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Performance Analysis of a Natural Dye Based Dye Sensitized Solar Cell

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Abstract: ***The dye-sensitized solar cell (DSSC) technology, taken as a new generation of photovoltaics, is an efficient and economical way to directly convert solar energy into electricity. The significant recent development of the DSSC technology has demonstrated its promise for future renewable solar electricity generation. In this paper a solar cell using DSSC technology has been proposed where a common Bangladeshi seasonal fruit, blackberry (syzygium cumini) has been used as the sensitizer. TiO_2 has been used as the n-type semiconductor material and for the experimental purpose a 500 Watt halogen lamp has been used. The performance has been analyzed by using platinum counter electrode. The experimental study has been performed in the Laboratory of University of Dhaka.***

Keywords: Solar Cell, DSSC, Natural Dye, Platinum electrode, SEM, Absorption Spectrum.

1. Introduction

A solar cell (also called photovoltaic cell) is an electrical device that converts the energy of light directly into electricity by the photovoltaic effect. Photovoltaic is the field of technology and research related to the practical application of photovoltaic cells in producing electricity from light, though it is often used specifically to refer to the generation of electricity from sunlight.

Fossil fuels are being depleted and produces by-product like carbon dioxide, carbon monoxide, sulphur dioxide which contributes to global warming[1]. There is a need to find alternative source of energy. Some alternative energy sources such as hydroelectricity or wind are limited to areas with windy environments or flowing rivers. On the other hand, sun allows all parts of the world to use its energy. Solar energy is not only environmentally safe, but also a source of energy that will exist for billions of years. The solar cell with the highest efficiency currently, 25%, is a silicon p- n junction solar cell [2]. The production cost of these crystalline solar cells is very high, and that is one of the hurdles for the mass use of this technology. In 1991, Michael Gratzel created a low-cost dye sensitized solar cell (DSSC) with titanium (IV) oxide (TiO_2) as a wide band-gap semiconducting oxide and a ruthenium based dye to sensitized TiO_2 and obtained a solar cell efficiency of 10.4% [3].

The dye sensitized solar cell (DSSC) technology has been developed for low-cost, high-efficiency solar-to-electricity conversion. A DSSC with an effective area of 1.004 cm^2 under global AM1.5 spectrum (1000 Wm^{-2}) at 25 °C exhibits a short-circuit current of 21.8 $mAcm^{-2}$ and an open-circuit voltage of 0.729 V with a fill factor of 0.652 and an efficiency of 10.4 ± 0.3 % [4]. The submodule mode of DSSC with an effective area of 26.48 cm^2 has achieved an efficiency of 7.9 ± 0.3 %. In fact, the theoretical efficiency for the terrestrial cell can reach as high as 30 % [5] indicating that there is much room for enhancing the energy conversion efficiency of DSSC. Despite the fact that the prices of conventional fuels are rising, the DSSC has been following the trend of declining costs and eventually it will constitute 20% or greater proportion in the growing solar-to-electricity market [6].

In this paper we have constructed a DSSC for the first time in our university. As the wide band gap semiconducting oxide we have used nano particle TiO_2. TiO_2 is widely available and is common in everyday household items, such as sunscreen. To sensitize the oxide we have used a natural dye extracted from blackberry (*syzygium cumini*), a seasonal fruit in Bangladesh. As the counter electrode we have used platinum. We also have used an iodide/tri-iodide couple electrolyte solution in the solar cell as a charge carrier.

In laboratory we have used a halogen bulb as the light source to get the Current-Voltage characteristic of the cell. Power-Voltage characteristic was also obtained. This was understandable since dye from black berry absorbs light in the UV region while our light source didn't have any light in that region.

2. Theoretical Background

When the light from the sun falls on any solar cell, three basic operations consists of absorption, separation and collection are held [7] .For DSSC, it applied absorption process to absorb the photon from the sun rays. The DSSC are fabricated by sandwiching a dye anchored mesoporous metal oxide, known as photoelectrode, between two conducting glass plates (such as fluorine-doped indium tin oxide (FTO)) in the presence of an electrolyte [8] Basically, there are four main components in DSSC such as light source, semiconductor, sensitizer and the electrolyte [9] which play important role in the DSSC. Each of the components has their own function.

The DSSC principle is applied from the photosynthesis process and diffusion is a major mechanism for electron to travel through the oxide layer [10]. The electronic process in DSSC involved several steps as shown in Figure 1 & 2.

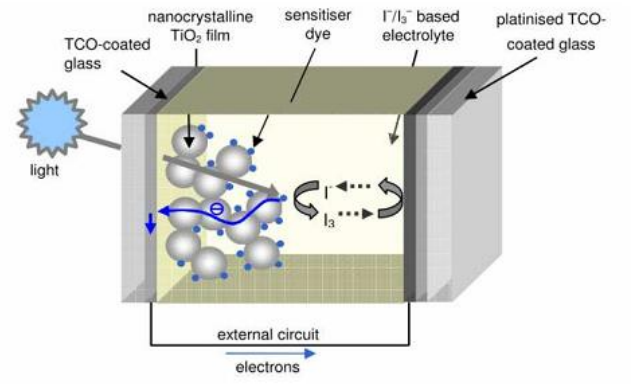


Figure1: Schematic of a liquid electrolyte DSSC with external circuit [11]

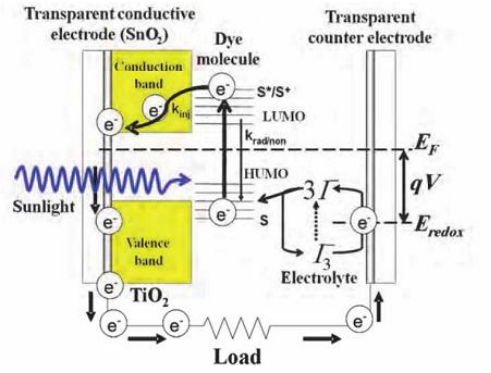


Figure2: Schematic illustration of electron movement of dye sensitized solar cell [12].

The steps involve:

(a) When the photon from the sunrays enters into the DSSC device. According to Eq. (1), the sensitizer, S absorbs a photon of wavelength, hν corresponding to the energy difference between its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) which leads to excited sensitizer state, S* known as photo excitation.

(b) Photo excitation, S* of this sensitizer is then injected the electron,e refer to Eq. (2), which travel through the nanostructured film by diffusion into the conduction band of the semiconductor (mesoporous),usually using TiO_2 (high band gap: 3.2 eV) to reach TCO on glass substrate as a current collector. Meanwhile according to [13], the hole generated by photon excitation remains on the molecule during this process, since the HOMO of dye is separated from all other energy levels of the device. There is no energy channel for the hole to diffuse into TiO_2photoanode. As a result, the hole is eventually filled up by electrons from electrolyte ions, which conduct current between the cathode and the dye molecule.

(c) The injected electron,e flows through the semiconductor network to arrive at the back contact by through the external load.

(d) By referring Eq. (3), the injected electron,e at back contact react in reduction of oxidized dye by iodide produces triiodide, I^{-3} to reduce the redox mediator. At the same time, the triiodide, I^{-3} diffuses to counter electrode and accepts electrons from external load, regenerating the iodides [14].

(e) Then, iodide wills donates electron to the oxidized sensitizer, S^+ that obtained at anode from Eq. (2) and regenerates the sensitizer which in turn regenerates the sensitizer as shown in Eq. (4). This process occurs quickly and results in no net chemical change [15]

(f) However, Eqs. (5) and (6) are undesirable reactions either with oxidized sensitizer or with the oxidized redox couple at the TiO2 surface. Consequently, performance of the cell will be affect.

This process goes in cycle and consequently current flows through the external circuit as long as light are incident on the cell [16]. The equations below show the reaction of the sensitizer and electron in the DSSC [17-20] that have been explained.

$$S_{(absorbed)} + h\nu \rightarrow S^*_{(absorbed)} \quad (1)$$

$$S^*_{(absorbed)} \rightarrow S^+_{(absorbed)} + e^-_{(injected)} \quad (2)$$

$$I_3^- + 2\,e^-_{(cathode)} \rightarrow 3I^-_{(cathode)} \quad (3)$$

$$S^+_{(absorbed)} + \frac{3}{2}I^- \rightarrow S_{(absorbed)} + \frac{1}{2}I_3^- \quad (4)$$

$$S^+_{(absorbed)} + e^-_{(TiO2)} \rightarrow S_{(absorbed)} \quad (5)$$

$$I_3^- + 2\,e^-_{(TiO2)} \rightarrow 3I^-_{(Anode)} \quad (6)$$

By referring the above figure, it shows the illustration of electron movement in the first step until to last step. This process will go on continuously as long as the sun rays incident on the cell. According to Fig. 2, the maximum voltage in DSSC is determined by the energy separation between Fermi level and the electrolyte chemical potential (Eredox). The photocurrent level is dependent on the separation level of HOMO-LUMO as example, if the energy separation of LUMO is increase, it will improve the electron injection into the conduction band of TiO2 effectively [21]. Besides, if the HOMO level accept the donated electrons from redox mediator effectively, it show that the energy different between the HOMO and redox mediator is positive. We can conclude that photo voltage is generally determined by the energy difference between the Fermi level of TiO2 and redox potential of electrolyte. The anode-cathode potential difference, namely, the open-circuit voltage Voc, is mainly determined by the difference between conduction band bottom and electrolyte anion energy level [22]. At short-circuit condition, the Fermi energy level decreases in the direction of the back contact (charge collector) due to difference in electron concentration with TiO_2 film distance. On the other hand, at open- circuit condition the Fermi energy level is constant across the entire film [23].

One of the most important problems is the recombination of the photo injected electrons in the conduction band of the semiconductor with the oxidized dyes and the triiodide in the electrolyte. In DSSC, the individual particle size is so small that the formation of a space charge region is impossible [24-25]. This indicates that the recombination rate of the photo injected electrons is very high due to the absence of an energy barrier at the electrode/electrolyte interface [25]. So many studies to reduce the recombination at the interface were tried such as fabrication of bilayer electrode,

preparation of composite semiconductor electrode, and passivation of semiconductor electrode using electro polymerization method and so on [25]

3. Experimental Details

For the experimental study, several DSSC sample was made the following procedure was followed for that.

3.1 FTO Coated Glass

We used Fluorine doped tin oxide [FTO] coated Glass as a substrate in our experiment. FTO coated glass is generally of float (soda-lime) glass using polished and unpolished substrates. These products are for use in spectro-electrochemistry, liquid crystal display [LCD] research and development, organic light emitting diode [OLED] research and development, phosphor research and quality control, electro- luminescent display [ELD] development, photovoltaic development, and other applications that require the properties of FTO coated glass such as:

- Electrically conductive and optically transparent.
- High VIS-NIR light transmission.
- High quality glass substrate.
- SiO_2 barrier layer.
- Low roughness.
- Low sheet resistance ~14ohm/sq.
- Uniform transmission up to ~90%.
- Reflecting in the infrared range.

3.2 Platinum coating

FTO coated glass plates were cleaned using following procedure:

- Washed with detergent water in ultrasonic bath for 10 minutes.
- Then cleaned in distilled water for 10 minutes.
- Cleaned with acetone for 10 minutes in ultrasonic bath.
- Finally Cleaned with isopropyle alchohol for 10 minutes in ultrasonic bath.

We have placed FTO glass plate into the sputter coater. Then we have made a thin platinum layer on conducting side of FTO glass plate.

3.3 Preparation of TiO_2 coated slide:

At first TiO_2 paste was made adopting the following procedure: 9 ml vinegar is added to 6 g titanium dioxide and mixed until it became smooth. Then one drop of dishwashing detergent is added to the suspension and kept in that condition for 15 minutes.

We took one piece of FTO glass plate which has been cleaned thoroughly as described before and have put 0.04mm thickness scotch tape on two sides of the conducting side of FTO glass. Then we used a small paintbrush to distribute a thin layer of the TiO_2 solution across the conducting surface of a FTO glass shown in Figure 3.

Figure 3: TiO_2 substrate

So the thickness of the TiO_2 layer is 0.04mm. We allowed the slide to dry for a few minutes, placed the TiO_2 coated slide on a hotplate at 300°C for around 20 minutes. Then we turned off the heater so that slide can come back the room temperature slowly.

3.4 Preparation of Dye Solution

We took four dry black berries and collected their barks and made a paste with them, then immersed the paste in 2 ml ethanol kept it there for overnight so that dye can be absorbed in ethanol effectively. Next morning we have put the solution in ultrasonic bath for 30 minutes. Finally we filtered to solution to collect dye.

3.5 Sensitizing with dye

For that we put a drop of dye on top of the previously prepared TiO_2 coated substrates. For the blackberry dyes we had to keep the dye on top of TiO_2 coated surface for several hours for the dye to properly stain the TiO_2 matrix. After staining we rinsed the slides with distilled water and allowed them to dry for a few minutes.

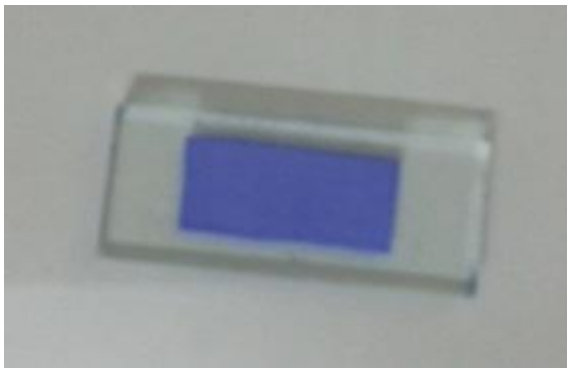


Figure 4: Dye sensitized TiO_2 substrate

3.6 Preparation of Iodide Electrolyte Solution

We have dissolved 0.127 g Iodine in 10 ml of ethylene glycol. Next added 0.83 g Potassium Iodide (KI), then stirred and stored in a dark container.

3.7 Assembly of the Solar Cell

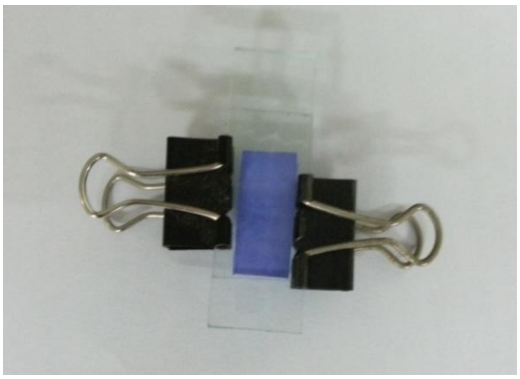
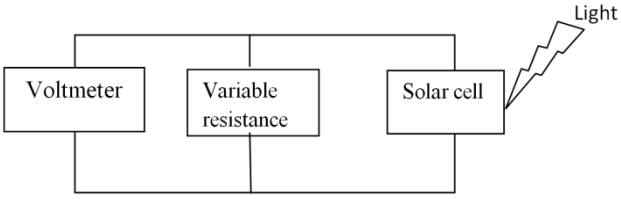


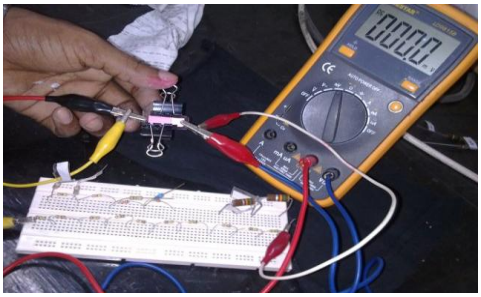
Figure 5: Assembly of the Solar Cell

We have put 0.181mm thickness scotch tape (acts as spacer) on two sides of dye sensitized TiO_2 coated side. We then placed the platinum coated slide face down on top of the TiO_2 coated slide. So cell thickness is 0.181 mm. We used two binder clips to hold the two slides together as shown in fig.-5. Then with a dropper, added one to two drops of liquid iodide/iodine electrolyte solution to the space between the two slides. The solution was drawn into the cell by capillary action .Attached the alligator clips to the two overhanging edges of the slides and attached the clip l to multi-meter with the negative terminal attached to the TiO_2 coated slide, and the positive terminal attached to the platinum coated slide

3.8 Photocurrent Measurement:



(a)



(b)

Figure 6: (a) Circuit diagram, (b) Measurement of I-V characteristics

- Solar cell is connected as shown in figure 6 using cables.
- Light from a 500 watt halogen bulb is used as a light source and the sample cells were always 70 cm away from the light source for all the I-V measurements for all the cells discussed in this thesis.
- At first the load resistance was fixed at the maximum value and the corresponding voltage was recorded later the resistance was decreased gradually and the corresponding voltages was recorded.
- The photocurrent was calculated for each recorded data using Ohm's law.

$$I = V / R$$

- Also the power for each load resistance was calculated using the following formula.

$$P = V \times I$$

4. Results and discussion

4.1 SEM Image of TiO_2 coated glass slide

We have used 100nm TiO_2 to make the paste, but from the image we see that nano particles were clustered together with an average size around 200nm-300nm. From the image we can also observe that there are lots of pores in TiO_2 matrix.

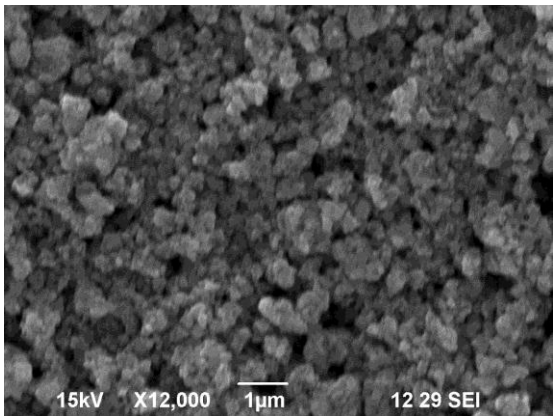
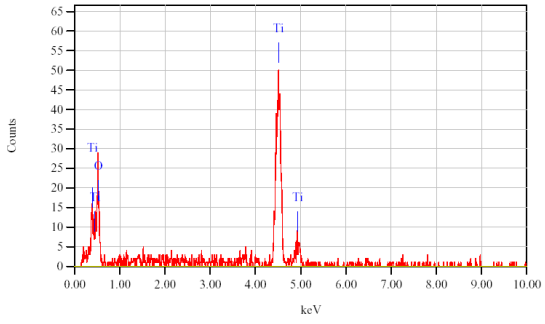


Figure 7: Image of TiO_2

This is very important so that dye can enter the matrix and properly stain the maximum area possible of the TiO_2 matrix.

4.2 Energy dispersive spectroscopy (EDS)



ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.4718

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
O K	0.525	42.16	0.38	68.58				20.0473
Ti K	4.508	57.84	0.33	31.42				79.9527
Total		100.00		100.00				

Figure 8: Graph of elemental analysis of TiO_2 thin film

From the EDS report we see that TiO_2 thin filmcontains 68.8% oxygen (O) and 31.42% titanium (Ti) as expected.

4.3 I-V and P-V data

4.3.1 Study of blackberry dye as sensitizer

As mentioned before we have used blackberry dye for sensitizing TiO_2. Data for I-V and P-V measurement are plotted below.

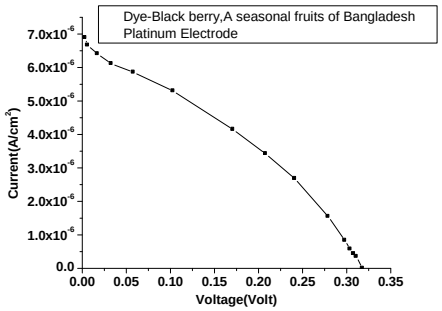


Figure 9: Cell Voltage (volt) Vs Cell current (A/cm^2)

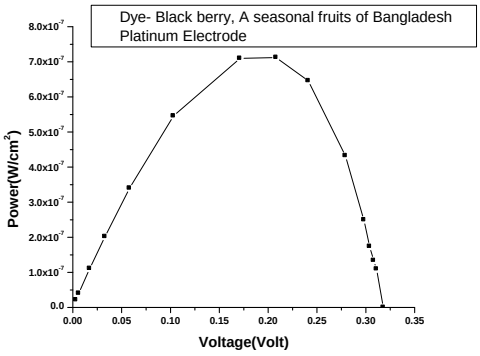


Figure 10: Cell Voltage (Volt) Vs Power (W/cm^2)

The maximum power along with the short circuit current and open circuit voltage of the cell are given below:

Table 1: Data for Short circuit current, Open Circuit Voltage, Maximum Power and Fill factor

Short circuit current (I_{SC}) (A/cm$^{2)}$)	Open Circuit Voltage (V_{OC}) (Volt)	Maximum Power (P_{max}) (W/cm^2)	Fill factor
6.96x10^{-6}	0.318	7.14x10^{-7}	32.26%

To explain the result we need to study the light spectrum of halogen bulb in comparison to solar light and also we need to know the absorption spectrum of the dyes used. These are discussed below.

4.3.2 Halogen spectrum

As mentioned before since we didn't have a solar simulator we used a 500 watt halogen bulb as the light source. The spectrum of halogen light is shown in the figure 11 and it showed that halogen light gives ray from 500nm to 1000nm with a maximum intensity at around 750nm. This showed that unlike sun there is no UV light emitted by this source.

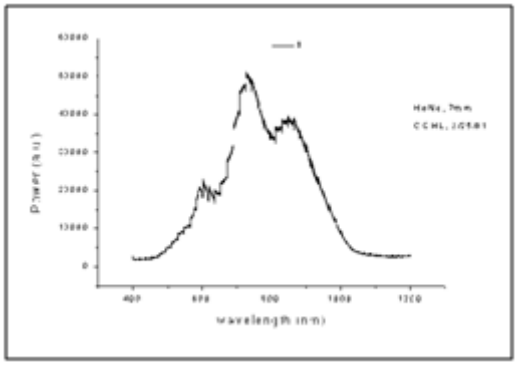


Figure 11: Halogen spectrum [26]

For comparison purpose we have also added the sun's spectrum from literature [27] in the next figure12.

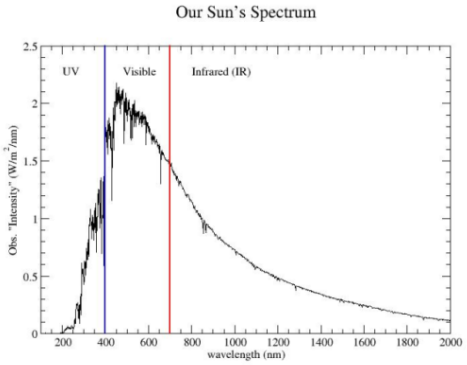


Figure 12: solar spectrum [27]

It is clear that absence of UV light from around 200 nm to around 400 nm in the halogen bulb is responsible for smaller power generated in our DSSCs in comparison to the power obtained by the others [28].

4.3.3 Absorption spectrum of dyes

We have taken the absorption spectrum of Syzygium cumini (Blackberry) using a UV-Vis spectrophotometer (Model no Shimadzu: UV-1800). The data is presented in figure-13. Also the wavelength corresponding to the maximum efficiency and the range of wavelength where appreciable absorption happens is tabulated in the Table 2.

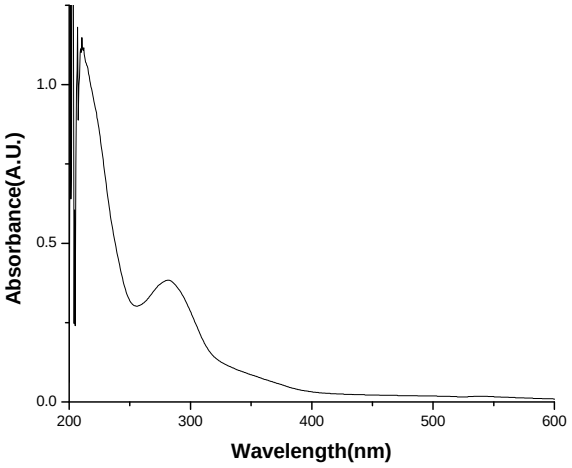


Figure 13: Graph of absorbance measurement

Table 2: Range of absorbance and peak position for *Syzygium cumini*(Blackberry)

Peak position (λ_{max}) in nm	Range of absorbance (nm)
282	200 – 400

Analyzing the above data tells us that cell sensitized with dye extracted from black berry absorbs light from 200 to 400 nm. Although the halogen bulb that we have used does not produce any light in the 200 to 400 nm range as evident from the discussion from the earlier section from dye extracted from black berry there is appreciable absorbance from 200 to 350 nm and after that the absorbance decreases and becomes negligible up to 580nm.

Since halogen bulb doesn't produce any light in the UV region and dye extracted from black berry doesn't absorbs much light in the visible region so the energy conversion efficiency for this cell was very low. If we could do the experiment using full solar spectrum simulator then the power obtained from the cells would have been more. Besides the use of 100nm TiO_2 powder contributed towards the lower performance of the cells since using even smaller particles more surface area can be exposed to solar light and thus there will be a considerable increase of the possibility of more solar light harvesting.

5. Conclusion

In this work we have constructed a DSSC for the first time in our university. We have used Platinum as electrode in this work. We have recorded the I-V and P-V characteristic curve for the cell.

We have used dye extracted from black berry (Syzygium cumini) for sensitizing TiO_2 and made cell with Platinum electrode. Data for I-V and P-V measurement showed that the power generated is much lower than that of conventional cells. To find an explanation of the above behavior we took absorption spectra of the dye extracted from black berry used in our study, the spectra showed that even the halogen bulb that we have used does not produce any light in the 200 to 400 nm range, dye extracted from black berry has an appreciable absorbance from 200 to 350 nm. That is the main reason for lower power produced by the cell using dye extracted from black berry. If we could do the experiment using full solar spectrum simulator then the power obtained from the cells would have been more. Besides the use of 100nm TiO_2 powder contributed towards the lower performance of the cells since using even smaller sized particles, more surface area can be exposed to light and better output power can be achieved.

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