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# The performance and stability of anthocyanin local dye as a photosensitizer for DSSCs

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**ABSTRACT**

*Development of renewable energy resources in the near future is an urgent issue. One strategy is the development of dye-sensitized solar cells (DSSCs); they are extremely promising, because they are made of low-cost materials and they do not need elaborate apparatus to manufacture. Titanium (iv) oxide is the most promising material for the electrode of DSSCs, while ruthenium complexes remains one of the best sensitizers for $TiO_2$. We studied the performance of anthocyanin-dyed $TiO_2$ as a DSSC material. Anthocyanin dye is an extract from hibiscus sabdariffa which is an adible plant called zobo by Nigerians. Optical absorbance measurements showed that anthocyanin-dyed $TiO_2$ electrode could absorb incident solar radiation beyond the ultraviolet region. Comparison of current-voltage characteristics with those of a bare (unstained) solar cell revealed that the anthocyanin-dyed cell has an outstanding better photovoltaic behaviour than the bare cell. Out-door diurnal power variation measurements showed that the anthocyanin-stained $TiO_2$ electrode was not stable under exposure to incident solar irradiation.*

**Keywords:** Gratzel, natural dye, $TiO_2$, photovoltaic performance.

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## INTRODUCTION

The quality of human life depends largely on the availability of energy. However, the world is heading towards a global energy crisis due to a decline in the availability of cheap oil so that a decreasing dependency on the fossil fuel is recommended [1]. The importance of the utilization of renewable energies such as photovoltaics has grown remarkably because of the escalation of fossil energy costs and demand for $CO_2$ reduction in order to prevent global warming [1,2]. To fulfill these requirements, some new candidates of solar cells or photovoltaics have been invented and developed.

Dye-sensitized solar cell (DSSC) which was invented by Gratzel in 1991 is expected to be one of the next-generation photovoltaics because of its environment friendly properties, low manufacturing cost and low manufacturing energy consumption [1-5]. Recently, higher energy conversion efficiency was achieved on a small-sized DSSC than practical amorphous-type solar cells. Gratzel's group has successfully developed a high power conversion efficiency of about 11% with thick spin-coated nanoporous $TiO_2$ films as a photoelectrode [1,4,6]. Soon ZnO is seemed to be promising material for solar cell applications, since its band gap energy (3.37 $_e$v) is similar to $TiO_2$ [4,7-14]. Now, the remaining problems of DSSC for practical use are concerned with the unit cell size and structural design, fabrication process of cells and modules, and long term stability under out-door operation [2,5,15].

Any solar cell is a device that causes a voltage difference between the outer contacts at open circuit under incident photon irradiation. The dye-sensitized solar cell based on nanoporous titanium dioxide shows high conversion efficiency and stands out as a prototype of the new heterogeneous solar cells [3,5]. DSSC are distinct from conventional p-n junction devices by the distribution of the functions of light absorption, electron transport and hole transport to different materials [3,5,16]. These new features have caused a scientific controversy, in respect to whether the origin of the open-circuit voltage in DSSCs should be interpreted in terms of built-in potentials, which is suggested by some authors and denied by others [17-19].

The central idea in DSSC fabrication is to separate the light absorption process from the charge collection process, mimicking natural light harvesting procedures in photosynthesis, by combining dye sensitizers with semiconductors [5,15,20,21]. This enables the use of wid-egap but cheap oxide semiconductors such as $TiO_2$. Early DSSC designs involved transition metal coordinated compounds (e.g. ruthenium polypyridyl complexes) as sensitizers because of their strong visible absorption, long excitation lifetime, and efficient metal to ligand charge transfer [5,20,22]. Although highly effective, with current maximum efficiency of 11% [1,4,6,20], the costly synthesis and undesired environmental impact of those prototypes call for cheaper, simpler, and safer dyes as alternatives. Natural pigments, including chlorophyll, carotene, and cyanin, are freely available in plant leaves, flowers, and fruits and fulfill these requirements [16,20,21]. Hence, this work studies the photovoltaic performance of a DSSC fabricated with *anthocyanin* dye (a local dye extracted from *hibiscus sabdariffa*) by comparing its characteristics with those of un-dyed solar cell. Out-door diurnal power variation study was carried out to ascertain the stability of *anthocyanin* dye.

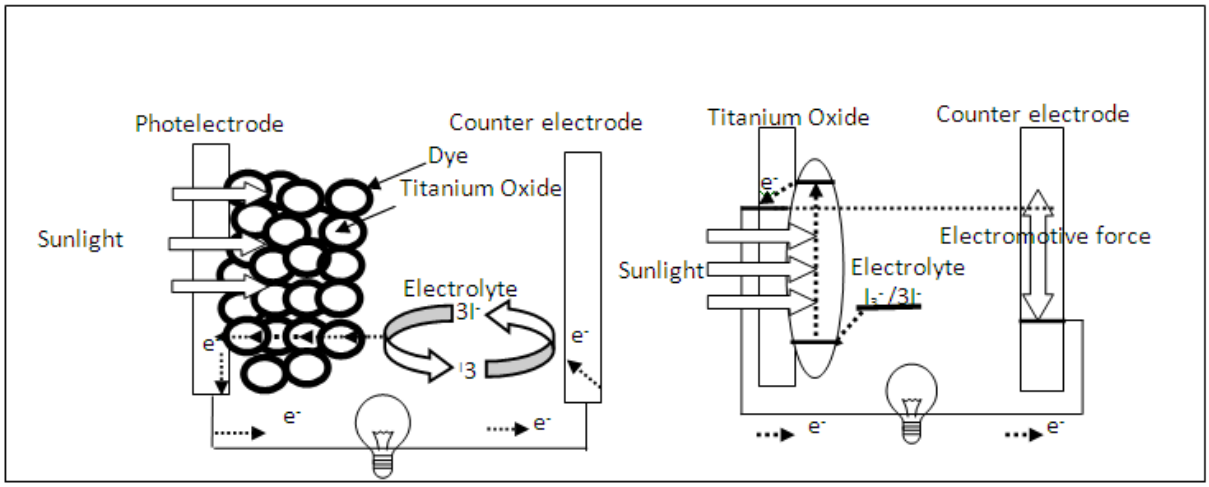


**Figure 1. The structure (left) and principle of operation (right) of dye-sensitized solar cell**

## MATERIALS AND METHODS

### 2.1 Electrode preparation

In this work, an equal amount of well blended powdered activated carbon (PAC) and a kind of natural graphite powder (NGP) was used as counter electrode for both cells. The deposition of our counter electrode on fluorine-doped tin oxide (FTO) glass substrate was enabled through the sol-gel process and doctor- blading method. The conducting side of a 2.5cm x 2.5cm FTO was identified and covered on each of the two parallel edges with a double layer of masking tape to control the thickness of the $TiO_2$ film (Fig. 2). The covered FTO edge measuring 2.5cm x 8mm provided the electrical contact area. Before deposition, the glass substrate was cleaned with acetone, then methanol and etched through plasma treatment for 1min. The carbon paste which was prepared through sol-gel technique was applied at one of the edges of the conducting glass and distributed with a squeegee sliding over the tape-covered edges. A hot air blower was used to dry the electrode for about 3 minutes before removing the adhesive tapes. The edges were cleaned with ethanol. The carbon electrode was sintered at $150^0$C in a furnace (carbolite 201 tubular furnace) for about 15 minutes.

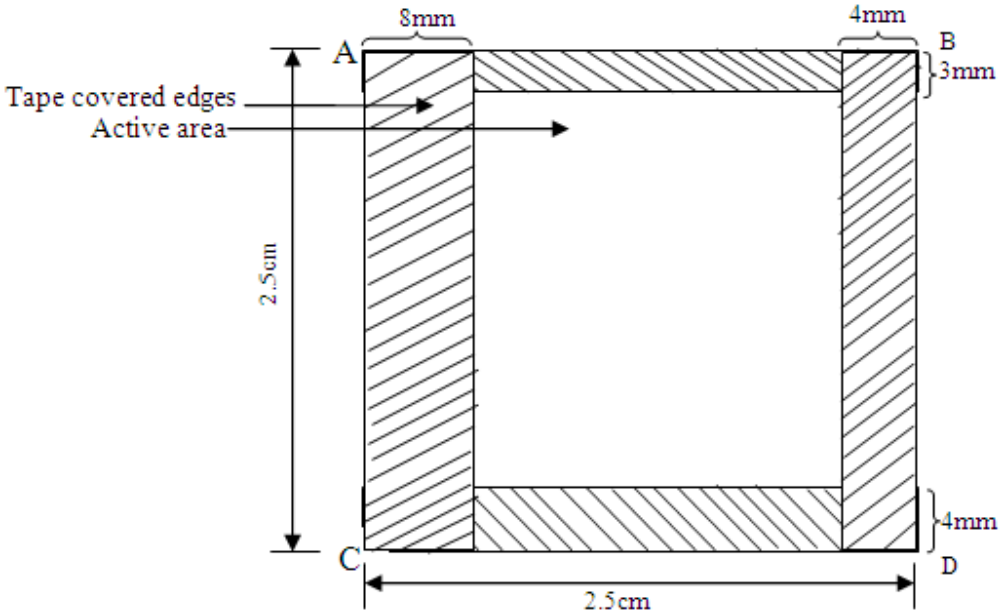


**Figure 2. Preparation of the FTO for electrode deposition**

Nanocrystalline titanium (iv) oxide (Ti-nanoxide T/sp) was used as photo-electrode. The same blade method was adopted in depositing the $TiO_2$ layer and the film was allowed to dry naturally without blowing before removing the adhesive tapes. The edges were also cleaned with ethanol. The electrode was sintered for 30 minutes at 400 $^0$C using the same carbolite 201tubular furnace.

**2.2 Dye sensitization**

The *anthocianin* dye used in sensitizing the mesoporous $TiO_2$ film was extracted from hibiscus sabdariffa which is a common edible plant called zobo by Nigerians. Extraction of the pigment from hibiscus sabdariffa was achieved through this simple process:

(i) Blend the hibiscus sabdariffa using electric blender.
(ii) Add 90% ethanol and continue blending.
(iii) Use sieve to extract the pigment which forms our dye.

The $TiO_2$ photo-electrode was immersed into a solution of the local dye overnight. The electrode was preheated at 80$^0$C for 15 minutes before it was dipped into the dye solution. Another photo-electrode was prepared without sensitization.

**2.3 Cell fabrication**

Sealing gasket (SX 1170 – 60 PF) brings the ease of using a 60µm thick hot melt foil for sealing the cells (Figure 3). The sealing gasket was cleaned in ethanol before it was rightly placed on the dyed working electrode. The counter electrode was gently placed on top of the frame and held in position with a clamp with the conducting carbonized side towards the working electrode. The set up was held over a hot plate for 1 min at 150 $^0$C before allowing it to cool for a few minutes. We introduced few drops of the electrolyte (Iodolyte R-150) through one of the 3mm holes by capillary action. The holes were then sealed using Amosil 4R sealant. Electrical contacts were made by applying silver paint along the conducting side of each electrode. A second cell was assembled using the un-dyed $TiO_2$ electrode to obtain our plain cell. The active surface area of the *athocyanin*-dyed cell was 1.54cm$^2$ and that of the plain cell was 2.25cm$^2$.

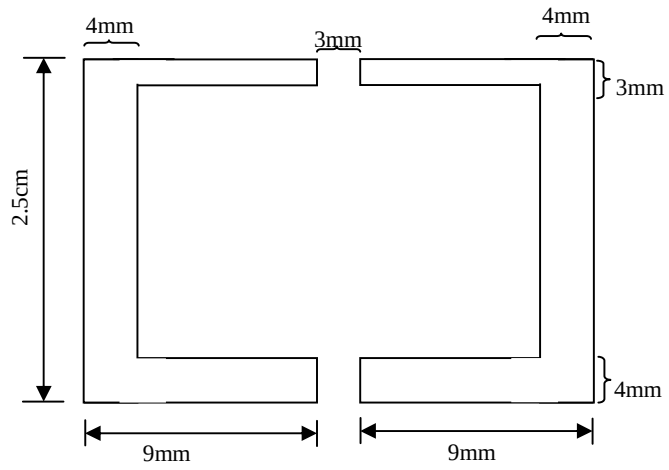


**Figure 3. The sealing gasket**

**2.4 Solar cell characterization**

The thickness of both electrodes was measured using Dektak stylus 7.0 surface profiler. The sheet resistance of the carbon counter electrode was measured using dual-Pro 301 (auto calculating 4 pt. Probe resistivity test system). The optical absorbance of the *anthocyanin*-stained $TiO_2$ was measured using Avaspec 2.1 spectrophotometer. The current-voltage (I-V) characteristics were measured using an Oriel class A solar simulator (AM 1.5, 100mW/cm$^2$). Outdoor output power measurements were carried out using a copper/constantan thermocouple and Mastech MY64 digital multi-meter. This diurnal measurement was carried out on top of a zinc roof measuring 6.5m from ground, for three non-consecutive days within a space of three weeks.

## RESULTS AND DISCUSSION

The thickness and sheet resistance of the carbon counter electrode were 4.2µm and 15.4Ω/square respectively while the thickness of the photo-electrode was 6.2µm. *Anthocyanin*-stained $TiO_2$ electrode showed an outstanding optical absorbance within the wavelength range of 283nm – 516nm. Peak absorbance of 2.16A.U., 2.26A.U. and 2.38A.U. were recorded in the UV region at 324.45nm, 344.87nm and 369.35nm respectively (Figure 4). Appreciable absorbance was recorded in the visible region with two outstanding peaks; 2.26A.U. and 2.16A.U. at the wavelength of 405.99nm and 426.47nm respectively. Meanwhile, Lee and Kang, 2010 [23] studied an unstained nanoporous $TiO_2$ and obtained optical absorbance of 1.3A.U. and 1.2A.U. at 200nm and 350nm respectively but no optical absorption was recorded beyond UV region. Also, a bare $TiO_2$ nanowire studied by Meng et al, 2008 [20] showed no optical absorbance beyond 400nm. Hence, the *anthocyanin* dye greatly improved the optical absorbance of the $TiO_2$ electrode.

Figure 5 and Figure 6 are the photocurrent-voltage characteristics of DSSCs fabricated with the *anthocyanin*-dyed and un-dyed electrodes respectively. The cell parameters obtained for the *anthocyanin*-dyed cell were; open circuit voltage (0.33V), short circuit photocurrent (2.60mA/cm$^2$), fill factor (0.68) and photoelectric conversion efficiency (0.58%); while the results obtained for the plain cell were; open circuit voltage (0.24V), short circuit photocurrent (0.20mA/cm$^2$), fill factor (0.63) and photoelectric conversion efficiency (0.03%). The performance of the dyed cell could be compared to the results obtained by Sirimanne *et al*, 2008 and Waita *et al* 2006 [15,22].

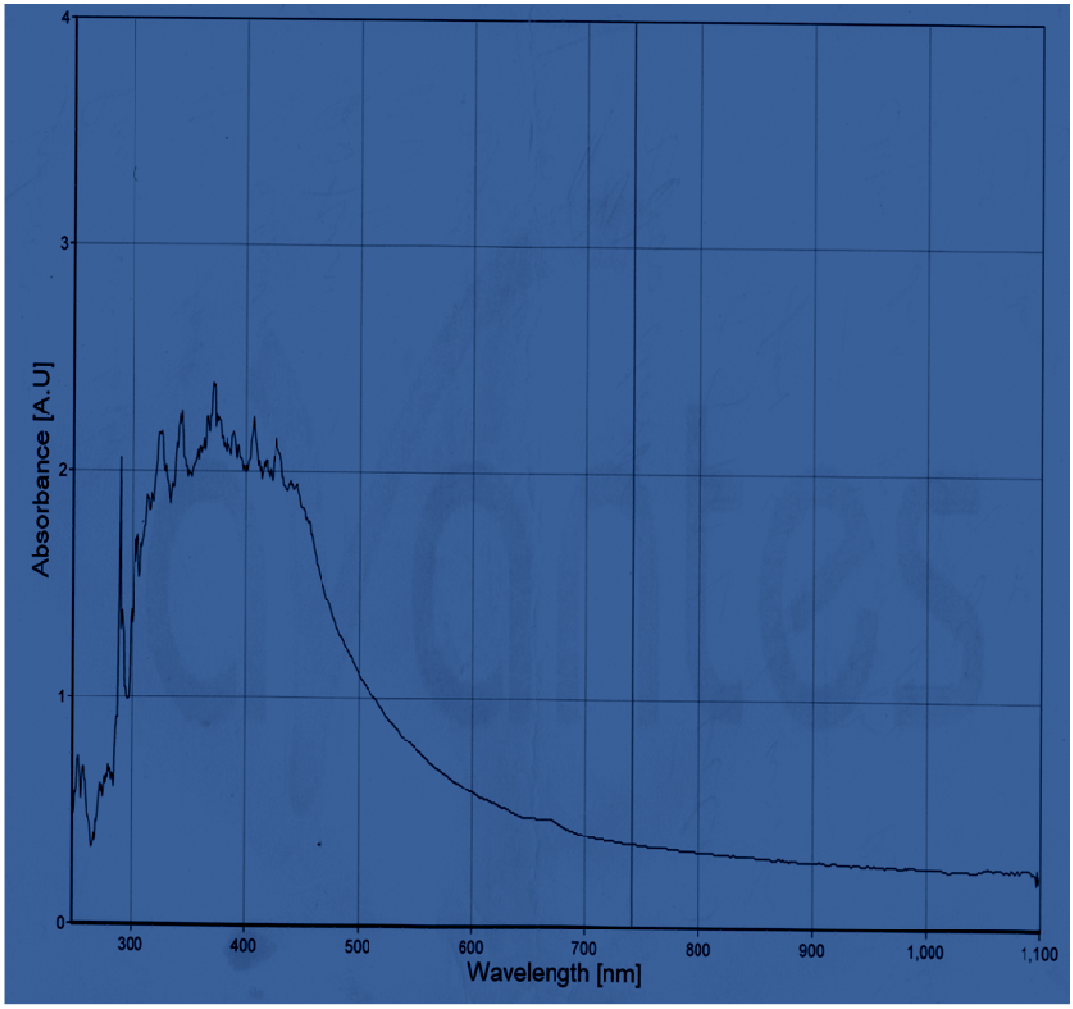


**Figure 4. Optical absorbance of *anthocyanin*-stained $TiO_2$ electrode**

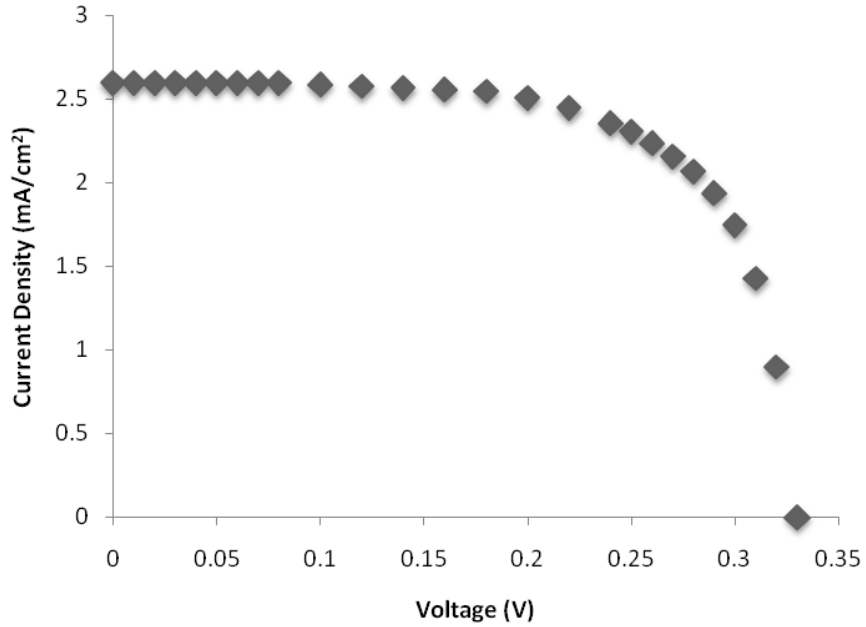


**Figure 5. The I-V curve of the cell sensitized with *anthocyanin* dye**

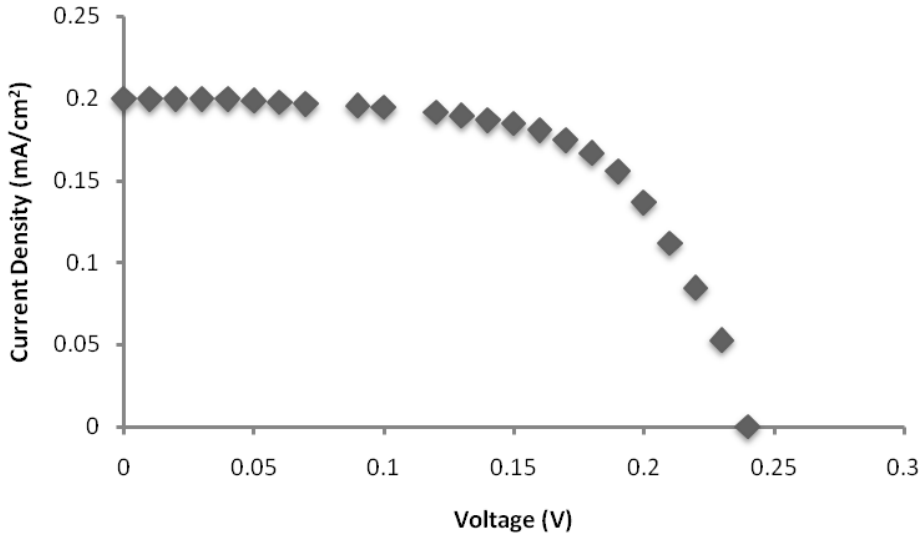


**Fig. 6. The I-V curve for the plain cell**

Figures 7, 8, 9, 10 and 11 are the results of the outdoor power variation study. The *anthocyanin*-dyed cell performed better than the plain cell on days 1 and 2 but exhibited a poorer photovoltaic behavior on the third day. The astonishing poor photovoltaic performance of the *anthocyanin*-dyed cell under out-door operation can be clearly observed in Figure 10,whereas Figure 11 revealed that the plain cell was relatively stable after exposure to out-door solar irradiation.

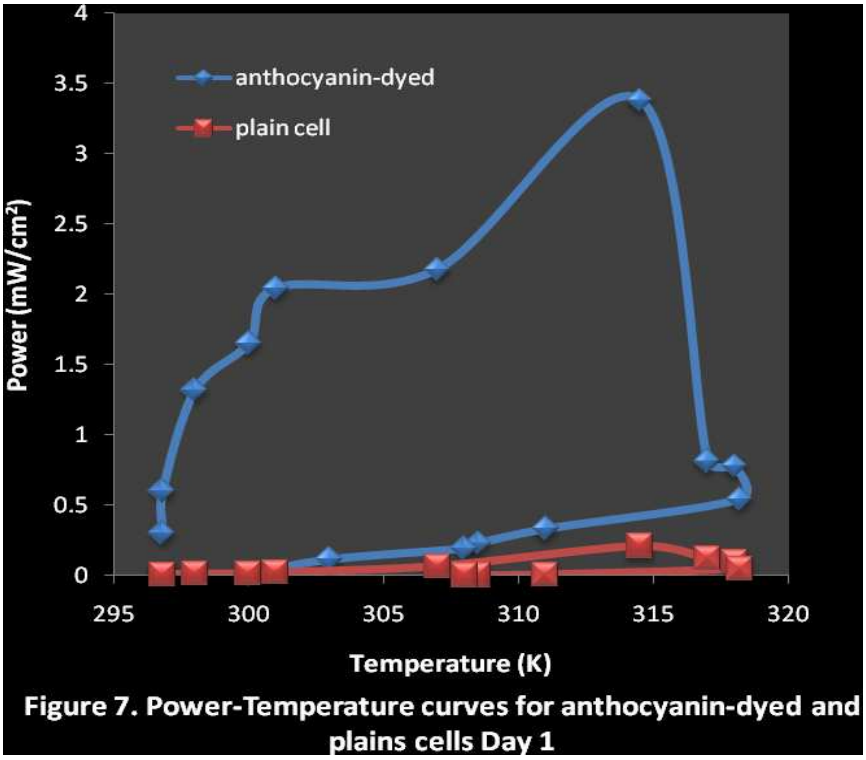


**Figure 7. Power-Temperature curves for anthocyanin-dyed and plains cells Day 1**

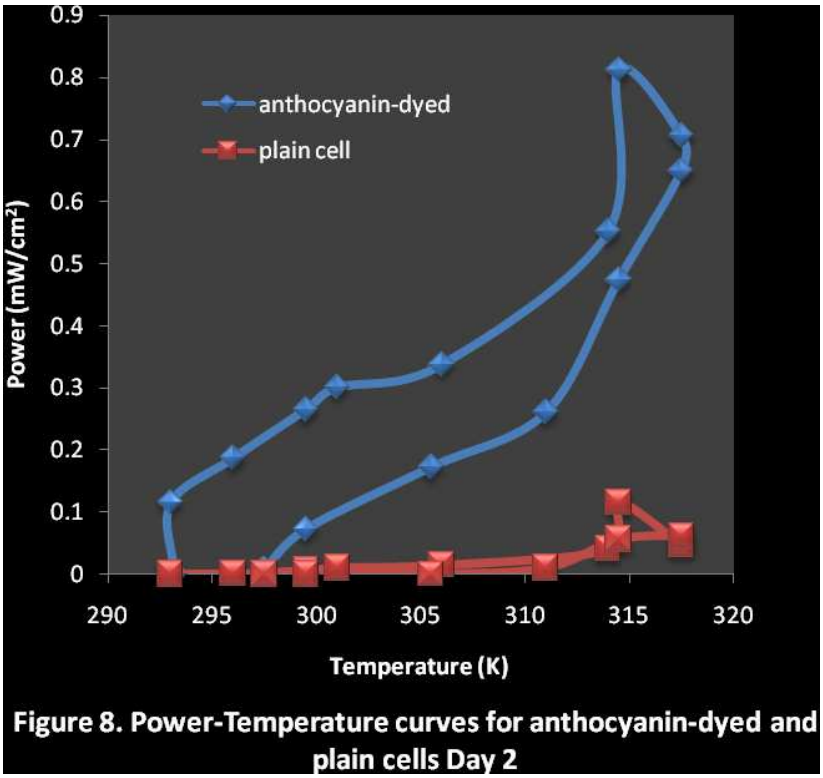


**Figure 8. Power-Temperature curves for anthocyanin-dyed and plain cells Day 2**

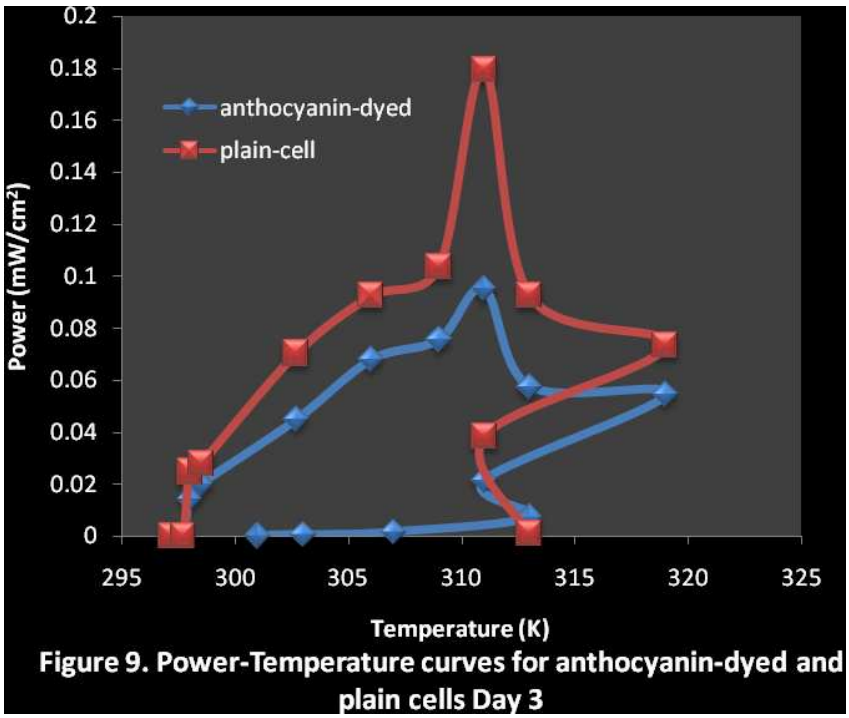


**Figure 9. Power-Temperature curves for anthocyanin-dyed and plain cells Day 3**

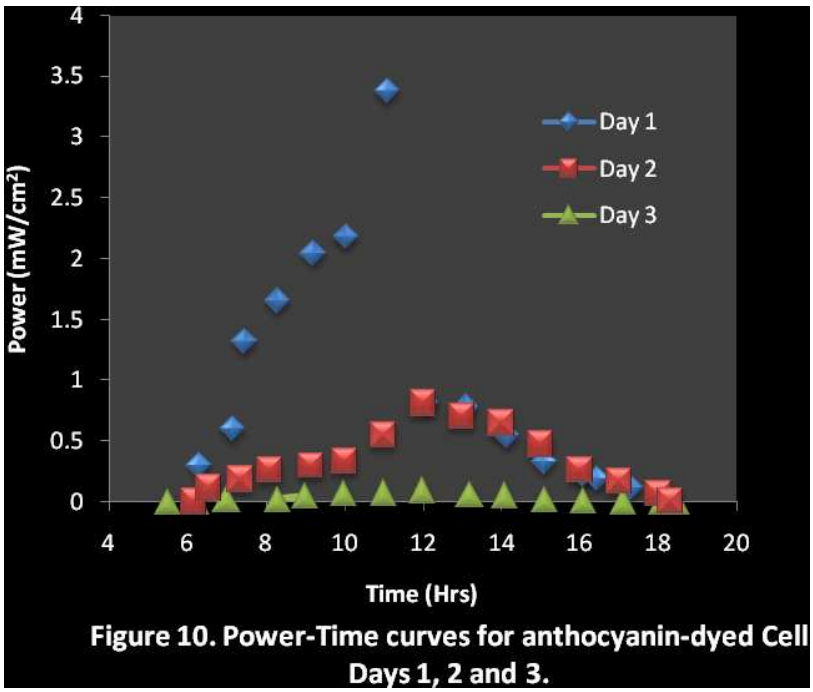


**Figure 10. Power-Time curves for anthocyanin-dyed Cell Days 1, 2 and 3.**

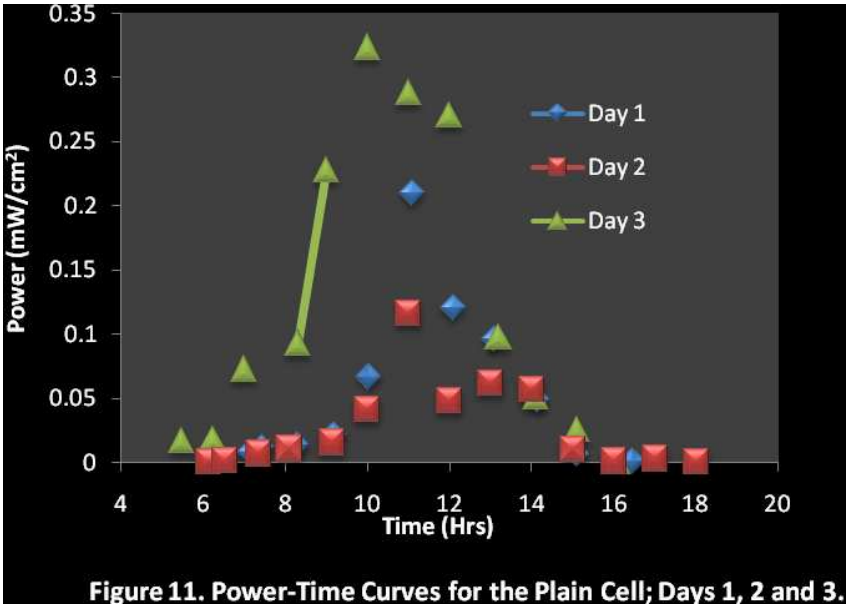


**Figure 11. Power-Time Curves for the Plain Cell; Days 1, 2 and 3.**

## CONCLUSION

Nanocrystalline titanium (iv) oxide was sensitized using *anthocyanin* dye, which is an extract from hibiscus sabdariffa. Dye sensitized solar cell based on *anthocyanin* dye and a second plain-cell were successfully fabricated and characterized. The effect of this local dye on the optical absorbance of the wide band gap $TiO_2$ semiconductor and the photovoltaic behavior of the cells were studied. The sensitized photoelectrode was able to absorb incident solar radiation beyond the ultraviolet region. The incident solar light to electric energy conversion efficiency was found to be 0.58% and 0.03% for the *anthocyanin*-dyed cell and the un-dyed cells respectively. The *anthocyanin*-dyed cell showed an impressive out-door photovoltaic behaviour, but could not maintain stable characteristics. Generally, the *anthocyanin* dye is a viable photo-sensitizer for nanocrystalline titanium dioxide, though the local dye need to be improved to ensure its stability under out-door operation.

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