Comparative Study Between Zobo and Tomato Dye on the Fabrication of Dye Sensitized Solar Cell Using ITO/TiO\textsubscript{2}/ZnO/Dye Sensitized

Eyekpegha O.F; Ezeh M.I

Department of Physics
Delta State University Abraka, Delta State
Email:seyekpegha@yahoo.com

Abstract

A photoanode of dye-sensitized solar cells based on a ZnO/TiO\textsubscript{2} composite film was fabricated on a transparent conductive glass substrate using spray pyrolysis and screen printing techniques 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 0.33.8765, which further gave a short circuit current density of 0.000236 and the efficiency calculated to be 0.031. While the solar cell sensitized with the tomato dye produced an open voltage of 0.334 V, at a fill factor of 0.44.4027, which further gave a short circuit current density of 0.000236 and the efficiency calculated to be 0.035.

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

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 the utilization 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. 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 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 TiO\textsubscript{2} between iodide/triiodide electrolyte solutions. The process by which the cell creates electrical energy can be represented by the following series of redox reactions:

\begin{align*}
\text{Dye} + \text{hv} & \rightarrow \text{Dye}^* \\
\text{Dye} + \text{TiO}_2/\text{ZNO} & \rightarrow \text{TiO}_2 + \text{Dye}^* \\
\text{TiO}_2 + \text{CE} & \rightarrow \text{TiO}_2 \text{ CE}^* + \text{Energy} \\
\text{Dye}^* + \Gamma & \rightarrow \text{Dye} + \text{I}_3^- \\
\text{I}_3^- + \text{CE} & \rightarrow \Gamma + \text{CE} \\
\text{Overall \ hv} & \rightarrow \text{Energy}
\end{align*}

Where hv represents light and CE represents electrode. As illustrated when light is shined on the stained TiO\textsubscript{2} an electron from the conjugated system of the dye structure becomes excited (1) [2]. When an electron reaches a certain excitation state, the dye will give up the electron to the TiO\textsubscript{2}/ZNO (2). And travel through the load to the carbonized counter electrode, creating electrical energy (3). The iodide/triiodide electrolyte solution reactivates the dye so it is able to undergo the process again by giving an electron back to the dye (4) [3] and picking another electron up from the counter electrode (5).

This work compares the effect of two different dyes in the solar cell. The dyes used are lycopene from tomato and anthocyanin from zobo leaf.

Lycopene with molecular formula C\textsubscript{40}H\textsubscript{56}, molar mass 536.87 g/mol, insoluble in water. Lycopene three
absorbance maxima 443 nm, 471 nm, 503 nm. A peak at 360 nm would indicate the presence of certain cis –
isomers.

Sussane R et;al (2009)
Anthocyanin has the molecular formular C_{15}H_{11}O and the structure is shown below

Andersen, and Qyvind (2011)

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.
The indium tin oxide conduction glass should not be
touched with bare fingers to avoid contaminations and when touched should be washed with ethanol and dried
using a drier.

Cleaning the ITO Glass
First the ITO is carefully washed with detergent and water, then rinse 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
A solution with 0.1 molarity was prepared by mixing zinc acetate salt of 99.9995 % purity with distilled and
de-ionized 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
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 droplet size was measured from the photography of the
sprayed jet, the droplet velocity is determined from the measurement of the air pressure from the nozzle. The
mean droplet size and velocity were 2.50 µm and 1 cm/s respectively.
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
First we stir well the Nano crystalline TiO$_2$ pastes before use. The TiO$_2$ paste is prepared by mixing
titanium dioxide salt with 5 ml of acetic acid. The thickness of the adhesive tape determined the thickness
of the titanium dioxide deposited on the glass. We use scotch magic tape from 3 m having a thickness of ~50
µm. This type of tape 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 µm, 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
~10 ml/cm$^2$ of titanium dioxide paste with a rigid squeegee is a microspic slide, preferably with polished
edges. A glass rod could also the job. Let dry electrode or gently dry it with a hair dryer till the solvent is
evaporated with the Ti-nanoxide D paste, the 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.
Screen Printing
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 to gather 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 first turns brownish, sometimes it releases fumes and later it turns yellowish-white due to the temperature dependent band gap narrowing in the pure titanim 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 by 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 dissolving it in an ethanol solution. Put slowly the sintered electrode heated at ~ 70 °C into the sensitizer’s solution, its face up. When impregnating large electrodes put them really gently and slowly into the usually cold sensitizer’s solution in order to avoid cracking of the glass. The impregnation process can be 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 sensitive to ambient humidity they turn orange colour after several weeks of ambient exposure such orange coloured electrode cannot work properly.

Carbon Deposition
The carbon electrode was deposited from a burning candle to form carbon soot on the ITO glass. The ITO glass with the same size of with that carrying the TiO$_2$ electrode was placed with the conducting side facing down about 10 cm above the flame. The carbon deposited on the glass was carried from the smoke of the burning wax. The process was quick in order to avoid damaging the ITO glass from overheating. The glass was allowed 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 Feeling
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.

The cells are filled with electrolyte as soon as the electrodes are put together. Otherwise, the stained thin film will be exposed to the air solon that degradation may possibly occur.

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

Drops of electrolyte were placed at the interface of the two glass plates with a pipette, and the liquid was allowed to be drawn into the cell by capillary effect. This operation was repeated until the entire internal surface of the solar cell is wetted with electrolyte.

Completing the Cell
Excess liquid was wiped off from the cell with a paper towel 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.
RESULTS

For Tomato Dye

TABLE 1.1: for the current to voltage in dark reaction

<table>
<thead>
<tr>
<th>Voltage_1 (1)</th>
<th>Current_1 (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+3.438494E-04</td>
<td>-6.353009E-07</td>
</tr>
<tr>
<td>+1.114312E-01</td>
<td>+1.861659E-04</td>
</tr>
<tr>
<td>+2.224305E-01</td>
<td>+1.865979E-04</td>
</tr>
<tr>
<td>+3.367300E-01</td>
<td>+2.827760E-04</td>
</tr>
<tr>
<td>+4.447159E-01</td>
<td>+3.423128E-04</td>
</tr>
<tr>
<td>+5.557644E-01</td>
<td>+4.657056E-04</td>
</tr>
<tr>
<td>+6.670106E-01</td>
<td>+5.870567E-04</td>
</tr>
<tr>
<td>+7.802828E-01</td>
<td>+6.648444E-04</td>
</tr>
<tr>
<td>+8.890325E-01</td>
<td>+2.027389E-03</td>
</tr>
<tr>
<td>+1.000162E+00</td>
<td>+2.857973E-03</td>
</tr>
</tbody>
</table>

TABLE 1.2: for the current to voltage in light reaction

<table>
<thead>
<tr>
<th>Voltage_1 (1)</th>
<th>Current_1 (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.36E-04</td>
<td>-1.70E-02</td>
</tr>
<tr>
<td>5.58E-02</td>
<td>-1.33E-02</td>
</tr>
<tr>
<td>1.12E-01</td>
<td>-1.20E-02</td>
</tr>
<tr>
<td>1.67E-01</td>
<td>-1.01E-02</td>
</tr>
<tr>
<td>2.22E-01</td>
<td>-7.89E-03</td>
</tr>
<tr>
<td>2.78E-01</td>
<td>-5.24E-03</td>
</tr>
<tr>
<td>3.34E-01</td>
<td>-2.71E-03</td>
</tr>
<tr>
<td>3.89E-01</td>
<td>5.77E-04</td>
</tr>
<tr>
<td>4.45E-01</td>
<td>3.98E-03</td>
</tr>
<tr>
<td>5.00E-01</td>
<td>7.00E-03</td>
</tr>
</tbody>
</table>

Discussion

From the graphs in fig 2 and 3 the liquid dye sensitizer (lycopene dye 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).

Efficiency of the cell

Solar conversion efficiency can be determined by the relation below

\[ \eta = \frac{V_{oc} \times J_{sc} \times FF \times 1000}{100} \]

Where

- \( \eta \) 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

\[ \eta = \frac{0.3944 \times (-0.00226) \times (-44.4027) \times 1000}{100} \]

\[ \eta = 0.034999 \approx 35 \% \]

For Zobo Dye

Tables 1.3 for the current voltage for dark reaction

<table>
<thead>
<tr>
<th>Voltage_1 (1)</th>
<th>Current_1 (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.36E-04</td>
<td>-1.70E-02</td>
</tr>
<tr>
<td>+5.58E-02</td>
<td>-1.56E-02</td>
</tr>
<tr>
<td>+1.12E-01</td>
<td>-1.38E-02</td>
</tr>
<tr>
<td>+1.67E-01</td>
<td>-1.14E-02</td>
</tr>
<tr>
<td>+2.22E-01</td>
<td>-1.14E-02</td>
</tr>
<tr>
<td>+2.78E-01</td>
<td>-6.14E-03</td>
</tr>
<tr>
<td>+3.34E-01</td>
<td>-3.14E-03</td>
</tr>
<tr>
<td>+3.89E-01</td>
<td>-3.14E-03</td>
</tr>
<tr>
<td>+4.45E-01</td>
<td>+3.58E-03</td>
</tr>
<tr>
<td>+5.00E-01</td>
<td>+6.22E-03</td>
</tr>
</tbody>
</table>

Table 1.4 for the current to voltage curve for light reaction

<table>
<thead>
<tr>
<th>Voltage_1 (1)</th>
<th>Current_1 (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1.420346E-04</td>
<td>+4.352408E-09</td>
</tr>
<tr>
<td>+1.117176E-01</td>
<td>+3.645927E-04</td>
</tr>
<tr>
<td>+2.225788E-01</td>
<td>+1.953811E-04</td>
</tr>
<tr>
<td>+3.337425E-01</td>
<td>+3.337843E-04</td>
</tr>
<tr>
<td>+4.448222E-01</td>
<td>+6.280288E-04</td>
</tr>
<tr>
<td>+5.557271E-01</td>
<td>+8.522584E-04</td>
</tr>
<tr>
<td>+6.666557E-01</td>
<td>+1.462236E-03</td>
</tr>
<tr>
<td>+7.779317E-01</td>
<td>+2.369534E-03</td>
</tr>
<tr>
<td>+8.890170E-01</td>
<td>+3.510679E-03</td>
</tr>
<tr>
<td>+1.000158E+00</td>
<td>+4.761126E-03</td>
</tr>
</tbody>
</table>

Discussion

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 (fig 2). And also at a wavelength set at 300 nm there is a transmittance of 0.04 % which increases as the wavelength increases (fig 3).
Efficiency of the cell
Solar conversion efficiency can be determined by the relation below

\[ \eta = \frac{V_{oc} \cdot J_{sc} \cdot ff \cdot 1000}{100} \]

Where
\( \eta \) 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

\[ \eta = \frac{0.399 \times (-0.0002 \times (-33.8765)) \times 1000}{100} \]

\[ \eta = 0.031 \approx 31\% \]

Fig 1 Graph of liquid absorbance of lycopene dye from tomato

Fig 2 Graph of liquid transmittance of lycopene dye from tomato
Fig 3: I.V curve for the solar cell in dark

Fig 4: I.V curve for the solar cell in light.

The graphs shown in fig 1 to fig 4 are for the solar cell with lycopene dye.
**Fig 5** Graph of liquid absorbance of Zobo dye

**Fig 6** Graph of transmittance of liquid in zobo dye
**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. The cell 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 dye 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.

References.

Andersen, Quvind M.; Anthocyanins, Encyclopedia of life sciences 2011


Wang, Z, L., Zno nanowire and nanobelt platform for manotechnology, materials science and engineering R-reports, 2009. 64 (3-4): P. 33-70
