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The Investigation of the Effects of Blackberry Dye as a Sensitizer in TiO_2 Nano Particle Based Dye Sensitized Solar Cell

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ABSTRACT— ***Alternative energy source is needed for next generation due to the shortage of Fossil fuels in world. 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. Dye sensitized solar cells (DSSC) technology attracted the researcher for its low-cost, high-efficiency solar-to-electricity conversion. An investigation was conducted to study of the effects of blackberry dye (syzygium cumini), a seasonal fruit in Bangladesh as a sensitizer. In this work we have constructed a DSSC where we have used nano particle TiO_2 as the wide band gap semiconducting oxide. To sensitize the oxide we have used a natural dye extracted from blackberry (syzygium cumini). As the counter electrode we have used photosensitive materials carbon. We also have used an iodide/tri-iodide couple electrolyte solution in the solar cell as a charge carrier.***

Keywords—Solar cell, DSSC, Dye of Black berry, Carbon Electrode, SEM, Emission Spectrum of Incandescent bulb.

1. INTRODUCTION

Dye-sensitized solar cells (DSSC) are a new type technology for converting light energy into electrical energy. Due to its low fabrication cost, environmental compatibility, and the simplicity of the process, interest in DSSC has been grown day by day. Fossil fuels are being depleted and produces by-product like carbon dioxide, carbon monoxide, sulphur dioxide which contributes to global warming[1]. 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 work we have constructed a DSSC, 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 a photosensitive materials namely carbon. We also have used an iodide/tri-iodide couple electrolyte solution in the solar cell as a charge carrier.

In laboratory we have used an incandescent bulb as the light source to get the Current-Voltage characteristic of the cell. Power-Voltage characteristic was also obtained.

2. ELECTRONIC PROCESS OF DSSC

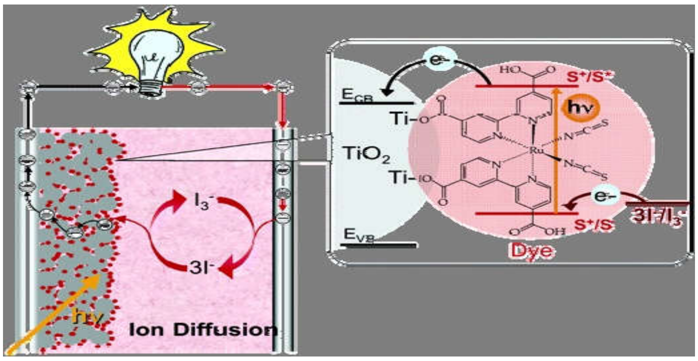


Figure 1: Representation of DSSC [7]

When sunlight falls on DSSC, then Photons enter through the photoactive electrode and can be absorbed by sensitizer molecules (S) at various depths in the film. The sensitizer's molecules (S^*) excited in this way inject electrons into the conduction band of the adjacent TiO_2 particles (e^-_{CB}), leaving an oxidized sensitizer molecule (S^+) on the TiO_2 surface [8]:

$$S^* \rightarrow S^+ + e^-_{CB} \; \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The injected electrons percolate through via the interconnected TiO_2 particles to the TCO substrate and are fed into an electrical circuit, where work can be delivered. The oxidized sensitizer is reduced by the electron donor (I^-) present in the electrolyte, filling the pores:

$$2S^+ + 3I^- \rightarrow 2S + I_3^- \; \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The triiodide (I_3^-) produced in this way diffuse to the counter electrode, where it is reduced back to iodide by metallic platinum under uptake of electrons from the external circuit:

$$I_3^- + 2e^- \rightarrow 3I^- \; \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The efficiency of a DSSC depends on four energy levels of the component: the excited state (approximately LUMO) and the ground state (HOMO) of the photo sensitizer, the Fermi level of the TiO_2 electrode and the redox potential of the mediator (I^-/I_3^-) in the electrolyte [9]

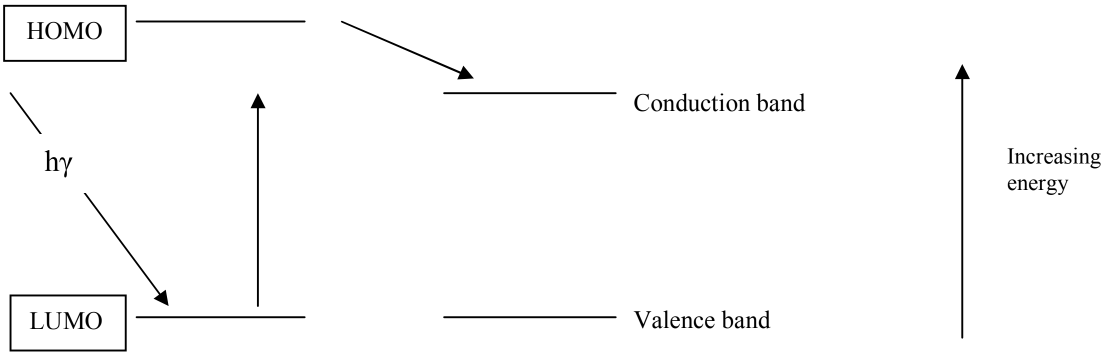


Figure 2: Process of excitation

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 [10-12]. 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 .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 [11]

3. EXPERIMENTAL DETAILS

3.1 Materials Needed:

A list of the materials needed are given below

- Nanocrystalline Titanium Dioxide Powder (100nm size) supplied by Sigma-Aldritch
- FTO coated glass slides
- Distilled white vinegar
- Dish washing detergent
- Small paint brush
- Hotplate
- Dyes (Blackberries(*Syzygium cumini*))
- Distilled water
- Binder clips
- Iodide electrolyte solution
- Connecting Wire
- Digital multi-meter
- 200W incandescent lamp

3. 2 Preparation of carbon electrode

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 used flame from a burner to deposit carbon on a FTO coated surface to be used as a counter electrode.

3.3 Preparation of TiO_2 coated slide

Figure 3: TiO_2 substrate

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 Figure 3. 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 the paste was immersed in 2 ml ethanol and kept there for overnight so that dye would be absorbed by ethanol effectively. Next morning we put the solution in ultrasonic bath for 30 minutes. Finally we filtered the 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.

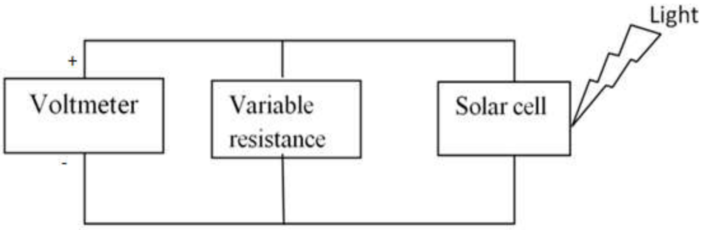
3.6 Preparation of Iodide Electrolyte Solution

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.

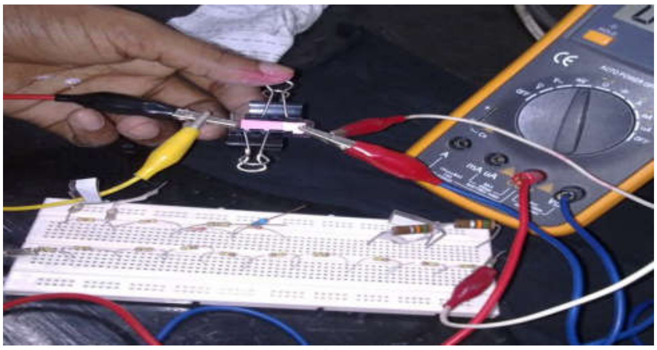
3.7 Assembly of the Solar Cell

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 carbon 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. 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 to multi-meter with the negative terminal attached to the TiO_2 coated slide and the positive terminal attached to the carbon coated slide.

3.8 Photocurrent Measurement



(a)



(b)

Figure 4: (a) Circuit diagram, (b) Measurement of I-V characteristics

- Solar cell is connected as shown in the above figure using cables
- Light from a 200 watt incandescent bulb is used as a light source and the sample cells were always 40 cm away from the light source for all the I-V measurements
- 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

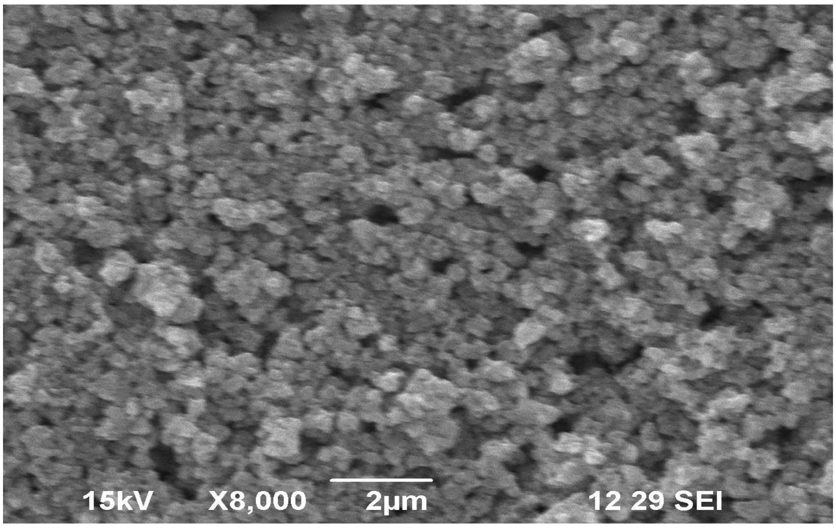


Figure 5: Image of TiO_2

From the image we see that nano-particles were clustered together with an average size around 200nm-300nm although we have used 100nm TiO_2 to make the paste. From the image we can also observe that there are lots of pores in TiO_2 matrix. So that dye can enter the TiO_2 matrix through pores and properly stain the maximum area possible of the TiO_2 matrix.

4.2 I-V and P-V data

4. 2.1 Study of blackberry dye as sensitizer

Data for I-V and P-V measurement are plotted below for the TiO_2 based DSSC, where blackberry dye was used to sensitize the TiO_2 matrix.

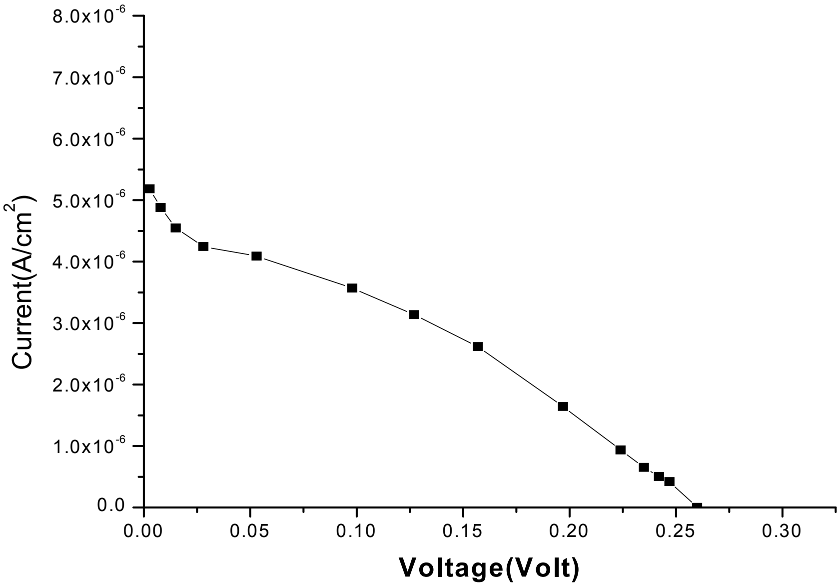


Figure 6: Cell Voltage (volt) Vs Cell current (A/cm^2)

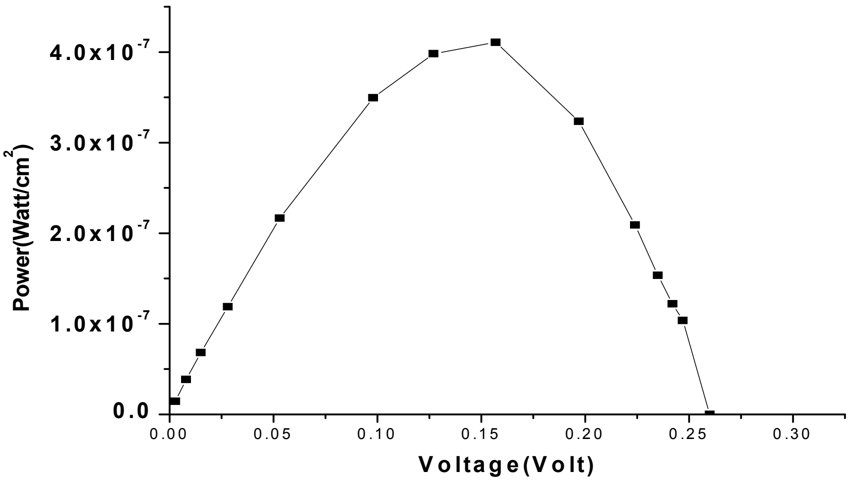


Figure 7: Cell Voltage (Volt) Vs Power (W/cm^2)

From figures 6 &7, the short circuit current per square area, open circuit voltage and the Maximum Power per square area of the cell have been found 5.27×10^{-6} A/cm^2 , 0.260 V and 4.11×10^{-7} W/cm^2 respectively with 33.34% fill factor, which determines the performance of the cell.

To explain the result, the light spectrum of incandescent bulb and also the absorption spectrum of the dyes extracted from blackberry have been studied. These are summarized below.

4. 2.1.1 Spectrum of incandescent bulb.

We used a 200 watt incandescent bulb as the light source due to lack of a solar simulator. The spectrum of incandescent light is shown in the figure 8 and it showed that incandescent light gives ray above 200nm with a maximum intensity at around 575nm

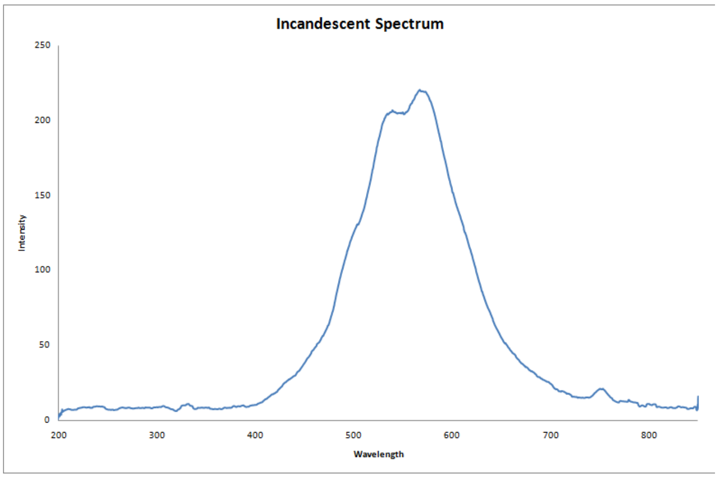


Figure 8: Emission spectrum of incandescent bulb [13]

4. 2.1.2 Absorption spectrum of dye

The absorption spectrum of *Syzygium cumini* (Blackberry) has been taken using a UV-Vis spectrophotometer (Model no Shimadzu: UV-1800). The data is presented in figure 9. Also the wavelength corresponding to the maximum efficiency and the range of wavelength where appreciable absorption happens is tabulated in the Table 1.

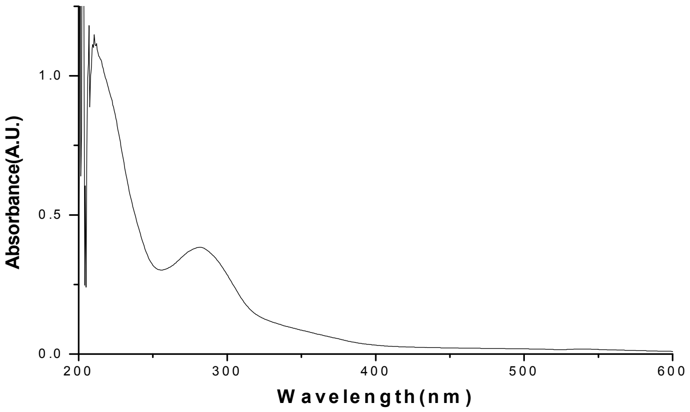


Figure 9: Graph of absorbance measurement [14]

Table 1: Range of absorbance and peak position for *Syzygium cumini*(Blackberry)

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

It is clear from data that cell sensitized with dye extracted from black berry absorbs light from 200nm to 400 nm. The incandescent bulb that we have used as the light source produces light above 200nm, which has been discussed in the earlier section. From the absorption spectrum of dye it is found that the dye extracted from black berry has an appreciable absorbance from 200nm to 400 nm and the absorbance decreases with the increasing the value of wavelength. Since incandescent bulb produces low intensity light in the 200 to 400nm regions (UV) and dye extracted from black berry doesn't absorbs much light in the visible region, so the energy conversion for this cell was very low. If we could do the experiment using smaller TiO_2 particles, more surface area can be exposed to solar light and thus there will be a considerable increment of the possibility of more solar light harvesting. A DSSC with blackberry dye as a sensitizer will perform better at midday (around11am to 2pm) because the greatest amount of UV reaches on the Earth from the sun at that time.

5. CONCLUSION

A DSSC has been constructed, where carbon has been used as electrode in this work. The I-V and P-V characteristics curve has been recorded for the cell. Dye extracted from black berry *(Syzygium cumini)* were used for sensitizing TiO_2 and made cell with carbon electrode. Data for I-V and P-V measurements showed that the power generated is much lower than that of conventional cells. To find an explanation of the lower power generation behavior, we studied the absorption spectrum of the dye extracted from black berry and the emission spectrum of incandescent light used in our work, the spectra showed that incandescent light that we have used as the light source produces light above 200nm with a maximum intensity at around 575nm but intensity of light in ranges from 200nm to 400nm is very low. Dye extracted from black berry has an appreciable absorbance from 200 to 400 nm in the lower intensity of emission spectrum of incandescent light. That is the main reason for lower power produced by the cell using dye extracted from black berry and another reason for lower power production is the carbon electrode. We hope above information will help the researcher about the DSSC with using natural dye, namely blackberry as a sensitizer. If we could do the experiment using lower sized TiO_2 powder the performance of the cells would be increased since smaller sized particles have more exposed surface area to light and the better output power could be achieved.

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