PROPERTIES OF TIO2 AND DYE IN ENHACEMENT OF DYE-SENSITIZED SOLAR CELLS’ EFFICIENCY

Capstone Design

13th April, 2017

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Supervised by Dr. A. Khaldoune
Capstone Report

“The designer has applied ethics to the design process and in the selection of the final proposed design. And that, the designer has held the safety of the public to be paramount and has addressed this in the presented design wherever may be applicable.”

_____________________________________________________

SOFIA ABID

Approved by the Supervisor(s)

__________________________

Dr. Asmae Khaledoune
ACKNOWLEDGEMENTS

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ABSTRACT
Dye-sensitized solar cells (DSSCs) are considered to be third generation photovoltaics special cell that efficiently converts visible light into electrical energy. Invented in 1991 by Professor Michael Graetzel and Dr. Brian O’Regan, it is given the name because it mimics the photosynthesis process by absorbing natural light. What makes this technology a promising light is its use of low-cost, sustainable and clean materials. It is also very promising in terms of surface optimization since these solar cells are typically used as windows and rooftops interfaces, and thus reduce surfaces usages. They are also esthetically pleasant and can be used more casually in homes. The key property of this technology as far as research is concerned is the study of oxides properties (such as ZnO and TiO$_2$) and Nano coating potential to be used in the DSSC’s. In this project, we built four prototypes of DSSC’s using TiO$_2$ as oxide layer, ZnO, ZnO+TiO$_2$, all with natural dye and another ZnO+TiO$_2$ using synthetic dye. We then calculated their efficiencies and found that the ZnO+TiO$_2$ exhibits the highest efficiency. The natural dye prototype exhibits highest power output while the synthetic dye prototype exhibits great resistance to degradation and aging.

1. INTRODUCTION
Solar electricity is a steadily growing energy technology today and solar cells have found markets in variety of applications ranging from small-scale electronic devices to large scale power plants. Although Morocco has a huge solar energy potential, no research has been conducted in the field of dye sensitized solar cells (DSSCs). The conversion efficiency of silicon based solar cells have reached an efficiency of 25.6% for mono-Si and 20.4% for Poly-Si. The second generation solar cells are based on thin film technologies. Amorphous Si (10.1%), CdTe (19.6%) are some of the well-established second generation solar cell devices. The third generation solar cell devices like Organic (10.7%), and dye sensitized solar cells (14.1%) [1]. Dye-sensitized solar cells (DSSCs) are considered to be one of the most promising alternatives to conventional silicon-based photovoltaic devices due to their easy fabrication, flexibility, low production cost which is around 1/5 of the production cost of Silicon-based PV solar cells. However, DSSC are substantially cheaper and easier to manufacture and promising laboratory research revels interesting and fast progress in the efficiency of the DSSC. Consequently, dye sensitized solar cells DSSCs emerged as a new class of low cost energy conversion devices with simple manufacturing procedures [2].Moreover, DSSC shows higher conversion efficiency than polycrystalline Si in diffuse light or cloudy conditions. It is believed that monocrystalline photovoltaic devices are becoming viable contender for large scale future solar energy converters [3]. However, the efforts are continually being undertaken to improve the performance of DSSC and hence the competitiveness of this technology in the world Market [4]. It is now possible to completely depart from the First and the second generation’s solar cells devices by replacing the phase contacting the semiconductor by an electrolyte thereby forming a dye sensitized solar cells.
2. Steeple Analysis:

2.1. Societal:
Demographically, our societies are ever-growing, and with this demographical expansion comes an increase in demand concerning many primary consumption resources, mainly energy. With a world population that is expected to double in two decades, the energy need and usage would grow as well. DSSC’s are a smart technology to provide clean energy from the sun, help reduce electricity bills and surface usage.

2.2. Technological:
Research done on DSSC’s generally and this work particularly focus on the enhancement of the materials used mainly the oxide and dye. The objective is to get the maximum efficiency from these materials at the lowest cost and longest time. The progress made on this technology would mainly improve the manufacturing of these solar cells and effectively move it from research laboratories to industrial manufacturing.

2.3. Economical:
Nowadays, governments, agencies and private corporations are willing to invest in green renewable energies. In Morocco, The Ministry of Energy, Mines, Water and Environment, along with other governmental parties are setting millions of dirhams investment in the sector. Other agencies such as MASEN invested more than 5 million dirhams in project Noor and invest in many Renewable energies project.

2.4. Ethical:
The techniques used in both research and manufacturing of DSSC’s are ethical and sustainable. In other terms, no harm (including testing) is done on humans or animals. No toxic chemicals are used in research nor manufacturing and no chemical waste is thrown in nature. There’s no intensive use nor depletion of natural resources.
2.5. **Political:**
Following the Intergovernmental Panel on Climate Change (IPCC), the Paris agreement of COP 21 and the international agreements made in Marrakech during COP22, Morocco is orienting its politics towards a more sustainable and environmental friendly model. The National Energy Institute is working on integrating development models that enhance sustainable energy use and develop economical models for a green energy plan.

2.6. **Legal:**
According to the Moroccan Law on Renewable Energies and according to the *dahir n°1-63-226 du 14 rabii I 1383 (05 août 1963)*, every initiative concerning the production, installation, manufacturing and commercialization of technologies using renewable energies are subject to declaration, authorization and standardization (according to national and international standards of renewable energies production) by the certified governmental agencies an authorities.

2.7. **Environmental:**
The core purpose of this whole project is to develop a technology for a green energy supply. Considering the rapid increase of the global carbon dioxide level in the atmosphere from 290 ppm to 390 ppm within the last 100 years and the effects on the world climate, measures to reduce greenhouse gas emissions have gained substantial attention within the last few year [5]. IPCC reports states in its latest report that the majority of additional CO2 emissions is due to the combustion of fossil fuels in power plants. Supplying energy from the sun will considerably reduce the CO2 emitted from the power plant. Plus, DSSC’s uses lass and natural dye which are clean materials and do not use nor emit any substance harmful to the environment or the human body.
3. Theoretical Background:

3.1. A Brief History of photovoltaics and DSSC’s:
The photovoltaic effect, also known as the process of converting sunlight into electricity directly, was first discovered in 1839 by Becquerel, a French physicist and Nobel Laureate upon observing light dependency voltage between electrodes emerged in an electrolyte [6]. In 1954, the first silicon solar cell was manufactured with an overall conversion efficiency of 6% [7]. Gerischer and Tributsch, both German scientists, worked on the principle of power generation by dye-sensitized solar cells in the 60’s and 70’s [8]. In the 90’s, Grätzel, a Swiss scientist and professor at Ecole Polytechnique Fédérale de Lausanne in Switzerland, introduced the Nano porous electrodes which helped improve the conversion efficiency of the dye-sensitized solar cells to 7% [9], which opened up the portal to extensive research on this technology.

3.2. Working Principle of Dye-Sensitized Solar Cells:
In its general format, a DSSC is composed of an anode and a cathode, with an oxide layer in between them, sensitized by a layer of dye and an electrolyte [10].
The anode is transparent, just like glass, so that the sunlight is absorbed by the inner parts of the solar cell [11]. Between the anode and the cathode is a mesh of oxide (typically Titanium Dioxide) nanoparticles that act like a roadway for the electrons [12]. These particles are coated with a light absorbing dye that converts photons (light) into electrons (electricity) [13]. An electrolyte (Iodide in our case) fills the space between the nanoparticles and help transfer electrons from the cathode to the dye molecules [14].

⇒ The anode sends electrons from the solar cell through a wire to whatever the cell is powering, then the electrons loop back to the cathode [15].

⇒ The electrons travel through the electrolyte and the TiO₂ nanoparticles to create an electric current [15].
TiO₂ nanoparticles are used as conductors because of their unique ability to be welded together and form one huge network for the electrons to travel through [15].

The electrons originate from the dye molecules coating the TiO₂ nanoparticles when they’re hit by light. Different color dyes can absorb different wavelength of light, which in turn carry different amount of energy [16].

The electrons travel randomly from one TiO₂ nanoparticle to another until they reach the anode [17].

When a photon strikes a dye molecule, the energy from the photon is transferred into the dye molecule. This molecule enters an excited state and emits and electron, which travel through the TiO₂ nanoparticles until it reaches the anode [17].

The dye-coated TiO₂ molecules are immersed in a solution of iodide which is able to replace the electrons lost by the dye molecules [18].

The iodide molecules in the iodide solution can give up an electron to a dye molecule that needs it. The iodide molecules are oxidized into triiodide which will float around until it comes in contact with the cathode [19].

The triiodide recovers its missing electrons from the cathode which reduce triiodide back to three iodide molecules [20].

The electrons emitted from the dye flow from the anode to whatever the solar cell is supplied and then flow back into the cell through the cathode [20].

The electrons from the cathode restore the electrons needed by the dye molecules and the whole process starts over again [20].
Figure 1 Principle operation of dye-sensitized solar cells

A Summary of the Process

Summary of Dye Sensitized Solar Cell

Figure 2 Summary Of DSSC Composants and Reactions
The dye is the photoactive material of the DSSC that can produce electricity once it is sensitized by light.

The dye catches photons of the incoming light and uses their energy to excite electrons.

The dye injects the excited electrons into the titanium dioxide.

The electro, is conducted away by the Nano-crystalline titanium dioxide.

A chemical electrolyte closes the circuits so that the electrons are returned back to the dye.

The movement of these electrons create energy which can be harvested into a rechargeable battery or any other electrical device.
3.3. Efficiency Parameters of a Dye-Sensitized Solar Cell:
The total efficiency of dye sensitized solar cells depends on optimization and compatibility of each of the constituents cited above, especially between TiO$_2$ semiconductor and Dye molecules. There is a very important factor is the high surface area and the thickness of the TiO$_2$ semiconductor film which leads to increased dye loading and improving the electron transport [21]. Also, the spectral response of a dye-sensitized solar cell (i.e. the relative efficiency of the DSSC’s in detecting the light and absorbing the photons) depends on the absorption properties the dye used. Thus, the device’s efficiency is measured through the quantum yield for the overall charge injection process and is referred to as the Incident Photon to Electrical Conversion Efficiency (IPCE) [22]. This quantity can be measured experimentally, in the laboratory by UV lights, using monochromatic light (single wavelength source) excitation. We would, typically, measure the photocurrent under closed circuit $I_{sc}$ which is the integrated sum of IPCE measured over the entire solar spectrum [23]:

$$I_{sc} = \int_{0}^{\infty} IPCE(\lambda).I_{sum}\lambda \, d\lambda$$

$$IPCE = 1240 \frac{I_{sc}}{\lambda \Phi}$$

Where;

$I_{sum}$: is the incident irradiance as a function of the wavelength $\lambda$.

$I_{sc}$: is the current at short circuit (mA/cm$^2$).

$\Phi$: is the incident radiant flux (W/m$^2$).
Then, we can express the overall sunlight to electric power conversion efficiency of a DSSC is expressed as:

\[ \eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{Isc \cdot V_{oc} \cdot FF}{P_{\text{in}}} \]

Where:

- **FF**: is the Fill Factor is the defined ratio \( I_{\text{max}} \cdot V_{\text{max}} / I_{sc} \cdot V_{oc} \).

- **P_{in}**: Solar Power Input into the solar cell.

- **V_{oc}**: The voltage across the open circuit.

⇒ The four values ISC, VOC, FF, and the conversion efficiency \( \eta \) are the key performance parameters of the solar cell.

**4. Experimental**

In this project, we will work on building four DSSC’s prototypes: One using TiO\(_2\) for the oxide layer, the second one using ZnO as the oxide layer and the third using both oxides. Both these prototypes will use natural dye (Extract from raspberries juice), conducting glass (A typical glass coated with ITO). The objective is to test both prototype, over the spam of twenty days, in an attempt to compare the impact of the materials on the overall efficiency.
4.1. **Dye Preparation:**
First, we prepare a sample of the dye that will be used. It is important to note that the desirable dye molecule should meet certain criteria such as matching with the solar spectrum, having a long-term operational stability and roughness of the semiconductor surface as well as a high redox potential. For our case, we used natural dye from raspberries juice (Fig.3 & 4). We started with crushing raspberries. Then we added 12 ml of 95% ethanol to the crashed strawberries as well as 12 ml of acetic acid. We then filter the dye until we end up with an evenly red liquid.

4.2. **Electrode and Electrolyte Preparation:**
The next thing is to make the redox couple that will act as a mediator that facilitates the regeneration reaction. In our case we used KI/I\(_2\) as redox couple (0.5 M of I\(_2\) and 0.05 M of KI). We got I\(_2\) as little grains that we mixed with water and stirred to get a liquid. We then added KI I powder form and stirred the whole mix with water until we got a brownish liquid: our redox couple.
1.1. Conducting Glass and TiO\textsubscript{2} Layer:

The main property that makes TiO\textsubscript{2} a very useful material is that it is highly hydrophilic. In other words, it has the particularity of dissociating the water it absorbs. This property is photo-activated by the ultraviolet radiation and is exploited in the windshield of vehicles or in the windows of buildings. Besides being hydrophilic, TiO\textsubscript{2} can easily be reduced so as to increase its conductivity. It can also decompose organic molecules which can be used for purification of water, air or cleaning surfaces. Moreover, when its composition is stoichiometric, TiO\textsubscript{2} behaves as an insulator while a few impurities are sufficient to make it a semi-conductor [24]. In our case, we used a conducting glass with active area of 9cm\textsuperscript{2}, pre-coated with TiO\textsubscript{2} (Paste). Typically, there are two types of conducting glass: Indium-doped conducting glass (ITO) and fluorine doped tin oxide (FTO). Ours was of ITO with a thin film of TiO\textsubscript{2} (thickness 5mm) deposited on the glass. For the other glass, we had to dope it with a conducting compounds. For our case, we chose graphite as a simpler alternative.

4.3. The Prototype Assembly:

Next, we put the conducting glass with the TiO\textsubscript{2} layer into the strawberries dye. We make sure it’s all emerged in the red liquid and we leave it there for around 15 minutes. After that, we take the glass off the dye and heat it on a Bunsen burner for around 3 minutes. We brought the two pieces of conducting glass together: the heated one coated with TiO\textsubscript{2} and the one coated with graphite. We add five drops of our liquid redox couple on one piece of glass and stick the two pieces of glass together leaving a little indentation on both sides. To secure our system, we clip the glasses together with paper clips. The procedure cited above breaks down the steps to make the DSSC’s using oxide titanium, pre-coated on conducting glass, with a layer of 5 mm thickness. The steps cited above are valid for both the prototype using ZnO as well as the prototype using both TiO\textsubscript{2} and ZnO. However, some changes have been made when it comes to the nature of the oxide and the deposition techniques.
4.4. ZnO, TiO$_2$+ZnO, TiO$_2$+ZnO with Synthetic Dye Prototypes:
✓ ZnO prototype:

For the prototype using ZnO as oxidant, we have used Oxide Zinc powder. It can be purchased from chemical manufacturers and is easily found in laboratories. The prototype I used was from the Laboratory of Chemical Engineering Department at l’Ecole Mohammed des Ingénieurs (EMI) in Rabat, where I have built this prototype. Concerning the oxide deposition method, I started by mixing 5 mg of zinc oxide powder with 5 ml of Ethanol and stirred it until I got a paste-like substance. I then deposited the paste on the conducting glass, while tapping the edges to center the deposition (Fig. 5). After this, the rest of the process is similar to the steps detailed above.

✓ ZnO + TiO$_2$:

In order to build this prototype, for comparison purposes, we decided to go with a TiO$_2$ pre-coated conducting glass, to which we added a thick layer of our ZnO-based paste (Made with the ZnO powder and Ethanol). The available conducting glass was pre-coated (Nano-coating techniques) from the source laboratory. The extra ZnO layer was deposited in our laboratory using a simple technique of paste deposition. The rest of the making of the DSSC’s is similar to the one detailed above (See TiO$_2$ prototype).
✓ ZnO+TiO$_2$ with Synthetic Dye:

In the next section (Results and Findings), we will discuss the particular interest exclusively oriented towards this particular prototype. The interesting results gotten from this particular sample pushed us on modifying one of the key elements related to the efficiency of the DSSC’s to test its effect on the power generated and life span of the cells. For this, we replace the organic dye (from the raspberry juice as explained above) with synthetic dye. At this point, the choice of the dye is very sensitive. We need to make sure that the dye, even if synthetic, matches the experimental thresholds (i.e. Strong light absorption, high solubility in organic solvents, sufficiently high LUMO, sufficiently low HOMO, high thermal and chemical stability).

Studies and research in the field, over the last twenty years, have identify potential synthetic dyes that fit these threshold and guarantee the processing of the redox reaction and electrons transfer [24]. The most used candidates are metals-based molecules of dye such as Pt, Cu, Fe [25] and are often considered and referred to as Transition Metal Complexes [25]. The most popular choices for this applications are: Our choice for that prototype was Porphyrin (Fig.6).

![Prophyrin Dye Molecule](image)

This choice is based on performances factors retrieved from previous researches and publications in which many dye molecules have been tested as for their light absorption properties [26]. The dye we used was ordered from an international distributor. We got a 50
ml sample from which we used only to 10 ml. Following the procedure above, we used the dye as received with no chemical additives (No ethanol). Following-up, we used the dye for the same purpose in the same manner we used the raspberry juice. In other words, we merge the conducting glass with both layers of TiO₂ and ZnO into our synthetic dye and leave it there for 15 minutes, again, until the white ZnO layer is slightly reddened. We then carry on with the standard procedure detailed above.

4.5. Measurements:
At the beginning of the measurements process, our focus was mainly on the three first-made prototypes (TiO₂, ZnO and TiO₂+ZnO). The interest on the fourth one (Synthetic dye) will raise at a later stage while fetching some relevant results concerning one of the prototypes. It is important to clearly outline the objective of our measurements: measuring different prototypes efficiency. Other conclusions can, subsequently, be drawn. The idea is to measure the power output from our prototypes. To this end, measurements of current and Voltage Potential Difference are to be taken. Our measurements time span was set to 20 days. Every day during these days, we would expose our cells to sunlight or, eventually, a projector lighting, depending on the meteorological conditions (Fig.7).
It is worth noting that the measurements were conducted in two cities: both Rabat and Ifrane. This information is relevant only in terms of sunlight intensity and light spectrum absorption, since the sunlight intensity differs slightly between the two locations. However, for the sake of simplification, we discard the difference and work with a unified and standardized solar power input ($P_{in}$). Each day, current and voltage values were fetched, as the solar cells were exposed to sunlight. To calculate the current and voltage (closed circuit), we connect the cathode (+) and anode (-) of our cell to the positive and ground inputs of our Multimeter. Voltage and current values were recorded. For days in which the weather did not permit sunlight harvesting, we used a light projector, available in the Physics and Engineering lab. It was important to get current and voltage values all throughout the 20 days’ time period, as it is a critical index for our cells aging study. In the next section (Results & Findings), we will display tables of the current and voltage values fetched during these twenty days for the three different-oxide-based prototypes, as well as final power output values and overall efficiency. Also, a table displaying values of current, voltage and power of a TiO$_2$+ZnO prototype using synthetic dye. For this, only ten days of measurements were recorded and were relevant enough for comparison sake.

*Figure 8 ZnO, TiO$_2$, ZnO+TiO$_2$ Prototypes*
5. Results & Findings:

The following three tables exhibit the values for the voltage, current and power gathered during the 20 days spam, for each one of the prototypes. This values will, then, be used to calculate the Net Power Output of every prototype. The power Output will be used to calculate he overall prototypes’ efficiency. We calculate the power and efficiency as follow:

Power Output:

\[ P_{\text{out}} = U_{\text{max}} \times I_{\text{max}} \]

- \( U_{\text{max}} \): Maximum Potential Difference of Voltage (Represented by the daily recorded values in Volte).
- \( I_{\text{max}} \): Maximum Current (Represented by the daily recorded values in mA).

Overall Efficiency:

\[ \eta = \frac{P_{\text{max}}}{P_{\text{in}}} \]

We discussed above how the efficiency formula is found and represented mathematically.

- \( P_{\text{max}} \): Maximum Power Output calculated as shown above.
- \( P_{\text{in}} \): Power Input from the Sun. The value we worked with is a standardized value from research done by Grätzel, which is set between 600 and 800 Watts per meter square.

5.1. ZnO Prototype:
## ZnO Prototype

<table>
<thead>
<tr>
<th>Day</th>
<th>Current Measured (mA)</th>
<th>Voltage Measured (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3,044</td>
<td>4,2</td>
</tr>
<tr>
<td>2</td>
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<td>4,2</td>
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<td>5</td>
<td>2,926</td>
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</tr>
<tr>
<td>20</td>
<td>0,822</td>
<td>1,32</td>
</tr>
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</table>

## Power Output (mW)

- 12,7848
- 12,7722
- 12,4804
- 12,04
- 9,42172
- 8,95806
- 8,7265
- 7,94864
- 7,67382
- 6,5564
- 4,91904
- 3,7638
- 3,7638
- 3,29
- 2,50425
- 2,45125
- 1,76925
- 1,62324
- 1,33764
- 1,08504

**6,2934925**
These values are the Net Power Output for every single day. In order to calculate the efficiency, we computed an average of these values.

\[ P_{\text{avg}} = 6.29 \text{ mW} \]

The overall efficiency is given by:

\[ \eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{62934925}{240} = 0.0262 \]

\[ \eta = 2.62 \]

5.2. TiO2 Prototype:

<table>
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<td>4,021</td>
</tr>
<tr>
<td>12</td>
<td>2,91</td>
<td>4</td>
</tr>
<tr>
<td>13</td>
<td>2,852</td>
<td>3,988</td>
</tr>
<tr>
<td>14</td>
<td>2,786</td>
<td>3,852</td>
</tr>
<tr>
<td>15</td>
<td>2,542</td>
<td>3,52</td>
</tr>
<tr>
<td>16</td>
<td>2,32</td>
<td>3,33</td>
</tr>
<tr>
<td>17</td>
<td>1,75</td>
<td>3,012</td>
</tr>
<tr>
<td>18</td>
<td>1,73</td>
<td>1,92</td>
</tr>
<tr>
<td>19</td>
<td>1,42</td>
<td>1,9</td>
</tr>
<tr>
<td>20</td>
<td>1,03</td>
<td>1,852</td>
</tr>
<tr>
<td>Power Output (mW)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16,5158</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16,6725</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15,3615</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15,0696</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14,9386</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14,49053</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14,43888</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13,51728</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12,719676</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12,364784</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11,878034</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11,64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11,373776</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10,731672</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8,94784</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7,7256</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5,271</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3,3216</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,698</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,90756</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

11,0792116

Similarly, we compute an average value of the power outputs in order for us to compute the overall efficiency:

\[ P_{\text{avg}} = 11.079 \text{ mW} \]

The overall efficiency is given by:

\[ \eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{11.079}{240} = 0.046 \]

\[ \eta = 4.62\% \]

5.3. TiO2+ZnO Prototype:
## Tio2+ZnO Prototype

<table>
<thead>
<tr>
<th>Day</th>
<th>Current Measured (mA)</th>
<th>Voltage Measured (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4,112</td>
<td>5,12</td>
</tr>
<tr>
<td>2</td>
<td>4,104</td>
<td>5,1</td>
</tr>
<tr>
<td>3</td>
<td>4,025</td>
<td>5,1</td>
</tr>
<tr>
<td>4</td>
<td>4,013</td>
<td>5,08</td>
</tr>
<tr>
<td>5</td>
<td>4,002</td>
<td>5,06</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>5,02</td>
</tr>
<tr>
<td>7</td>
<td>3,952</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>3,912</td>
<td>4,95</td>
</tr>
<tr>
<td>9</td>
<td>3,908</td>
<td>4,92</td>
</tr>
<tr>
<td>10</td>
<td>3,852</td>
<td>4,85</td>
</tr>
<tr>
<td>11</td>
<td>3,812</td>
<td>4,852</td>
</tr>
<tr>
<td>12</td>
<td>3,742</td>
<td>4,823</td>
</tr>
<tr>
<td>13</td>
<td>3,652</td>
<td>4,812</td>
</tr>
<tr>
<td>14</td>
<td>3,522</td>
<td>4,711</td>
</tr>
<tr>
<td>15</td>
<td>3,221</td>
<td>4,45</td>
</tr>
<tr>
<td>16</td>
<td>3,12</td>
<td>4,32</td>
</tr>
<tr>
<td>17</td>
<td>3,04</td>
<td>4,227</td>
</tr>
<tr>
<td>18</td>
<td>2,96</td>
<td>4,05</td>
</tr>
<tr>
<td>19</td>
<td>2,5</td>
<td>3,23</td>
</tr>
<tr>
<td>20</td>
<td>2,321</td>
<td>2,2</td>
</tr>
</tbody>
</table>

## Power Output (mW)

- 21,05344
- 20,9304
- 20,5275
- 20,38604
- 20,25012
- 20,08
- 19,76
- 19,3644
- 19,22736
- 18,6822
- 18,495824
- 18,047666
- 17,573424
- 16,592142
- 14,33345
- 13,4784
- 12,85008
- 11,988
- 8,075
- 5,1062
- 16,8400823
The average net power output for this prototype is given by:

\[ P_{\text{avg}} = 16.84 \text{ mW} \]

The Overall Efficiency is, then, calculated by:

\[
\eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{16.84}{240} = 0.0702
\]

\[ \eta = 7.02\% \]

5.4. Synthetic Dye Prototype:

The TiO\textsubscript{2}+ ZnO prototype is of particular interest since it has shown an efficiency considerably greater than the two other prototypes. Thus, we chose to use the multi-oxidants layer to study the effect of synthetic dye on the aging of the solar cell. The following are the results we got for a ten days’ time span.

<table>
<thead>
<tr>
<th>Day</th>
<th>Current Measured (mA)</th>
<th>Voltage Measured (V)</th>
<th>Power Output (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.52</td>
<td>4.09</td>
<td>14,3968</td>
</tr>
<tr>
<td>2</td>
<td>3.48</td>
<td>4.07</td>
<td>14,1636</td>
</tr>
<tr>
<td>3</td>
<td>3.44</td>
<td>4.06</td>
<td>13,9664</td>
</tr>
<tr>
<td>4</td>
<td>3.41</td>
<td>4.02</td>
<td>13,7082</td>
</tr>
<tr>
<td>5</td>
<td>3.36</td>
<td>3.98</td>
<td>13,3728</td>
</tr>
<tr>
<td>6</td>
<td>3.36</td>
<td>3.97</td>
<td>13,3392</td>
</tr>
<tr>
<td>7</td>
<td>3.31</td>
<td>3.94</td>
<td>13,0414</td>
</tr>
<tr>
<td>8</td>
<td>3.28</td>
<td>3.93</td>
<td>12,8904</td>
</tr>
<tr>
<td>9</td>
<td>3.26</td>
<td>3.93</td>
<td>12,8118</td>
</tr>
<tr>
<td>10</td>
<td>3.26</td>
<td>3.93</td>
<td>12,8118</td>
</tr>
</tbody>
</table>

Similarly to what we did with the other prototypes, we calculate an average value for the Net Power Output. Again, the value will be used to calculate the efficiency.

\[ P_{\text{avg}} = 13,45024 \text{ mW} \]

The Overall Efficiency is, then, calculated by:
\[ \eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{13.45}{240} = 0.056 \]

\[ \eta = 5.604\% \]

In the next section, we will discuss the results found above and compare the different results found for different prototypes.

6. **Discussion & Analysis:**
From the results above, we can clearly see the difference in terms of efficiency between the three prototypes using different oxidants. The difference is apparent when looking at the current and voltage measurements.

6.1. **ZnO Prototype:**
For the ZnO prototype, the current goes from 3.044 mA on the first day to 0.822 mA on the twentieth day. The Voltage drops from 4.2 V in the first day to 1.32 V in the twentieth day. This gives a power difference of:

\[ \text{Power Difference } \% = \frac{12.7848 - 1.08504}{12.7848} \times 100 = 91.5\% \]

The Net Power Output with respect to time (our 20 days’ time span) is represented as follow:
6.2. TiO2 Prototype:

For the TiO2 prototype, the current goes from 3.514 mA on the first day to 1.03 mA on the twentieth day. The Voltage drops from 4.7 V in the first day to 1.852 V in the twentieth day. This gives a power difference of:

\[
\text{Power Difference \%} = \frac{16.5158 - 1.90756}{16.5158} \times 100 = 88.45\%
\]

The Net Power Output with respect to time (our 20 days’ time span) is represented as follow:
1.2. ZnO+TiO$_2$ Prototype:

For the TiO$_2$+ZnO prototype, the current goes from 4.112 mA on the first day to 2.321 mA on the twentieth day. The Voltage drops from 5.12 V in the first day to 2.2 V in the twentieth day. This gives a power difference of:

$$\text{Power Difference \%} = \frac{21.05344 - 5.1062}{21.05344} \times 100 = 75.75\%$$

The Net Power Output with respect to time (our 20 days’ time span) is represented as follow:
6.3. TiO$_2$+ZnO with Synthetic Dye Prototype:

From the results shown above, we can clearly conclude that the TiO$_2$+ZnO prototype exhibits the highest Net Power Output values and the highest efficiency (7.02% compared to 2.62% for ZnO and 4.62% for TiO$_2$). Following this significant results, we decided to choose this prototype to test the significance of replacing natural dye (Raspberry juice) by synthetic dye (Porphyrin). We should note that the testing and measurements done on the synthetic dye prototype were conducted on a ten days’ time span, rather than 20. Thus, we can compare our results with the results obtained from the TiO$_2$+ZnO prototype with natural dye, during the first ten days. The first difference is visible when it comes to the Average Net Power Output. It is very useful to look at this piece of information since the average power output reflects the proximity of values with one another. In the case of the Synthetic dye prototype, the first value of power input recorded was 14.3968 mW in the first day and dropped to 12.8118 mW, which is a drop of 1.585 mW between the first and tenth day and a percent difference of 11%. Whereas, for the Natural Dye prototype, the first Net Power Output
recorded value was 21.05344 mW on the first day and 18.6822 mW on the tenth day (out of the twenty days recording). This a drop of 2.37 mW and a percent difference of 13%.

From these results, we can conclude that using Porphyrin significantly slows down the aging of the solar cells. However, it does decrease the efficiency, compared to natural dye.

We can see from the results of the above section that the overall efficiency of the Natural Dye prototype is 7.02% and that of the Synthetic Dye prototype is 5.604% which is a significant difference of 1.416% in terms of efficiency. The difference between decay/aging and efficiencies of the two prototypes can be represented by the following graph:

![Power Output Vs Days](image)

### Figure 12 Power Output of Synthetic Dye Prototype Vs. Natural Dye Prototype

6.4. Results Explanation:

- **Zinc Oxide Vs. Titanium Dioxide:**

From the result found below, our interest shift to properties of ZnO and TiO$_2$ when mixed together and used as a multi-layer oxidant for our DSSC’s. Both oxidants are used as Nano-particles coated into the surface of our conducting glass. Again, the main role of the oxidant
in the DSSC is to create a pathway for the electrons to move from the cathode to the anode. In other words, it is important for the oxidant layer used in the fabrication of the cells to be able to create a welded pathway and create a large transfer network (The Nano particles of the oxidant should be able to be welded together easily in order to ease the electrons transfer).

In this attempt to explain the highest efficiency obtained when combining ZnO and TiO$_2$ together, we start by setting the optimal properties for an ideal oxidant layer in a DSSC:

✓ The more defects in the oxidant layer, the highest the risk of the electrons getting lost in the iodide solution.

✓ The smaller the oxide nanoparticles for a fixed volume, the more surface area we can coat with dye.

✓ The lower density of nanoparticles, the fewer paths for the electrons to take in order to reach the anode.

Now, ideally, we should be able to find the optimal size and density of TiO$_2$ nanoparticles and create the maximum amount of surface area while creating the maximum number of safe pathways for the electrons.

Now, we look at properties of both ZnO and TiO$_2$: 
We will consider the properties of both oxidants at 300 k (Thermodynamically constant). For our discussion, we are mostly interested in the following properties: the lattice parameters and constants, the volume of the molecule and the density. We can see from the table above
that the ZnO particles have a ratio of lattice parameters of 1.602 (ratio of c to a), while the TiO\textsubscript{2} particles (considering the most widely used structure and the one we used for our experiment to be Anatase) have a ratio of lattice parameters of 0.64. We conclude that the smallest nanoparticles are ZnO, which means that ZnO coating frees more surface for dye to take place. Speaking of density, the density of ZnO is given by 5.606 g/cm\textsuperscript{3} while that of TiO\textsubscript{2} is 3.79 g/cm\textsuperscript{3}. Thus, electrons have fewer paths to take to get from the cathode to the anode. With a volume of 3.4061 nm\textsuperscript{3}, TiO\textsubscript{2} layer creates the maximum amount of surface area while creating the maximum number of safe pathways for the electrons.

\(\Rightarrow\) Thus, both these layers, optimize the threshold settings for a fully optimized pathway of the electrons between the anode and the cathode.

➢ **Natural Dye Vs. Synthetic Dye:**

Upon absorption, the dye used charges the TiO\textsubscript{2} particles positively by transferring most of its protons [27]. In other words, the degree to which a sensitizer is protonized needs to be optimized in order to achieve high conversion efficiency [27]. When using natural dye, the dye molecules exhibit a relatively stable photochemical behavior. However, it has been shown from research that organic dye degrades the TiO\textsubscript{2} particle [28]. It’s where the synthetic comes into play with metal alloys. In our case, by using synthetic dye, we’ve postponed the degradation factor, but also, affected the photochemical stability by replacing natural dye molecule by synthetic ones, lowering the overall efficiency.

➢ **Results Summary:**

From our comparative study, we have come to the conclusion that the use of a multilayer-oxidants (TiO\textsubscript{2}+ZnO) exhibit a greater overall efficiency than mono-layer oxidants. The efficiency increase is represented by a 2% factor, which can be significantly higher on big scale samples. We have also studied the effect of sensitization of the oxide layer through the
use of organic and synthetic dye. We have concluded, from experimental results that natural dye-based prototypes generate a higher overall efficiency than the synthetic-dye based prototype. However, the synthetic dye prototype exhibits a slower degradation to aging factor compared to the natural-dye prototype. This gives an opening to further research (an ongoing research on the field) to produce a dye that can resist degradation and aging while performing in the high end of the overall efficiency spectrum.

7. From Laboratory to Commercial Development:

7.1. Current PV Market Overview:

In 2010 alone, the photovoltaic industry is recorded to have generated 82$ billion in global revenue [29]. In the same year, the PV industry is estimated to have generated 20.5 GW of power [29]. The solar industry’s production is expected to grow at a growth rate between 20% and 30% for the next five years [29]. The figure below shows the distribution of the main solar manufacturers in the world. The top 3 includes: JA Solar (China), First Solar (USA) and Trina Solar (China) [29].

![World Top Solar Manufacturers 2009](source: Solarbuzz & EPRA)

*Figure 15 World Top Solar Manufacturers*
7.2. Third Generation PV Market Overview:
Over the last few interests, many PV manufacturers started showing interest in developing and manufacturing dye-sensitized solar cells, in their business reports. As in for 2016, many companies, such as G24/Gcell in Wales and Dongjin Semichem in South Korea started to commercialize DSSC technology [n]. The South Korean company has developed an automatic pilot production line for glass-based DSSC, in 2012 [30]. It can now produce ten thousands of modules per year [30]. Apart from their promising rendering in terms of energy efficiency, their aesthetics is attracting architects, construction materials companies, but mainly windows manufacturers. DSSC’s have the advantage of being made of glass (a transparent material) and can thus be used in windows, in buildings. Not only is the option aesthetically pleasing, it is also surface area optimized, since using solar panels in windows reduce the surface area on rooftops or others used by first and second generations solar panels. The pictures below show direct application involving DSSC’s. As for our next section, we are going to study the feasibility of integrating DSSC’s in offices to minimize electrical energy consumption. To portray this, we decided to choose as an example the Office of International Programs, here at AUI, for our energy audit and alternative implementation, in order for us to see the amount of potential savings (in terms of energy and cost) when integrating the model of windows-based dye-sensitized solar cells.

7.3. Integrating Window-Based DSSC’s: Case of OIP at AUI:
The first step in our implementation study is to perform an energy audit of the office. In other words, we will report and look at all the electricity consuming devices and depict how much energy that consume on a daily and monthly basis.

➢ OIP Energy Audit:
In order to perform the energy audit, we stopped by the OIP office and took note of all relevant electricity consuming devices. We got the following:

- 4 Desktop Computers
- 4 Desktop Printers
- 1 Scanner/Printer
- 1 Fax Machine
- 1 Coffee Maker
- 4 Office phones
- 18 lightbulbs
- 3 Heaters.

We will be discarding the energy consumption of heaters since we know that AUI heating system to the administrative buildings is based on bio mass (No burning of fossil fuels).

The following figures show the total monthly consumption and cost for the electrical appliances:

![Figure 16 Energy Consumption from Lighting](image)
From the figures above, we can conclude that the total monthly consumption and average monthly cost are as follows:

<table>
<thead>
<tr>
<th>Appliances</th>
<th>Monthly Consumption (KWh)</th>
<th>Average Monthly Cost (MAD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lighting</td>
<td>58.56</td>
<td>79.06</td>
</tr>
<tr>
<td>Office Appliances</td>
<td>133.2</td>
<td>179.82</td>
</tr>
<tr>
<td>Other Appliances</td>
<td>33.6</td>
<td>45.36</td>
</tr>
</tbody>
</table>

✓ The total Monthly Energy Consumption is: **225.36 KWh**

✓ The total Average Monthly Cost is: **304.24 MAD**

➢ **DSSC’s Integration and Energy Savings**
Now, we want to be able to calculate the energy output we’ll get after integrating the DSSC’s into the office’s windows. First, we need to keep in mind the efficiency formula, given by:

\[ \eta = \frac{P_{\text{max}}}{P_{\text{in}}} \]

We want to be able to fetch the power output when having the efficiency and sun power input. We can get the power input from the Gratzel standardized values cited above (600-800 W/m²). We consider the same value used for our prototypes efficiency calculations and that is 720 W/m².

The confirmed efficiency of laboratories DSSC’s is recorded to be 14.1% up to this day [31]. However, in manufacturing and industry, it is only set to be 12% [31]. We also now that the office has 4 large widows of area 2mx1m (2m²). Thus the maximum power output can be expressed as:

\[ P_{\text{max}} = P_{\text{in}} \cdot \eta = 720 \cdot 0.12 = 86.4 \text{ W} \]

We can get, for the total of the 4 windows, a power output of:

\[ P = 86.4 \cdot 4 = 345.6 \text{ W} = 0.3456 \text{ KW} \]

If we consider an average of 10 hours of sunlight per day, the net power per hour produced from our device, monthly, will be:

\[ P_t = 0.3456 \cdot 10 \cdot 30 = 103.68 \text{ Kwh} \]

In other words, the DSSC’s will cover 46% of the monthly energy consumption. This is equivalent to saving 140 MAD monthly on energy bills (103.68*1.35=139.986).
8. Conclusion & Future Works:

It goes without saying that dye-sensitized solar cells exhibits such promising insights when it comes to the solar energy particularly and energy efficiency in general. It is true that research regarding the topic has come a long way from its beginning a few decades ago. From the findings done by Gratzel, efficiencies of laboratory-based models keeps increasing over the years as teams of researchers from all over the world contribute to existing art. In the same line, efficiencies in the industry and manufacturing processes keep increasing as well. In this project, we’ve tried to explore one of the most researched area of the topic: The oxidant layer and nature of the dye. We’ve tried out different combination and got distinctive efficiencies. We could conclude that combining different oxidants does have a greater impact on the solar cells efficiencies. The most amazing thing about this topic is the infinite possibilities it opens in terms of research since very little is known about it to this day. Improvements constantly looks at aspects such as creating a dye alloy that combine both the aging properties of a synthetic dye and the high power output of natural dye. Overall, the research on DSSC’s will keep growing throughout the years as continuous progress is made in the field of nanotechnology, and particularly Nano-coating of materials.
9. REFERENCES


