*, vol. 84, no. 10, pp. 1833–1837, 2010.
- [11] Y. Jiao, F. Z. And, and S. Meng, "Dye Sensitized Solar Cells Principles and New Design," *Tech*, pp. 131–148, 2011.
- [12] T. W. Hamann, R. a. Jensen, A. B. F. Martinson, H. Van Ryswyk, and J. T. Hupp, "Advancing beyond current generation dye-sensitized solar cells," *Energy Environ. Sci.*, vol. 1, no. 1, p. 66, 2008.
- [13] M. Hamadanian, J. Safaei-ghomi, M. Hosseinpour, and R. Masoomi, "Uses of new natural dye photosensitizers in fabrication of high potential dye-sensitized solar cells (DSSCs)," *Mater. Sci. Semicond. Process.*, vol. 27, pp. 733–739, 2014.
- [14] K. E. Jasim, "Dye sensitised solar cells-working principles, challenges and opportunities," *Tech*, pp. 171–204, 2011.
- [15] B. I. Adamu, G. Babaji, M. H. Ali, C. E. Ndikilar, A. B. & Suleiman, and S. S. Abdullahi, "The Effect of Degradation of Electrolyte on TiO 2 Roselle Dye Sensitized Solar Cell," *Int. J. Pure Appl. Sci.*, vol. 6, no. 1, pp. 36–45, 2016.
- [16] I. Daut, M. Fitra, M. Irwanto, N. Gomesh, and Y. M. Irwan, "TiO ₂ Dye Sensitized Solar Cells Cathode Using Recycle Battery," *J. Phys. Conf. Ser.*, vol. 423, p. 012055, 2013.
- [17] T. O. Ahmed, P. O. Akusu, N. Alu, and M. B. Abdullahi, "Dye-Sensitized Solar Cell (DSC) Based on Titania Nanoparticles and Hibiscus sabdariffa," *Br. J. Appl. Sci. Technol.*, vol. 3, no. 4, pp. 840–846, 2013.