Comparative Study on Zobo and Tomato Dye on the Fabrication of Dye Sensitized Solar Cell Using ITO/TiO₂/ZnO/Dye Sensitized

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Abstract

A photoanode of dye-sensitized solar cells based on a ZnO/TiO_2 composite film was fabricated on a transparent conductive glass substrate using the spray pyrolysis and screen printing technique respectively. The resulting substrate is sensitized with the zobo and the tomato dye separately to form a dye sensitized solar cell.

The solar cell sensitized with the zobo dye produced an open voltage of 0.389 V, at a fill factor of -33.8765, which further gave a short circuit current density of -0.000236 and the efficiency calculated to be 0.0031. While the solar cell sensitized with the tomato dye produced an open voltage of 0.334 V, at a fill factor of -44.4027, which further gave a short circuit current density of -0.000236 and the efficiency calculated to be 0.0031. While the solar cell sensitized with the tomato dye produced an open voltage of 0.334 V, at a fill factor of -44.4027, which further gave a short circuit current density of -0.000236 and the efficiency calculated to be 0.0035. Therefore, cell produced with tomatoes dye is more efficient and cheaper to fabricate due to an improved annealing time.

Keywords:Dye sensitized solar cell; zobo dye; tomato dye; efficiency; comparative study

1.0 Introduction

The growing worldwide energy demand and the environmental impact of the extensive exploitation of fossil fuels during the last decades have motivated the search for alternative sources of energy. Special attention is paid nowadays to the development of new technologies allowing for the utilization of so-called renewable energy sources. Renewable energy is derived from natural processes that are replenished constantly. Tapping into these energy sources is desirable both from an ecological and an economic point of view [1]. Nowadays, renewable energy is the fastest-growing source of electricity generation with main contributions from hydroelectric and wind power. Furthermore, solar power generation has experienced accelerated growth during the last decade. The renewable share of worldwide electricity generation is expected to grow from 18 percent in 2007 to 23 percent in 2035. The optimization of the existing processes for power generation and the development of new technologies are, therefore, a matter of scientific, technological, economic and public concern. Dye-sensitized solar cells also known as Gratzel cells are a rising interest for use as alternative energy sources. These

miniature solar cells, typically made with titanium dioxide nanocrystalline mono layers, mimic the photochemical process of photosynthesis to convert light energy into electrical energy. The dye which is bound to the titanium dioxide plays the role of chlorophyll[1], which gives up an electron when excited by light Gratzel cells are essentially constructed by sandwiching the dyed TiO₂ between iodide/triodide electrolyte solutions. The basic idea of what a cell looks like at a magnified view is shown in Figure 1.

The process by which the cell creates electrical energy can be represented by the following series of redox reactions [2]:

$Dye + hv \rightarrow Dye^*$	(1)
$Dye + TiO_2/ZNO \rightarrow TiO_2 + Dye^*$	(2)
$TiO_2 + CE \rightarrow TiO_2 CE^* + Energy$	(3)
$Dye^* + I^- \rightarrow Dye + I_3^-$	(4)
$I_3^- + CE \rightarrow I^- + CE$	(5)
Overall $hv \rightarrow Energy$	(6)

Where hv represents light and CE represents electrode.

As illustrated when light is shined on the stained TiO_2 an electron from the conjugated system of the dye structure becomes excited as in equation (1). When an electron reaches a certain excitation state, the dye will give up the electron to the TiO_2/ZnO equation (2). And travel through the load to the carbonized counter electrode, creating electrical energy equation

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(3). The iodide/triodide electrolyte solution reactivates the dye so it is able to undergo the process again by giving an electron back to the dye equation (4) and picking another electron up from the counter electrode equation (5) [3].

This work compares the effect of two different dyes in the dye sensitized solar cell. The dyes used are from natural sources; tomato seed (Lycopene) and zobo leaf(Anthocyanin).

Lycopene with molecular fomula $C_{40}H_{56}$, molar mass 536.87g/mol, it is insoluble in water. Lycopene displays three absorbance maxima 443nm, 471nm and 503nm. A peak at 360nm would indicate the presence of certain cis-isomers. Anthocyanin has a molecular fomula $C_{15}H_{11}O$.

2.0 Methodology

Dye sensitized solar cell were fabricated on transparent conducting under photovoltaic operation. The conductive glass is indium tin oxide (ITO) due to low cost and stability. The TiO_2 Nano particles were fabricated by the aqueous hydrolysis of titanium alkoxides precursors, followed by autoclaving at temperature up to 240°C to archive the desired Nano particles dimensions and crystalline (anatase). The Nano particles are deposited as a colloidal suspension by screen printing.

Note that Indium tin oxide conducting glass should not be touched with bare fingers. When finger prints and other contamination are present we wash with ethanol, then dry using hair dryer.

Cleaning the ITO Glass

First the ITO is carefully washed with detergent and water, and then rinsed with distilled water. After rinsing with distilled water, the ITO glass is placed in a chamber. Finally, methanol is poured in the chamber, and the chamber is placed in an ultrasonic cleaning device.

Deposition of Zinc Oxide by spray pyrolysis

A solution with 0.1 molarity was prepared by mixing zinc acetate salt of 99.9995 % purity with distilled and deionized water in a capillary tube. The solution is mixed with the magnetic stirrer for 15 mins. The surface tension of the obtained solution is deduced by the height of the solution in the capillary tube.

Spray pyrolysis is the process in which the ZnO is deposited by spraying 10 ml of the zinc acetate solution on the conducting surface of the heated ITO, where the constituent reacts to form the chemical compound. The procedure is carried out in a fume chamber and gun. The ITO is placed on heat; such that the conductive side faced up, the nozzle is fixed 5 cm from the ITO holder. When the ITO is heated to 260° C the solution is sprayed on it until it cools to 220° C. This process is repeated until the 10 ml zinc acetate is sprayed on the ITO.

Titanium Deposition by screen printing

First we stir well the Nano crystalline TiO_2 pastes before use, not shake unless bubbles could be formed. The TiO_2 paste is prepared by mixing titanium dioxide salt with 5 ml of acetic acid. The thickness of the adhesive tape will determine the thickness of the titanium dioxide deposited on the glass we use scotch magic tape from 3m having a thickness of ~50 µm. This type can be easily removed from the glass without leaving traces of adhesive materials.

The transparent pastes are made to give a layer of 2 $-3 \mu m$, for a single layer of tape. So a low dry-out of the solvent and a progressive heating is necessary to ensure optimal adhesion of the titanium dioxide layer onto the zinc oxide thin filmed ITO glass.

The deposition process itself consist of spreading out a given volume of $\sim 10 \text{ ml/cm}^2$ of titanium dioxide paste with a rigid squeegee in a microscopic slide, preferably with polished edges. A glass rod could also do the job. Gently dry the electrode with a hair dryer till the solvent is evaporated with the Ti-nanoxide D paste, then electrode turns white or slightly translucent upon drying.

Note: There should be no signs of peeling off and also on the back side of the glass electrode and check if there are no air bubbles visible. Approximately 2.0 g of TiO_2 salt is mixed with 10 ml of acetic acid. A TiO_2 layer was screen printed on the sprayed ZnO thin film, on the conducting side of the ITO glass and then annealed at 450° C for 30 mins.

Annealing Process

The annealing process allows the titanium dioxide Nano crystals to melt partially together in order to ensure electrical contact and mechanical adhesion on the glass. Good results have been obtained using a hot air blower to heat up the electrode at 450° C for about half an hour. While heating up the electrode it first turns brownish, sometimes it releases fumes and later it turns yellowish-white due to the temperature dependent band gap narrowing in the pure titanium dioxide. This is the sign that the annealing process is completed and cooling rate is chosen to avoid cracking of the glass (cool down from 450° C to 60-80°C in 3 mins). The annealing process is carried out using the carbolyte machine.

Sensitizer Impregnation

The zobo which is a natural dye must be dissolved in pure ethanol in a concentration of 20 mg of dye per 100 ml of solution, while the tomato should be mashed before its been dissolved in an ethanol solution. Put slowly the sintered electrode heated at \sim 70 °C into the sensitizer's solution, its face up. When impregnating arge electrodes we put them gently and slowly into the usually cold sensitizer's solution in order to avoid cracking of the glass. The impregnation process was done at room temperature.

Note: No water should enter sensitizer solution, no water should contact impregnated electrodes otherwise the electrode is useless. Once stained, electrodes area issensitive to ambient humidity they turn orange color after several weeks of ambient exposure such orange colored electrode cannot work properly.

Carbon Deposition

The method used to deposit the carbon electrode is through the deposition of soot from a burning candle. Start with an ITO glass plate matching the size of the TiO_2 electrode being used for the assembly.

Light a candle and hold the piece of ITO glass, conductive side facing down, about 10 cm above the flame. The carbon from the combustion of wax is carried in the smoke and makes a black deposition on the conductive side of the ITO glass.

The process is very fast, so don't overdo it. A homogeneous gray to black layer is enough.

Allow the glass plate to cool on a suitable surface before further processing.

Sealing Electrodes

When the electrodes are put together, the active sides of the anode and the cathode will be facing each other. In other words, the stained TiO_2 will face the carbon of the counter-electrode. The gap left between the two glass plates will be filled with electrolyte during the next step.

This step can be accomplished using two different approaches. First, electrodes can be pressed together, and the electrolyte soaked in the resulting stack by capillary effect. Second, the two electrodes can be sealed together and the electrolyte injected via holes drilled through the cathode.

The first approach is called an "open cell" because the inner part of the solar cell is exposed to air. This is a very easy setup, but the electrolyte won't be confined in the cell and will eventually dry out. Such an assembly is practical for training courses, where results must be obtained quickly. However, the resulting solar cells won't last as long as in a sealed configuration.

The second approach is meant to give longer lasting solar cells. The electrodes are sealed together with a gasket so that the electrolyte is confined in the cavity. It certainly takes more effort to manufacture, but it allows the Dye Solar Cells to operate for an undetermined period of time.

Electrolyte Filling

The gap between the two electrodes can now be filled with electrolyte to complete the Dye Solar Cell. This is performed either by capillary effect in open cells, or by injection through the filling holes in sealed cells.

It is best to fill the cells with electrolyte as soon as the electrodes are put together. The stained thin film will otherwise be exposed to air for too long and possibly degrade.

The electrodes have been put together and held with binders, immediately start filling with electrolyte before air and moisture degrades the electrodes.

Place a few drops of electrolyte at the interface of the two glass plates with a pipette, and allow the liquid to be drawn into the cell by capillary effect. If necessary, repeat this operation until the entire internal surface of the solar cell is wetted with electrolyte.

Completing the Cell

Wipe off any excess liquid with a paper towel and manipulate the cell carefully to avoid skin contact with the electrolyte. The Dye Solar Cell is now operational and will last until the electrolyte solvent evaporates.

Since the assembly is open to ambient air, the performance of the cell will decrease over time. This assembly however will

give plenty of time to measure and demonstrate the electrical output of the photovoltaic device.

3.0 Results

3.1 For Tomato Dye

Voltage_1 (V)	Current_1 (A)
+3.438494E-04	-6.353009E-07
+1.114312E-01	+1.861659E-04
+2.224305E-01	+1.865597E-04
+3.336730E-01	+2.827760E-04
+4.447159E-01	+3.423128E-04
+5.557644E-01	+4.657056E-04
+6.670106E-01	+8.664844E-04
+7.780282E-01	+1.270817E-03
+8.890325E-01	+2.027389E-03
+1.000162E+00	+2.857973E-03

Table 1.1: For the current to voltage in dark reaction

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Table 1.2: For the current to v	voltage in light reaction
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Voltage_1 (V)	Current_1 (A)
-2.36E-04	-1.45E-02
5.58E-02	-1.33E-02
1.12E-01	-1.20E-02
1.67E-01	-1.01E-02
2.22E-01	-7.89E-03
2.78E-01	-5.24E-03
3.34E-01	-2.71E-03
3.89E-01	5.77E-04
4.45E-01	3.98E-03
5.00E-01	7.00E-03

4.0 Discussion

From the graphs in Fig 2 and 3 the liquid dye sensitizer (from tomato) shows that at the wavelength set at 300 nm there is an absorbance of 3 % and shows decrease in absorbability as the wavelength increases (Fig 2). And also at a wavelength set at 300 nm there is a transmittance of 0.01 % which increases as the wavelength increases (Fig 3).

In Fig. 4 and 5, the liquid dye sensitizer (zobo dye) shows that at the wavelength set at 300 nm there is an absorbance of 3 % and shows decrease in absorbability as the wavelength increases. And also at a wavelength set at 300 nm there is a transmittance of 0.04 % which increases as the wavelength increases. Fig. 6 shows an IV curve of the dye sensitized solar cell using Lycopyne dye (tomatoes dye) placed in a dark room and Fig. 7 shows the cell under Illumination. Likewise, Fig 8 and 9 shows the dye sensitized solar cell using anthocyanin dye from Zobo leaf, placed in a dark room and under illuminicence.

4.1 Efficiency of the Both Cells

4.2 Tomatoes Dye

Solar conversion efficiency can be determined by the relation

$$\eta = \frac{voc * jsc * ff * 100}{100}$$

Where

ŋ is the solar conversion efficiency Voc is the voltage of the open circuit Jsc is the short circuit current density of the cell Ff is the fill factor of the cell in percentage Therefore

$$n_{\rm f} = \frac{0.334 \times (-0.000236) \times (-44.4027) \times 100}{100}$$

 $n = 0.0034999 \approx 0.35$ %

4.3 Zobo Dye

Solar conversion efficiency can be determined by the relation

$$\eta = \frac{voc * jsc * ff * 1000}{100}$$

Where

 η is the solar conversion efficiency V_{oc} is the voltage of the open circuit J_{sc} is the short circuit current density of the cell

Ff is the fill factor of the cell in percentage Therefore

$$\mathfrak{n} = \frac{0.389 \times (-0.000236) \times (-33.8765) \times 100}{100}$$

 $\eta = 0.0031 \approx 0.31$ %

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4.4 For Zobo Dye

Tables 1.3: For the current voltage for dark reaction

ion of the current voltage for dark rea		
-2.36E-04	-1.70E-02	
+5.58E-02	-1.56E-02	
+1.12E-01	-1.38E-02	
+1.67E-01	-1.14E-02	
+2.22E-01	-1.14E-02	
+2.78E-01	-6.14E-03	
+3.34E-01	-3.16E-03	
+3.89E-01	-3.16E-03	
+4.45E-01	+3.58E-03	
+5.00E-01	+6.22E-03	

 Table 1.4 For the current to voltage curve for light reaction

 • For the current to voltage curve for h		
+1.420346E-04	+4.352408E-09	
+1.117178E-01	+3.645927E-04	
+2.225788E-01	+1.953811E-04	
+3.337425E-01	+3.337843E-04	
+4.448222E-01	+6.280288E-04	
+5.557271E-01	+8.522584E-04	
+6.666557E-01	+1.462236E-03	
+7.779317E-01	+2.369534E-03	
+8.890170E-01	+3.510679E-03	
+1.000158E+00	+4.761126E-03	



Figure 1Magnified image of a typical dye sensitized solar cell



Fig 2Graph of liquid absorbance of the dye from tomato

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Fig 3Graph of liquid transmittance of the dye from tomato



Fig 4 Graph of liquid absorbance of Zobo dye



Fig 5Graph of transmittance of liquid in zobo dye

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Fig 6: I.V curve for the solar cell in dark



Fig 7: I.V curve for the solar cell in light. The graphs shown in Fig 2 to Fig 7 are for the solar cell with tomatoes dye



Fig 8: I.V curve for the solar cell in dark

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Fig 9: I.V curve for the solar cell in light.

The graphs in Fig 4 to Fig 9 are for the solar cell with zobo dye.

5.0 Conclusion

In conclusion the stability factor of the cell tells more of its reactivity between the sensitizer dye and the redox electrolyte which does not reduce as a result of the reduction power of the electrolyte. It is advantageous because it is environmentally derived being that the dye was gotten from plant, it is easy to maintain and manage compare to silicon based cell, it is also easy to fabricate and design and it is a clean source of energy. To one cell connected in series of about 10 cells each can form a module and henceforth power light appliances. DSSC technology has an efficiency of above 11 % with a band gap for sensitizer of over 3.2 eV. For this work, the cell with zobo dye achieved an efficiency of 31 %, while the cell with tomato cell achieved the efficiency of 35 %, showing that the lycopene dye sensitized solar cell has a higher efficiency and should be a preferred dye to anthocyanin from zobo.

6.0 Acknowledgment

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