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FABRICATION AND CHARACTERIZATION OF DYE- SENSITIZED SOLAR CELL (DSSC) USING NATURAL DYE FROM *ALSTONIABOONEI* (STOOL WOOD)

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ABSTRACT
Natural dye from Alstonia boonei was used as a sensitizer to fabricate dye-sensitized solar cell (DSSC) using Doctor Blade method. The photoelectrochemical performance of the cell, showed an open circuit voltage (V_{oc}) of 0.514v, short circuit current density (J_{sc}) of 0.330mA/cm^2, a fill factor (FF) of 0.309 and a conversion efficiency of 0.052%. The cell absorbed light in the ultra violet (UV), visible and near-infra red (NIR) regions with maximum absorption peak at 4.842A.U. in the UV region. The cell with anthocyanin dye used as a control, gave a conversion efficiency of 0.019% with V_{oc} of 0.514v, J_{sc} of 0.376mA/cm^2 and a fill factor (FF) of 0.100 with maximum absorption peak of 4.773A.U. in the UV region. The efficiency of the cell with Alstoniaboonei dye gave a higher efficiency than the control cell which is also in line with the efficiency of other natural dyes earlier reported by other Scientists. Therefore, Alstonia boonei dye can be used as a sensitizer in DSSCs considering its conversion efficiency and its ability to absorb photon energy even in the near-IR (NIR) region

KEY WORDS*: Dye, sensitizer, solar, efficiency, absorption, voltage, cell, energy, sunlight, current.*

INTRODUCTION
One of the greatest challenges in the next fifty (50) years is the production of clean and renewable energy for human consumption [1]. Our current energy consumption depends mainly on fossil fuels that generate greenhouse gases, most notably, carbon dioxide (CO_2). Greenhouse gases are directly implicated in the rise of average global temperature over the last century, which has widespread effects on ocean levels, biodiversity, crop production, natural disasters, and other aspects of the ecosystem [2]. Renewable energy sources such as solar energy are considered as a feasible alternative because “More energy from sunlight strikes the earth in one hour in an entire year” [3]. Developing means to harvest a fraction of the solar energy reaching the earth may solve many problems associated with both energy and global environment. Therefore, intensive research activities have resulted in attention-grabbing, to the different classes of organic and inorganic based solar cells, capable of directly converting solar energy into electricity. The first-generation solar cells are based on silicon materials [4]. Second-generation solar cells rely on thin film such as cadmium telluride and copper indium selenide. However, indium, tellurium and selenium are relatively scarce. Cadmium is a very toxic heavy metal, and manning of this metal causes various environmental hazards [5]. Because of the high cost of the first-generation solar cells (due to high cost of silicon materials) and the hazardous effect of the second-generation solar cells, we must look for other technologies, if solar cells become environmentally and economically competitive with fossil fuels.Dye-sensitized solar cells (DSSC) are third-generation solar cells that exhibit many advantages over the previous generations of solar cells [7; 8]. One of the key materials in DSSC, is the photosensitizer (dye). Ruthenium complex dyes are capable of delivering DSSC with high conversion efficiencies [9]. However, ruthenium dyes are not suitable for environment friendly photovoltaic systems. Ruthenium is expensive and environmentally hazardous. Ruthenium compounds are highly toxic and carcinogenic. When ruthenium compounds are heated in the presence of air, they form ruthenium tetraoxide, which is a highly volatile and toxic compound that damages the eyes and upper respiratory system [5]. Natural dyes such as pigments used in food colouring are easily and safely extracted from plants [10]. It means that they do not require complex synthesis or toxicity test, and can be used in DSSC. Since natural dyes have low cost of

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synthesis and are environment friendly, they are considered as a viable option for dye-sensitized solar cells in future research [4]. Natural dyes in DSSC have shown overall conversion efficiency below 1% [4]. Until now, several natural dyes such as betalains [11; 12], anthocyanins [11; 13] and carotenes [14] have been used as sensitizers in DSSC. Betalains have the requisite functional group (–COOH) to bind better to the TiO_2 nanostructure [15]. In this research the possibility of using *Alstonia boonei*, a very large, deciduous, tropical-forest tree, as sensitizer in DSSC fabrication was harnessed.

MATERIALS AND METHODS

Materials and Equipment

Titanium (IV) oxide (n-TiO_2 solaronix T37/SP),Conductive glass (FTO 5x5cm), Platinum catalyst (Pt-catalyst T/SP),Electrolyte (Iodolyte AN 50), *Alstonia boonei* (Stool wood) leaves,Roselle (*Hibiscus sabdariffa*) leaves,Auto-calculating four point probe resistivity test system (Quad-Pro 301), Oriel Class-A Solar simulator (AM 1.5), Spectrophotometer (Avaspec 2.1),Surface profiler (Dektak stylus 7.0) and Electron microscope (Cetron).

Sample Collection

The photosensitizer (dye) used in sensitizing the mesoporous TiO_2 film, was extracted from *Alstonia boonei* leaves, obtained from Awka, Nigeria while the the standard dye (anthocyanin dye) used in the fabrication of the control cell was extracted from *Hibiscus sabdariffa* leaves, gotten from Abuja, Nigeria.

Preparation of Photosensitizer (dye)

11.4g of *Alstonia boonei* leaves were crushed in a porcelain mortar, with 100ml of distilled water added, to increase the fluid content. The resulting extract was filtered and kept in a plastic dish to be used for the staining process. 11.4g of Roselle leaves were placed in a beaker, 100ml of distilled water was added and it was heated for about 3-5minutes. After heating, it was allowed to cool to room temperature and then, it was filtered and kept in a plastic dish to be used also for the staining process.

Preparation of TiO_2 Film

The FTO glass sheet was gently cleaned with ethanol and cotton wool. The area on the conductive side of the glass was mapped out using scotch tape. The size of the final open area was 0.5cm x 4cm. Then, four drops of TiO_2 suspension was added onto the deposition area. The suspension was spread evenly using a glass stiring rod (squeegee). The slide was allowed to dry for approximately 5-10 minutes before removing the scotch tape. After the tape was removed, the glass was put on a hot plate and dried for about 30 minutes at 100℃. The glass slide was allowed to cool to room temperature before undergoing staining process with *Alstonia boonei* dye.Another TiO_2 film needed to be stained with anthocyanin dye, was also prepared using the same steps mentioned above.

Staining of TiO_2 Film with Dye

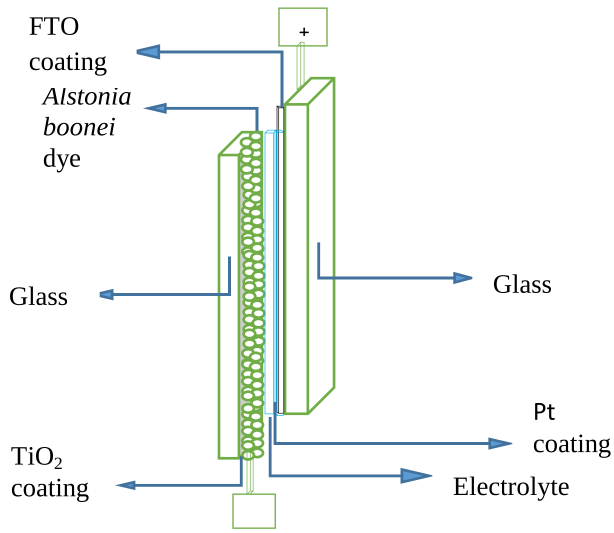
The cool glass slide with TiO_2 was placed in the plastic dish containing the *Alstonia boonei* dye. This was allowed to stay for 24 hours at room temperature for the dye to adsorb on the surface of the TiO_2 film. It was subsequently rinsed with ethanol and allowed to dry. Also, the other TiO_2 film was stained with the anthocyanin dye using the same steps stated above.

Preparation of Counter Electrode

Two unused FTO glasses were cleaned gently with ethanol and dried with cotton wool. The deposition areas on the conductive side of the glass slides were mapped out with scotch tape, which are equal to the deposition areas on the photoanodes. The areas mapped out were caoted with Platinum catalyst and annealed for about 400℃ on a hot plate.

Assembling of DSSC

The TiO_2 coated glass slide, which was stained with the *Alstonia boonei* dye, was put face to face with the platinum coated glass slide (counter electrode). These glasses were put slightly offset to allow enough room for electrical contacts. After that, both sides were held together using binder clips and a drop of iodolyte electrolyte was put at one end of the glass using pipette. The electrolyte solution penetrated into the cell by capillary effect and stained the entire cell. The gap between the glass slides was sealed using epoxide glue. Also, the DSSC with anthocyanin dye was assembled using the same steps mentioned above. These cells were now sent for characterization. In Fig. 1 is shown the schematic diagram of the assembled DSSC and the energy conversion process steps



$$TiO_2(S) + hv(photon) = TiO_2(S*) \quad (1)$$

$$TiO_2(S*) = TiO_2(S^+) + e^- \quad (2)$$

$$TiO_2(S^+) + e^- + CE = TiO_2(S) + e^-_{(CE)} \quad (3)$$

$$TiO_2(S^+) + 3I^- = TiO_2(S) + I_3^- \quad (4)$$

$$I_3^- + 2e^-_{(CE)} = 3I^- + CE \quad (5)$$

Fig. 1: Schematic diagram of the assembled DSSC and the energy conversion process steps

Characterizatization

Optical Characterization

Optical absorbance

The absorption spectrum of the DSSC with *Alstonia boonei* dye was obtained using an Avaspec 2.1 spectrophotometer. This was carried out as follows; the cell sample was placed on the sample holder of the instrument, the spectrophotometer was switched on and then, the absorbance at different wavelengths were recorded and displayed automatically by the machine. Then,the absorption spectrum was obtained from the plot of absorbance against wavelength. Also, that of the DSSC with anthocyanin dye was recorded and determined using the same instrument and steps stated above.

Optical transmittance

The optical transmittance spectrum of the DSSCs with *Alstonia boonei* dye and anthocyanin dye were both obtained using the same instrument used for optical absorbance but percentage transmittance was plotted against wavelength.

Morphological Characterization

Film thickness

The thickness of the sensitized TiO_2 film with *Alstonia boonei* dye was measured using a Dektak Stylus 7.0 Surface Profiler. This was carried out as follows; the sensitized film was placed in the binder clip of the machine, the machine was switched on and the film thickness was automatically measured by the machine. Also, the thickness of the film sensitized with anthocyanin dye was measured using the same machine and operational procedure used for the *Alstonia boonei* dye.

Cell active area

The cell active area of both cells with *Alstonia boonei* dye and anthocyanin dye were determined automatically using Oriel Class-A Solar Simulator.

Micrograph

The micrograph of the cell active area of the DSSC with Stool wood dye was obtained using Cetron electron microscope. The micrograph of the DSSC with anthocyanin dye was also obtained using Cetron electron microscope.

Electrical Characterization

Sheet resistance

The sheet resistance of the DSSC with *Alstonia boonei* dye was measured using Four Point Probe Resistivity Test System. This was carried out as follows; the machine pointer was placed randomly at four different points on the cell, the machine was switched on, and the average sheet resistance was measured and recorded automatically. Also, the average sheet resistance of the DSSC with anthocyanin dye was measured using the same machine and operational procedure stated above.

I-V characteristics

The I-V characteristics of the DSSC with *Alstonia boonei* dye was determined using Oriel Class-A Solar Simulator under the standard illumination light intensity of $1000W/m^2$. This was carried out as follows; the cell sample was placed under the power source (1000W white bulb), the machine was switched on and the current density and voltage of the cell were recorded automatically. Also, the I-V characteristics of the DSSC with anthocyanin dye was determined using the same machine and operational procedure stated above

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The fill factor (FF) of both cells were calculated using the formula [16].

$$FF = \frac{J_{mp} V_{mp}}{J_{sc} V_{sc}} \qquad 6$$

Where;

J_{mp} = maximum current density.

V_{mp} = maximum voltage.

J_{sc} = short circuit current.

V_{oc} = open circuit voltage.

The conversion efficiency (Ƞ) of both cells were also calculated using the fomula;

$$\eta = \frac{J_{sc}\, V_{oc}\;\, FF * 100}{P_{in}} \qquad 7$$

Where;

P_{in} = Power of incident light = $1000W/m^2$ or $100mW/cm^2$.

RESULTS AND DISCUSSION

Results of Optical Characterization and Discussion

Optical Absorbance

The result of absorption spectrum of DSSC with Stool wood dye is shown in Fig. 3.1.

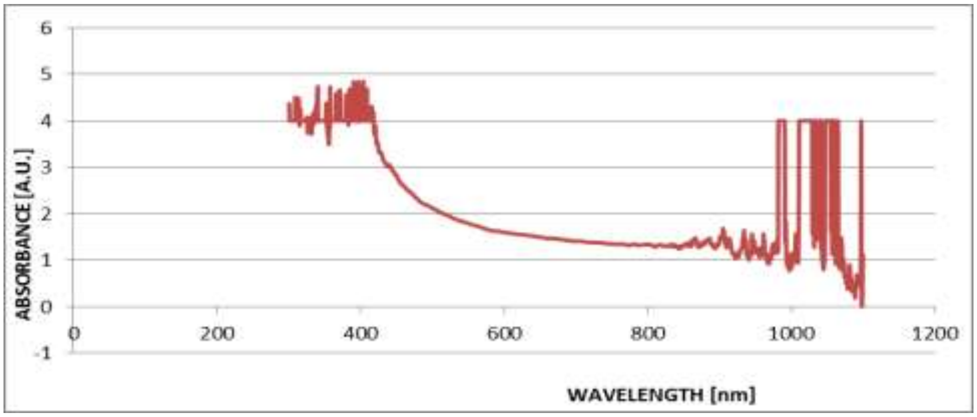


Fig. 2.1: Absorption spectrum for DSSC with Stool wood dye

DSSC with Stool wood dye absorbed ultra violet (UV), visible and near-infra red (NIR) lights in the wavelength range of 300–1100nm with the higest peak of absorbance (4.842A.U.) in the UV and visible region at wavelengths of 389.97nm and 396.45nm respectively according to Fig. 2.1. Hence, DSSC with Stool wood dye absorbed light of appropriate wavelength. This implies that, *Alstonia boonei* dye can be used as photosensitizer for wide-band gap semiconductors such as TiO_2 which alone can not absorb visible light [17].

The DSSC with anthocyanin dye which was used as a control, also absorbed UV, visible and NIR lights in the range of 300–1100nm with the highest absorbance peak (4.773A.U.) in the UV region at wavelength of 302.85nm according to Fig. 2.2.

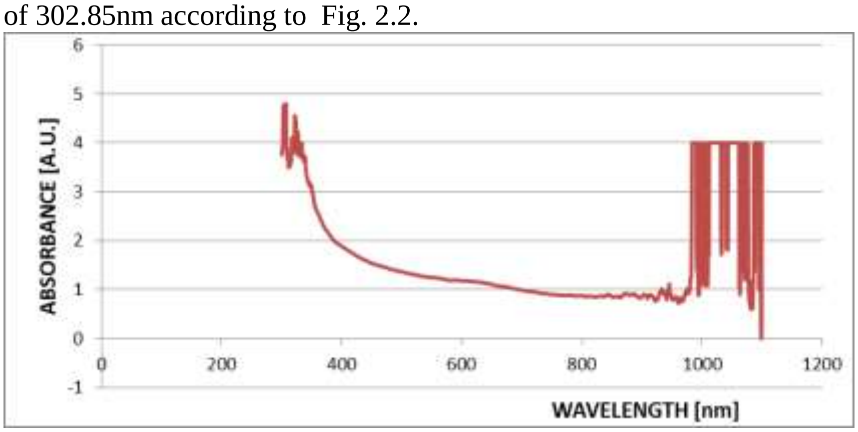


Fig. 2.2: Absorption spectrum for DSSC with Anthocyanin dye.

This shows that Stool wood dye is a better sensitizer than anthocyanin dye, obtained from *Hibiscus sabdariffa* (Roselle) in DSSCs.

Therefore, the high peak of absorbance exhibited by the DSSC with Stool wood dye, implies that, it is a better absorber.

Optical Transmittance

The result of optical transmittance spectrum for DSSC with Stool wood dye is shown in Fig. 2.3.

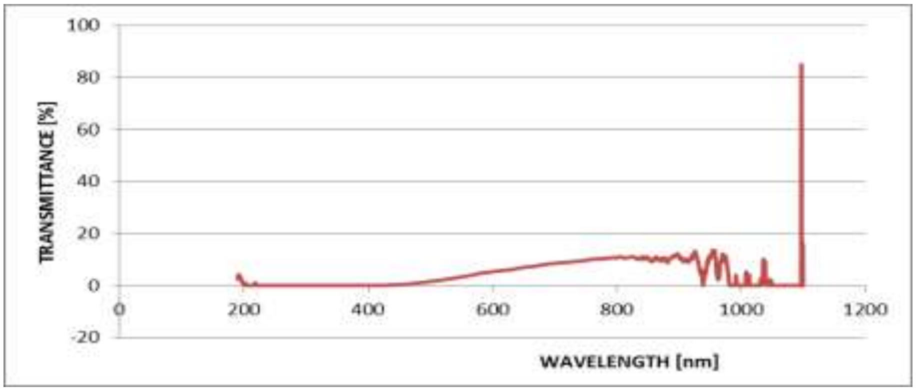


Fig. 2.3: Optical transmittance spectrum for DSSC with Stool wood dye.

The DSSC with Stool wood dye exhibited a very low percentage transmittance in the UV region with the highest peak of 3.81% at 200nm. The transmittance increased gradually in visible region with maximum transmittance of 9.30% at 734.62nm and then reached highest peak of 84.96% at 1097.54nm in the near-IR (NIR) region according to Fig. 2.3. This shows that Stool wood dye absorbed the highest amount of photon energy in the UV region compared to visible and NIR regions.

The anthocyanin dye also exhibited the same trend but with maximum peak of 3.31% at 200nm in the UV region, 8.37% at 723.29nm in the visible region and 52.36% at 1098.61nm in the NIR region according to Fig. 2.4.

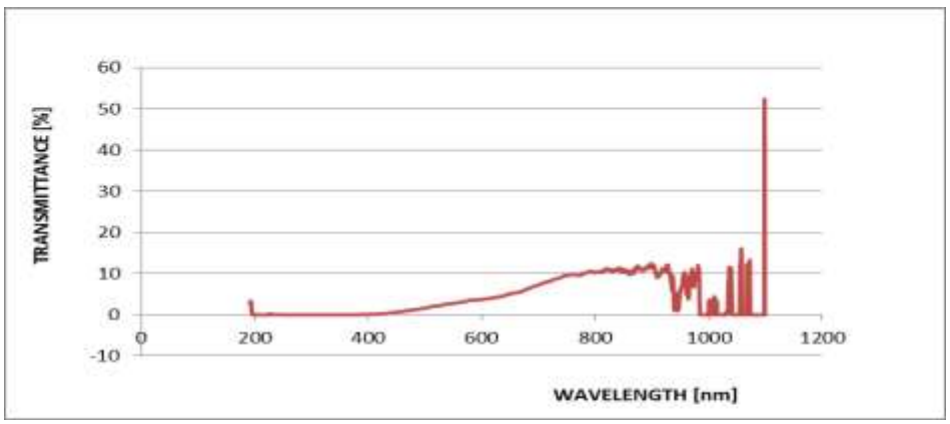


Fig. 2.4: Optical transmittance spectrum for DSSC with Anthocyanin dye.

From literature the wavelength ranges for UV, visible and NIR regions of electromagnetic radiation are; 10–390nm, 390–770nm and 770–2500nm respectively [18].
Therefore, the high transmittance exhibited by the DSSC with Stool wood dye, shows that, it can be used as a window material in solar cells application.

Band Gap
The TiO_2 film sensitized with Stool wood dye gave a band gap of 2.00eV according Fig. 2.5.

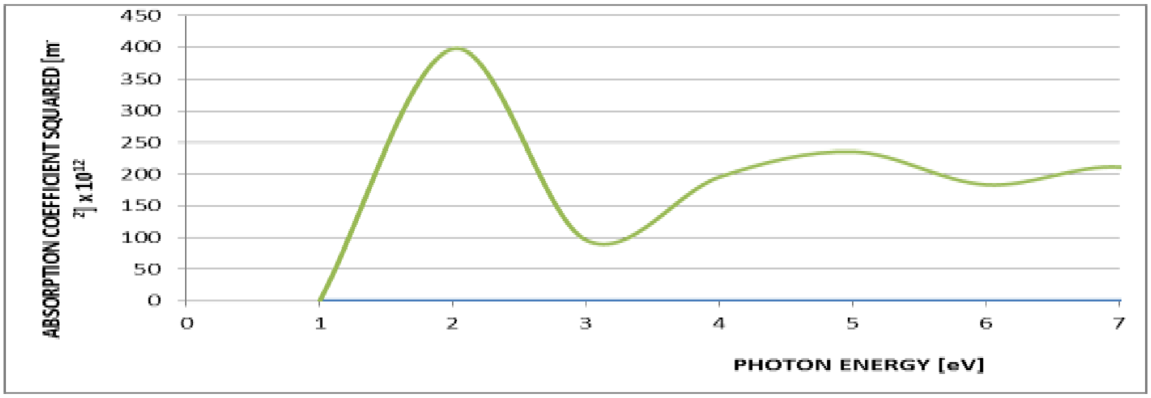


Fig. 2.5: Plot of Absorption coefficient squared against photon energy for DSSC with Stool wood dye.

While the DSSC with anthocyanin dye gave a band gap of 3.10eV according to Fig. 2.6.

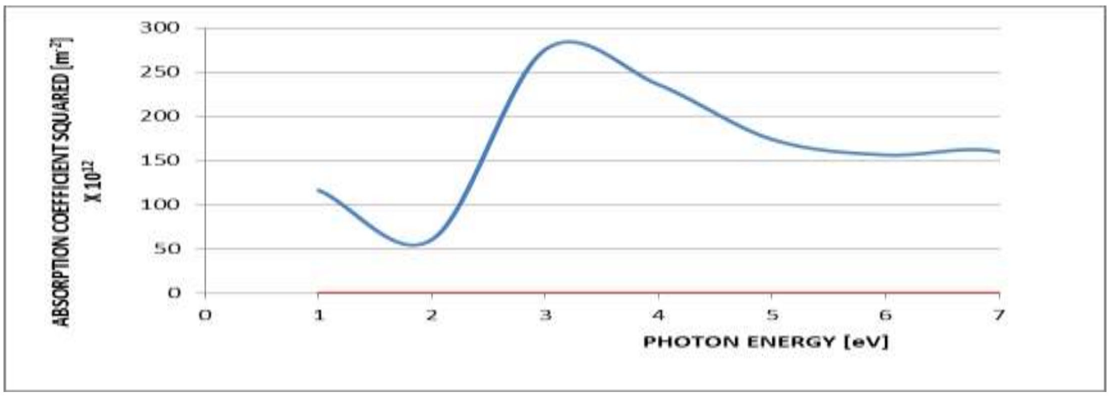


Fig. 2.6: Plot of Absorption coefficient squared against Photon energy for DSSC with Anthocyanin dye.

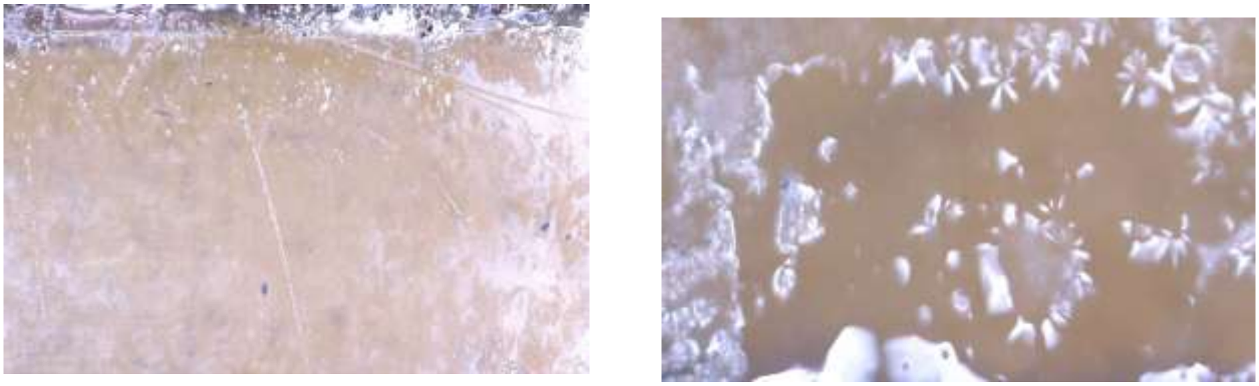
However, from another study [19], the band gap range of anatase TiO_2 was found to fall within 3.20–3.51eV. The band gap obtained for both cells, shows that the cells are semiconductors, since the band gap range for semiconductors is 0.2–4.5eV. The resulst compared well with other results of 3.20–3.51eV [19; 6].

Cell Active Area

The active area of the cell sensitized with Stool wood dye was measured to be 0.20cm^2.
The cell sensitized with anthocyanin dye was equally 0.20cm^2.

Micrograph

The micrographs for the cell active area of the DSSC with Stool wood dye at magnifications of 48.9x and 217x are shown in Fig. 2.7.

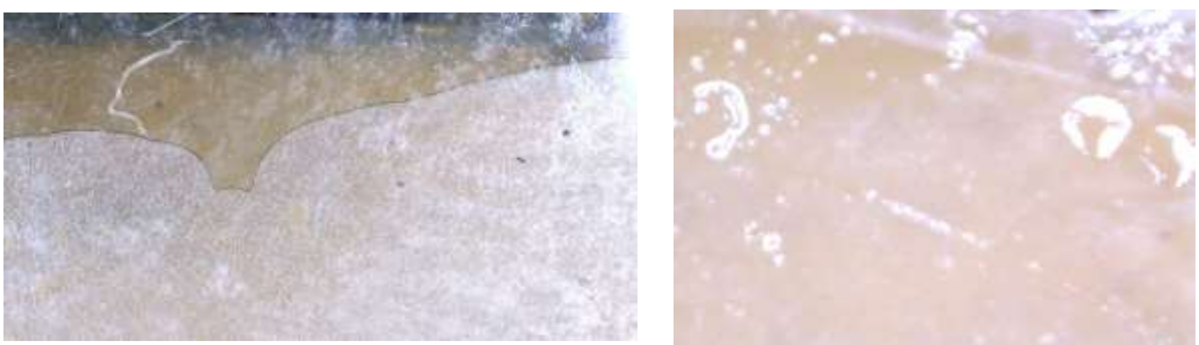


a. 48.9x b. 217x

Fig. 2.7a-b: Micrograph for Cell active area of DSSC with Stool wood dye.

At 48.9x magnification, the cell active area surface was virtually homogeneous with few spherical spots. Then at 217x magnification, the surface was covered with non-homogeneous cloudy-like particles which indicates the area covered by the Stool wood dye on the surface of the TiO_2 film.

The micrographs for the cell active area of the DSSC with anthocyanin dye at magnifications of 48.9x and 217x are shown in Fig. 2.8.



a. 48.9x b. 217x

Fig. 2.8a-b: Micrograph for Cell active area of DSSC with Anthocyanin dye.

There is a better interaction of the Stool wood dye with the titanium dioxide crystals as seen in Fig. 2.7b when compared with that of anthocyanin dye as shown in Fig. 2.8b. This interaction, could be linked to the better efficiency of the DSSC with Stool wood dye when compared to the DSSC with anthocyanin dye.

Results of Electrical Characterization and Discussion

Sheet Resistance

The average sheet resistance measured was 12.789 Ω for DSSC with Stool wood dye. The average sheet resistance obtained for the DSSC with anthocyanin dye was 14.330Ω. Therefore, there is a free flow of current in the DSSC with Stool wood dye because of the lower resistance exhibited by it when compared with the DSSC with anthocyanin dye which showed a higher resistance.

I-V characteristics

The results of the I-V characteristics for DSSC with Stool wood dye and anthocyanin dye are shown in Table 1.

Table 1: Results of I-V characteristics.

I-V characteristics	Stool wood (*Alstoniaboonei*) dye	Standard dye (Anthocyanin dye)
J_{mp} (mA/cm^2)	0.204	0.080
V_{mp} (V)	0.257	0.242
J_{sc} (mA/cm^2)	0.330	0.376
V_{oc} (V)	0.514	0.514
FF	0.309	0.100
η (%)	0.052	0.019

An efficiency of 0.052% was obtained for DSSC with *Alstonia boonei* dye. While the control cell (anthocyanin dye) gave an efficiency of 0.019% as shown in Table 1. This shows that the *Alstonia boonei* dye is a better sensitizer when compared with the anthocyanin dye extracted from *Hibiscus sabdriffa* (Roselle). The value is low when compared with other results of 1.43% efficiency for undoped ZnO and 0.6% for Al doped ZnO electrode[20], 0.192% efficiency using Anacardium occidentale [21], 0.193% and 0.234% efficiencies using Z-907 with CO $(DTBEST)_3$ and CO (DEEST) respectively as electron mediators [22]. The low efficiency obtained in this work could be difference in the size of the cell active area ($0.42cm^2$) which is larger as well as the type of dye used. *Alstonia boonei* dye is a natural dye and as such is environmental friendly.

The I-V curves for both DSSCs with *Alstonia boonei* dye and anthocyanin dye are shown in Fig. 2.9 and Fig. 2.10 respectively.

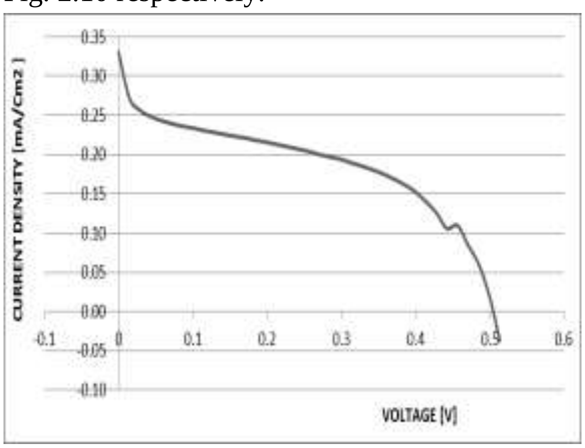


Fig. 2.9: I–V curve for DSSC with Stool wood dye.

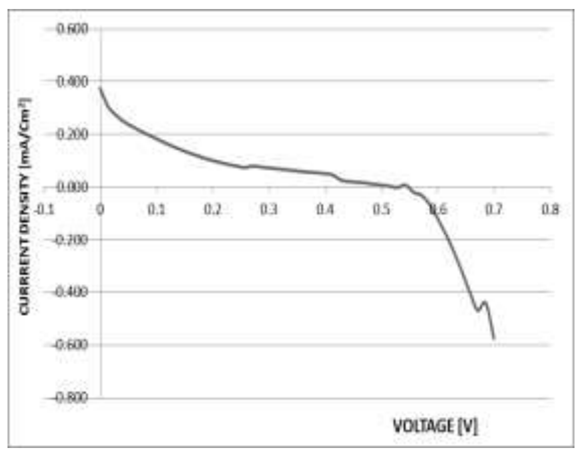


Fig. 2.10: I–V curve for DSSC with Anthocyanin dye.

CONCLUSION

Dye-sensitized solar cell (DSSC) using Stool wood (*Alstonia boonei*) was successfully fabricated using Doctor blade method and also characterized. Despite the fact that the size of the cell active area and film thickness used were small compared to other works, an efficiency of 0.052% was obtained. Also, the *Alstonia boonei* dye was able to narrow the band gap of the TiO_2 film to 2.00eV, for it to absorb light in the visible and even in the Near-Infrared (NIR) regions. This shows that *Alstonia boonei* dye is a good sensitizer for DSSCs. Therefore, DSSCs with *Alstonia boonei* dye, will produce clean and renewable energy which will serve as an alternative to the use of fossil fuel for energy production that has caused enormous environmental pollution

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CONFLICT OF INTEREST

We declare that there is no conflict of interest regarding this article

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