International Journal of Renewable Energy Resources 5 (2015) 38-44

DYE-SENSITIZED SOLAR CELL USING USED SEMICONDUCTOR GLASS AND NATURAL DYE: TOWARDS ALTERNATIVE ENERGY CHALLENGE

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ABSTRACT
Solar energy is an abundant and accessible source of renewable energy available on earth, and many types of photovoltaic (PV) devices like organic, inorganic, and hybrid cells have been developed to harness the energy. Dye Sensitized Solar Cell (DSSC) is considered to be one of the most promising technological developments in the field of Solar Cells. The nanocrystalline thin films like TiO_2 have various applications, among them dye-sensitized solar cells are more promising and low-cost alternative to conventional inorganic photovoltaic devices. We have sensitized TiO_2 nanocrystalline thin films with the natural dye anthocyanin and malvidin- 3-fructoside from raspberry and grape fruits, respectively. In this work we have also reported the interaction between the semiconductor and the dye as natural photosensitizer and studied its sensitization and Photo electrochemical activities. Dye-sensitized solar cells produce electricity through electron transfer. Sunlight passes through the conductive glass electrode. We get the efficiency of summer and rainy season at room temperature 12.3942%, 11.7326% and the sunlight 16.5557%, 11.9735% respectively with series connection by using 19.3548 cm^2 surface area of dye-sensitized solar cell. The solar intensity was about 300 W/m^2 inside the room during the all measurements. This paper also provides a comprehensive understanding on the behaviors of TiO_2 in DSSC from the conduction band shift and the mechanism of electron injection, transfer and recombination and a promising strategy to explore high efficiency DSSC.

Key words: Solar energy, dye-sensitize solar cell, photovoltaic cell, organic dye, mechanism of DSSC.

1. INTRODUCTION

The solar energy is the most capable of the alternative energy sources. Due to increasing Demand for energy and rising cost of fossil type fuels (i.e., gas or oil) solar energy is considered as an attractive source of renewable energy that can be used for electricity purposes in both homes and industries. Continuously the world energy demand is increasing and the world power consumption, which is 13 terawatts (TW) currently, is expected to reach about 23 terawatts (TW) in 2050 (Andrade et al. 2011). Fossil fuels, meet 80% of the energy requirement of the world, which are depleting rapidly (Li et al. 2006). Moreover, the amount of carbon dioxide in the atmosphere rises by burning of fossil fuels. Due to growing energy demand, global worming issues, and exhaustion of oil resources, there is a renewable and clean energy technology. Solar energy photovoltaic technology employing is considered as the most efficient technology among all the sustainable energy technologies such as solar thermal, tidal power, hydropower and biomass (Gong et al. 2012). The sun gives the solar radiation is approximately 3×10^{24}J per year, which is ten times the current energy demands (Millington, 2009). At the Bell laboratories, the first practical photovoltaic cell was designed in 1954 (Tsokos, 2008), using diffused silicon p-n junction technology with an efficiency of 6% (Perlin, 2004). Although the conversion of light to electricity efficiency of silicon based solar cells has reached 15% to 20% (Grant et al. 2002), the need for highly purified silicon, use of toxic chemicals in their manufacture, and the high cost has restricted their worldwide use. The search for friendly environment and low cost solar cells are encouraged by these constrains. O' Regan and Gratzel developed a new photovoltaic cell in 1991, working on the principle of plant photosynthesis. Dye-sensitized solar cells (DSSC) have attracted much attention as possible candidates for low cost, high stability, and high efficient solar cells (O'Regan and Gr¨atzel, 1991; Gr¨atzel, 2004). The efficiency of this PV cell, which became known as dye-sensitized solar cell (DSSC), was reported as 7.1% to 7.9%. In this emerging technology, there are many innovations such as new dyes which are absorbed at a wider range of wavelengths and the introduction of nanostructure titanium oxides (TiO_2) to increase surface area (Zhang et al. 2009; Ito et al. 2008; Kuang et al. 2006). The DSSC of thin films on transparent conducting oxide (TCO) coated glass with the nanostructure Porphyrins/titanium oxide dye can obtain a solar efficiency as high as 13% (Yella et al. 2011).

It has been reported the efficiency of 3.44% by using double light-scattering-layer ZnO film consisting of ZnO mono disperse aggregates as under layer and sub micrometer-size plate like ZnO as over layer used as photo anode, DSSC was fabricated (Jinlei et al. 2014). The highest power conversion efficiency of 7.89% and short circuit current density of 18.58 mA/cm^2 is obtained by using the co-doped with 0.075 at % Sr and 2.5 at % Cr (i.e. S7C25 solar cell) (Bakhshayesh and Bakhshayesh, 2015). The conversion efficiency of light to electricity is 7.2% and the maximum external quantum efficiency (EQE) at 530 nm is over 90% is fabricated by the TiO_2 nanostructural materials synthesized by electrospray and hydrothermal post-treatment (Bing and Baoshun, 2015). The dye-sensitized solar cell conversion efficiency, using gold nanoparticles is 6.06%, and is higher than the cells without gold nanoparticles, which is 5.42% and also studied light-scattering effects on the photo-electrode, different thickness of large particle size TiO2 (∼ 250 nm) coated onto photo-electrode to form double layer structure (Chao et al. 2015). By enhancing the spectral response of mesoporous ZnO films of dye-sensitized solar cells by incorporating metal-free organic sensitizer and using N719 dye, provides the conversion of light to electricity 4.67% (Ying et al. 2015).

Dye sensitized solar cell consists of a catalytic electrode with an electrolyte and a photo electrode between them. The measuring parameters of dye-sensitized solar cell such as open circuit voltage (V_{OC}), close circuit density (J_{SC}), interface charge resistance, fill factor (FF), electrical conversion efficiency (η) and an incident photo to current efficiency (IPCE) depend on the morphological properties of semiconductors, electrical properties of electrolytes and spectroscopic properties of dyes. It is an important type of thin film photovoltaic technology because of ease of fabrication, low cost of manufacturing and light weight product (Lenzmann and Kroon, 2007). In the near future, the venture of dye-sensitized solar cell as a competitive technology will thus be revealed. The latest efficiency of DSSC is more than 11% (Nazeeruddin et al. 2005).

The objectives of the dye-sensitized solar cells are the most important part of the green energy. It improves environmental impact and reduces greenhouse gas emission through reducing of electricity and burning fuel. It also imparts to produce electricity from used and natural ingredients which are available, low cost and environmental friendly. In this paper, we have reported the performance of two natural dyes extracted from raspberry and grape fruits and discussed as sensitizers for TiO_2 based dye-sensitized solar cells (DSSCs). To the best of our knowledge, the use of two fruits mixed dyes is being reported for the first time as sensitizers for TiO_2 based dye-sensitized solar cells.

2. MATERIALS & METHODOLOGY

2.1 Preparation of Conductive Glass and Titanium Dioxide Paste

The collection and preparation of conductive glass plates which are made of fluoride doped tin dioxide glass or other any kinds of glass plate that capable of conduct electrons as well as the sunlight simultaneously, Because of unavailability of fluoride doped tin dioxide glass, the collection of conductive glass plates from the LCD or LED display of the mobile and laptop. The commercially available titanium dioxide (TiO_2) and slowly added 20ml of an acetic acid solution (0.1675 ml CH_3COOH per 99.8225 ml water) to 12g of titanium dioxide powder. By adding the acid slowly, in addition to vigorously mixing the solution, will ensure a uniform paste, by using mortar and pestle.

2.2 Preparation of Dye-sensitized Solar Cell

Pulverized frozen raspberries and grapes into juice with a mortar and pestle and squeezed this solution through a cheese cloth to remove the largest pieces of pulp. Cover each of the conductive glass plate's four edges with a 2mm-thick piece of scotch tape (on the conductive side, as determined by a multimeter). This will create an ultra-thin "bowl" that will be filled with the titanium dioxide paste. Apply three drops of the TiO_2 paste to the electrode, and spread evenly and gently with a glass stirring rod. Anneal the glass plate with an oven (or other heat source) at 450ºC for 30 minutes. Soak the annealed electrode in the dye solution for ten minutes and dye molecules covalently bonded to the TiO_2 known as sensitization. Gently rinse off the glass plate with water once and ethanol twice so that remaining pulp and sugars are removed. The aluminum foil is used as a counter electrode or cathode of the other side of glass surface. To assemble the dye sensitized solar cell, first the cathode is placed on the anode such a way that the cathode and anode do not overlap each other, or there should have small amount of space between the two electrodes, that's next will fill-up with the KI electrolyte (25 ml of distill water to 2.06gm of KI), then connect the electrodes with wire to get the current outside of the cell.

2.3 Mechanism of Dye-sensitized Solar Cell

The dye molecules have strong power of absorbing photons from the sunlight. By absorbing photons from the sunlight the electron of Dye molecules goes to the ground state to the attain the excited state and the micro porous TiO_2 layer collects these excited electron and diffuse across the film and also pass toward the conductive glass plate (anode), the electrons travel the circuit and again come back to the cell through the another metal electrode (cathode) and then through KI electrolyte solution. The dye molecule, having lost an electron to the titanium dioxide, is now oxidized, which means it has one less electron than before. The dye wants to recover its initial state so it must obtain an electron. It obtains this electron from the iodine electrolyte and the dye goes back to ground state. This causes the iodine to become oxidized. When the original lost electron reaches the counter electrode, it gives the electron back to the electrolyte and thus electricity produced.

The absorption of light quanta of specific energy results in generation of charge carriers in solar cells. Dye molecules get excited due to absorption of sun light and shifted from the highest occupied molecular orbital's (HOMO) to the lowest unoccupied molecular orbital's (LUMO).

$$D + h\nu \rightarrow D^{*} \quad \text{……………………………….. (1)}$$

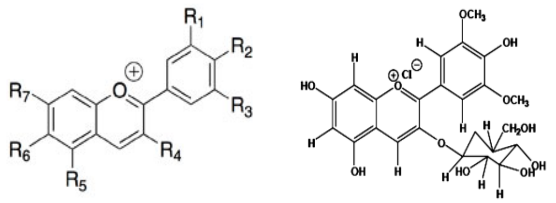

Figure 1 (left) Structure of anthocyanin (where R is –OH,-OHC3, and –H) obtained from raspberry fruit; (right) structure of malvidin-3-fructoside obtained from red grapes.

The dye molecule (photosensitizer) become oxidized, once an electron injected into the conduction band of the wide band gap semiconductor nano structured TiO_2 film.

$$D^{*} + TiO_2 \rightarrow D^{+} + e^{-}(TiO_2) \text{ ....(2)}$$

The work done is delivered as an electric energy after injected electron is transported between the TiO_2 nanoparticles.

$$e^{-}(TiO_2) + \text{Electrode} \rightarrow TiO_2 + e^{-}(\text{Electrode}) + \text{Energy} \text{ ....(3)}$$

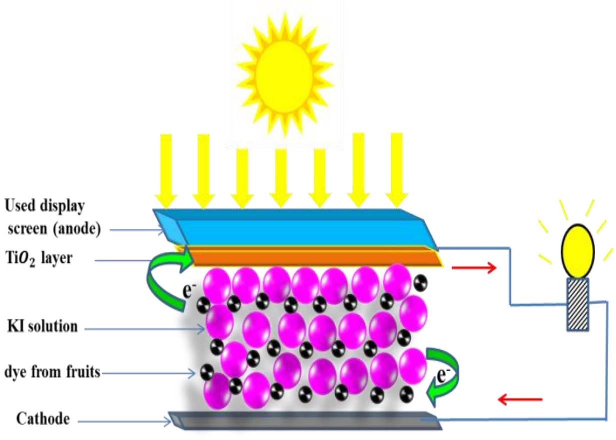

Figure 2 Schematic diagram of dye-sensitized solar cell.

The particular high content of the anthocyanins in raspberry and the accessibility of the fruit offer a great source of the anthrocyanins, which has the absorbance range complimentary to that of chlorophyll (Cherepy et al. 1997). In literature, the anthocyanins were also used in dye-sensitized solar cells (Gratzel and Michael, 2005). Willstatter and Zollinger (Heidari et al. 2004; Willstatter and Zollinger, 1915) reported malvidin 3-fructoside as the major pigment in grapes, and malvidin 3, 5-diglucoside and malvidin as the minor ones. Anthocyanins from grapes include mono and diglucosides of five different aglycones with the addition of monoacylation (Willstatter and Zollinger, 1916). The structure of malvidin 3-fructoside is shown in Figure 1.

3. RESULTS AND DISCUSSION

3.1 Effect of intensity of the sunlight

The dye-sensitized solar cell is arranged as a single, parallel and series connection either at room temperature or the sunlight during the summer and rainy season. Here it is showing that measured voltage and current was varying with time, because the temperature of the room is going both up and down. We also took our every single, parallel and series connected dye sensitized solar cell at sunlight, then the cells are offered some voltage and current. This voltage and current was increasing with respect to increasing time that means increasing the intensity of the sunlight with time.

3.2 Effect of a single connection

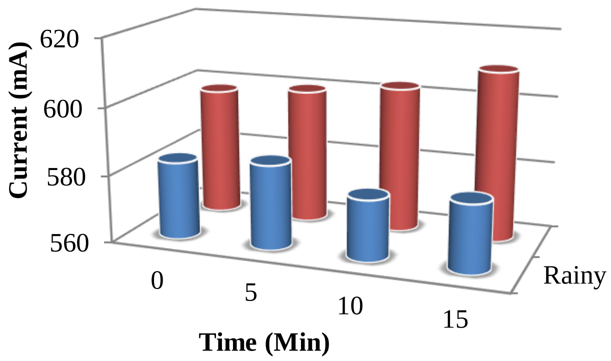

Figure 3 Response of current at room temperature.

A single connection of dye-sensitized solar cell at room temperature during the summer and rainy season and took some reading of the current within five minutes period (2 pm- 2.15 pm). We observed that the current offered by the cell during the summer season is higher than the rainy season. The figure 3 shows that the maximum 610 mA in summer season and 585 mA in rainy season at room temperature. In room temperature, the current is comparatively lower because lack of sufficient photons in the solar energy.

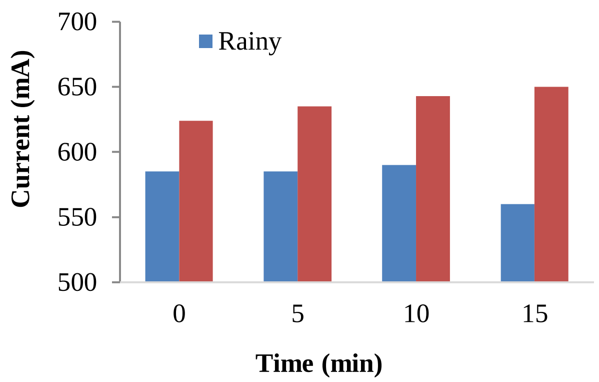

Figure 4 Response of current at sunlight.

Similarly a single connection of dye-sensitized solar cell at the sunlight during the summer and rainy season and took some reading of the current within five minutes period (2 pm- 2.15 pm). We observed that the current offered by the cell during the summer season is higher than the rainy season. The figure 4 shows that the maximum 650 mA in summer season and 590 mA in rainy season at room temperature. In room temperature, the current is comparatively higher because of sufficient photons in the solar energy.

3.3 Effect of a parallel connection

For parallel connection, three dye-sensitized solar cells were prepared.

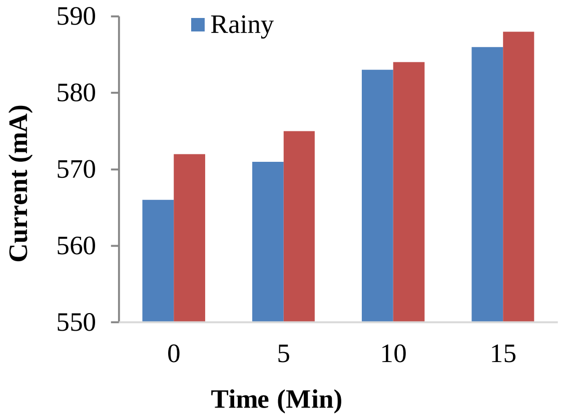

Figure 5 Response of current with parallel connection at room temperature.

The parallel connection of three dye-sensitized solar cells at room temperature during the summer and rainy season and took some reading of the current within five minutes period (2 pm- 2.15 pm). We observed that the current offered by the cell during the summer season is higher than the rainy season. The Figure 5 shows that the maximum 588 mA in summer season and 586 mA in rainy season at room temperature. The parallel connection is arranged for obtaining the higher current and in room temperature; the current is smaller due to lack of photons.

The parallel connection of three dye-sensitized solar cells at sunlight during the summer and rainy season and took some reading of the current within five minutes period (2 pm- 2.15 pm). We observed that the current offered by the cell during the summer season is higher than the rainy season. The Figure 6 shows that the maximum 705 mA in summer season and 640 mA in rainy season at the sunlight. For obtaining the higher current, the parallel connection is arranged, in the sunlight, the current is larger due to sufficient photons.

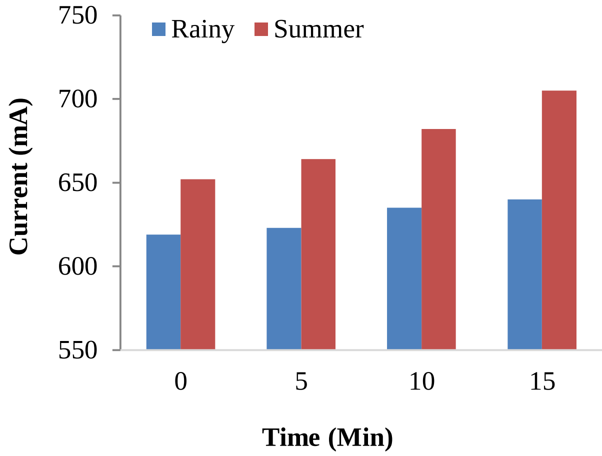

Figure 6 Response of current with parallel connection at the sunlight.

3.4 Effect of a series connection

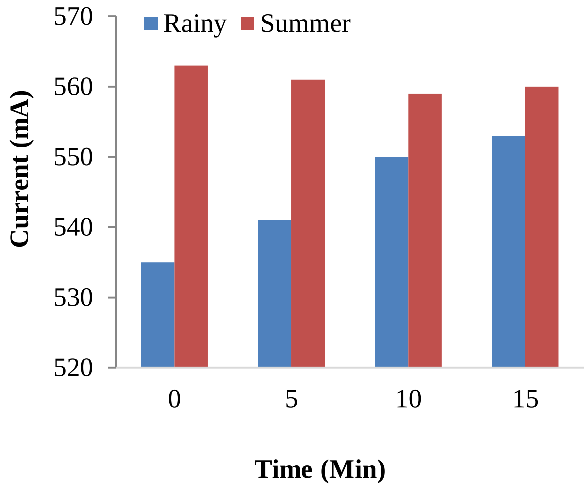

Figure 7 Response of current with series connection at room temperature.

The series connection of three dye-sensitized solar cells at room temperature during the summer and rainy season and took some reading of the current within five minutes period (2 pm- 2.15 pm). We observed that the current offered by the cell during the summer season is higher than the rainy season. Figure 7 shows that the maximum 563 mA in summer season and 553 mA in rainy season at the sunlight.

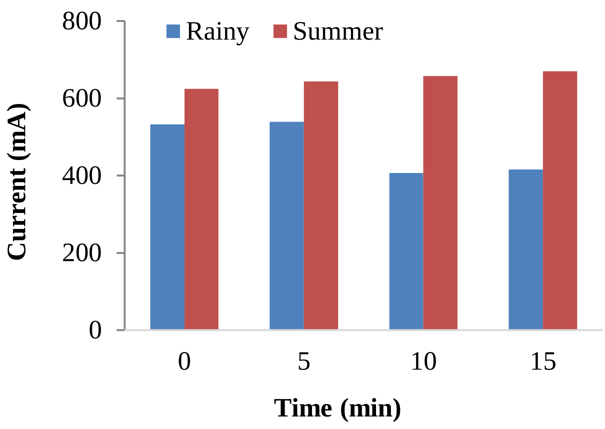

Figure 8 Response of current with series connection at the sunlight.

The series connection of three dye-sensitized solar cells at the sunlight during the summer and rainy season and took some reading of the current within five minutes period (2 pm- 2.15 pm). We observed that the current offered by the cell during the summer season is higher than the rainy season. The figure 8 shows that the maximum 670 mA in summer season and 539 mA in rainy season at the sunlight.

3.5 Efficiency of dye-sensitized solar cell

The absorption spectra of dye solutions and the dyes adsorbed on TiO_2 surface, surrounding with used display screen (anode). Solar energy conversion efficiency can be measured by using two computerized digital Keithley multimeter. Based on the I-V (Current-Voltage) for the room temperature and sun light illuminated black grape dye extract sensitized cell. Table 1 shows the performance of the dye-sensitized solar cell in terms open circuit voltage (V_{OC}), Short circuit photocurrent (I_{SC}), fill factor (FF), and energy conversion efficiency (η).
The fill factor is defined as the following equation.

$$V_{OC} = \frac{q \times V_{oc}}{nkT} \qquad (4)$$

$$\mathrm{FF} = \frac{V_{OC} - \ln(V_{OC} + 0.72)}{V_{OC} + 1} \qquad (5)$$

Obviously the efficiency of dye sensitized solar cell by the black grape and raspberry is significantly higher.

Table 1 Photochemical parameters of the dye-sensitized solar cell by using black grape and raspberry solvents

Connection	Conditions	Season	Open Circuit Voltage, V_{OC}, V	Short Circuit Current, I_{SC}, A	Fill Factor, *FF*	Input Power, P_{in}, W	Maximum Power, P_{max}, W	Efficiency, η, %
Single	Room Temperature	Summer	0.783	0.610	0.9689	10	0.4628	4.6278
		Rainy	0.761	0.585	0.9681	10	0.431	4.3098
	Sun Light	Summer	0.965	0.650	0.9739	10	0.6109	6.1089
		Rainy	0.780	0.590	0.9688	10	0.4458	4.4584
Parallel	Room Temperature	Summer	0.748	0.588	0.9677	10	0.4256	4.2562
		Rainy	0.742	0.586	0.9674	10	0.4206	4.2064
	Sun Light	Summer	0.832	0.705	0.9704	10	0.5692	5.692
		Rainy	0.762	0.640	0.9682	10	0.4722	4.7217
Series	Room Temperature	Summer	2.230	0.563	0.9872	10	1.2394	12.3942
		Rainy	2.150	0.553	0.9868	10	1.1733	11.7326
	Sun Light	Summer	2.500	0.670	0.9884	10	1.6656	16.5557
		Rainy	2.250	0.539	0.9873	10	1.1973	11.9735

The efficiency of single connection is lower than the series connection, because of lower open circuit voltage and short circuit current. In summer season, at single connection, the efficiency of the sun light is higher than the room temperature, due to greater electron transfer rate and resulting in the larger amount of open circuit voltage and short circuit current. Figure 9 shows that the efficiency of room temperature and sun light in summer season are 4.6278% and 6.1089% respectively.

The efficiency of parallel connection is considerably similar the single connection, because of open circuit voltage and short circuit current. Here we arrange the three dye-sensitized solar cells with average open circuit voltage is 0.748 V in room temperature and the sun light is 0.832 V and also the average short circuit current is 0.588A in room temperature and the sun light is 0.640A. Figure 10 shows that the efficiency at room temperature and the sun light are 4.2562% and 5.692% respectively.

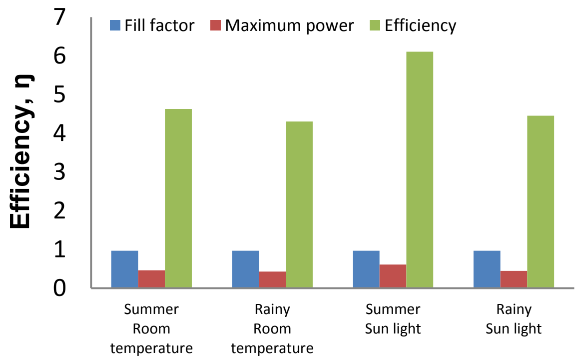

Figure 9 Efficiency of single connection.

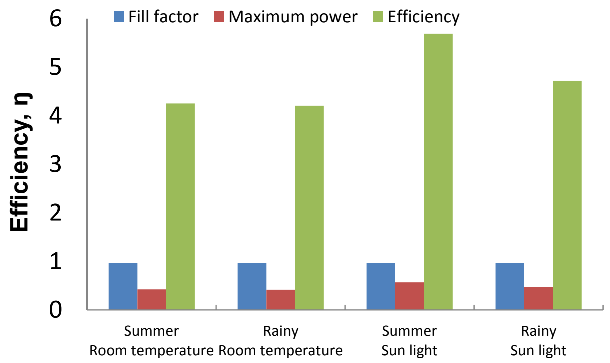

Figure 10 Efficiency of parallel connection.

The efficiency of series connection is higher than the single and parallel connection. It is the combination of the three dye-sensitized solar cells. This connection gives the higher open circuit voltage, short circuit current and also higher fill factor. Here the maximum power is higher than the single and parallel connection. Here we observe that the higher open circuit voltage but the lower short circuit current , because of obtaining the higher resistance according to Ohm's law, we get the lower short circuit current. Figure 11 shows that the maximum efficienct at room temperatue and the sun light are 12.3942% and 16.5557% respectively under the average solar intensity of 300 W/m^2.

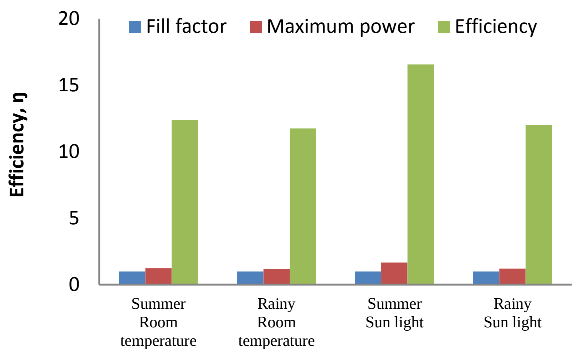

Figure 11 Efficiency of series connection.

5. CONCLUSION

The hungry for energy source is the most important topic for modern era and the need increasing very rapidly to overcome the want of energy sources and the bad effect of fossil fuel we have concentrated our mind to work on such topic of converting the sunlight to the electricity by using the very low cost and available raw materials compared to silicon based solar energy system. Although our project shows low electricity conversion but it also show the vivid future for energy conversion system as the sun is the simply endless source of energy.

For every single cell (2"×1.5") at room temperature we get the average current is about 610mA. At direct sunlight the cell offered maximum current is about 650mA. The parallel connections of three cells at room temperature provide an average current is about 588 mA. At direct sunlight the maximum current is about 705 mA and finally the series connection of three cells at room temperature provide an average current is about 563 mA. At direct sunlight the maximum current is about 670 mA. Predicted consumer uptake of DSSC will assist in decreasing our reliance on electricity generation derived from fossil fuels, thereby decreasing greenhouse gas emissions.

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