

**OPTICAL CHARACTERIZATION OF DYE-SENSITISED TiO₂ THIN
FILMS FOR SOLAR CELL APPLICATIONS**

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DECLARATION

This thesis is my original work and has not been presented for the award of a degree or any other award in any University

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DEDICATION

I dedicate this thesis to my parents, my husband and my three children for their moral support in the hardest times.

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ABBREVIATIONS AND ACRONYMS

CdS	Cadmium Sulphide
CdTe	Cadmium Telluride
CIGS	Copper Indium Gallium Diselenide
CIS	Copper Indium Diselenide
DSSC	Dye Sensitized Solar Cells
<i>eV</i>	electron Volt
FF	Fill Factor
I ₃ ⁻	Tri-iodide ions
InGaAs	Indium gallium arsenide
I _{sc}	Short-circuit current
ITO	Indium Tin Oxide
PSC	Photo-electrochemical Solar Cell
PV	Photovoltaic
STC	Standard Test Condition
TCO	Transparent Conducting Oxide
TCO	Transparent Conducting Oxide
TiO ₂	Titanium dioxide

ABSTRACT

The use of dye-sensitized solar cells to harness solar energy has gained interest because of their simplicity and are cheaper to manufacture. They can also be glazed on flexible substrates for improved conversion efficiency. Standard DSSC consist of materials made of transparent conducting oxides (TCOs) with titanium dioxide (TiO_2) used as semiconducting material. Synthetic dyes or natural dyes are utilized as sensitizers to modify the TiO_2 film. The goal of the current study was to find out the potential of organic dyes from blue berry and spinach as sensitizing agents for TiO_2 films by investigating their influence on optical properties of the films and energy conversion efficiency of DSSC employing the said films. The blueberry and the spinach dyes were extracted from blueberry fruit and spinach leaves respectively and were taken into the nano-porous titania substrates. The nano-porous TiO_2 paste was sourced from Solaronics SA and its film generated on the glass surface by employing screen printing technique. Ruthenium dye was used as a reference dye. Using DUV3700 spectrophotometer the TiO_2 film was characterized to obtain its optical properties which were transmittance, reflectance and absorbance for both sensitized and un-sensitized TiO_2 films. The optical results showed blue berry sensitized TiO_2 had low reflectance, transmittance and high absorbance compared to all other samples both sensitized and un-sensitized. Spinach sensitized TiO_2 films had high reflectance, transmittance and low absorbance. On energy conversion efficiency, the DSSC fabricated using Ruthenium dye had the highest efficiency of $\sim 2\%$. The DSSC fabricated with Blue berry dye followed closely at $\sim 1.5\%$ efficiency while the DSSC employing spinach dye had the lowest conversion efficiency of $\sim 0.6\%$. Diluting the dyes with distilled water improved conversion efficiency for DSSCs fabricated employing the blue berry and spinach dyes. From the study blue berry dye has shown a more promising potential for fabrication of the DSSCs. However, further study is required to optimize the concentration of the dyes as diluting the dyes enhanced the performance of the dye as a DSSC sensitizer.

CHAPTER ONE

INTRODUCTION

1.1 Overview of the study

Energy has great importance in addressing human development and comfort (Pasten & Santamarina, 2012). For instance, it is used in heating, cooling, transport and generation of energy both in the urban and rural areas. Energy harnessed from the sun's radiation is environmentally friendly as compared to other sources of energy since it does not create the harmful waste associated with other methods such as fossil fuel (Grätzel, 2005). Hydro power provides the majority of electricity supply in Kenya (Kiplagat *et al.*, 2011). With Kenya receiving a viable solar irradiance, this makes solar energy a good option for utilization in the energy mix (Rabah, 2005). Photovoltaic (PV) electricity production is achieved by employing a solar cell as the basic unit in the construction of solar modules (Alazraki & Haselip, 2007).

Currently, the solar radiation can be harnessed to produce electricity by the help of solar cells. These cells are classified into three broad categories namely; silicon based mono-crystalline cells (also known as 1st generation devices), thin film and amorphous silicon based devices (also known as second generation) and inorganic and organic solar cells (also referred to as the third generation devices). Inorganic solar cells comprises of group III–V compounds like copper indium/sulfide, cadmium telluride and indium gallium arsenide. Natural solar cells on the other hand comprises of plant extracted dye-sensitized solar cells and the polymer solar cell (Hara *et al.*, 2003). Currently, most of the solar panels accounting for 92% are made from amorphous Silicon(Si), Cadmium telluride(CdTe) account for 5% while CIGS and Amorphous Hydrogenated silicon account for 2% and 1%, respectively (Sarkar,

2014). The high cost of production is the main disadvantage behind the first generation C-Si cells. The high cost results from the sophisticated manufacturing process, cost of purchasing the wafers and expensive energy costs (Ramanujam & Singh, 2017). The second generation solar cells comprising of copper indium gallium diselenide (CIGS), amorphous hydrogenated silicon and cadmium telluride (CdTe) were introduced as a replacement of the first generation of solar cells. Of the three second generation solar cells, copper indium gallium diselenide (CIGS) fabricated solar cells are more promising alternative to the c-Si solar cells because it has high stability and reliability except in considerable humidity and heat. However, their drawbacks are brought about by scarcity and price of Indium (Ramanujam & Singh, 2017). Dye-sensitized solar cells (DSSCs) came as a more efficient way of harnessing solar radiation energy. Though their efficiencies are relatively low compared with silicon-based solar cells, they have stood out to be simple in construction since they require low cost materials (Hara *et al.*, 2003).

By careful selection of the dye sensitizer used, the efficiencies of these solar cells can be greatly improved (Zhang *et al.*, 2013). These solar cells use dyes and electrodes coated with wide band gap semiconductors to adsorb large amounts of energy (Hara and Mori, 2011). The efficiency of existing DSSCs reaches up to 12%, using Ru (II) dyes by optimizing material and structural properties (Sharma *et al.*, 2018). Integration of dye molecules with wide band gap semiconductor electrodes is a crucial factor in mounting a photo-electrochemical solar cell as presented in Figure 1.1

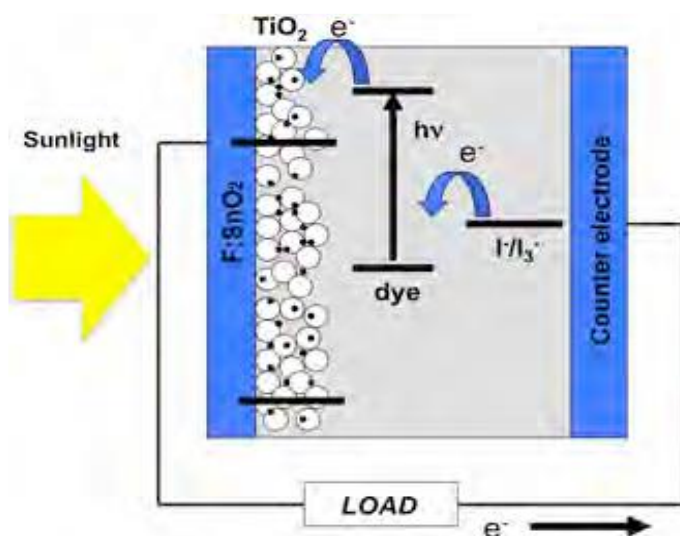


Figure 1. 1: A diagrammatic representation of a nanoparticle-based DSSC (Cherepy *et al.*, 1997).

This DSSC comprises of a glass coated (TCO) film, a dye-sensitized nanoparticle film (thickness of tens of μm), liquid electrolyte and a counter electrode (Cherepy *et al.*, 1997). These electrodes are transparent and good conductors. The titanium dioxide coated on one of the electrodes helps in holding the dye. The dye helps in trapping the light, exciting of the electrons from the iodide electrolyte which ultimately results in the cell current. To be able to reflect back the light, the bottom of the TiO_2 plate is galvanized with graphite or carbon (Trudeau *et al.*, 2002). Though different dye sensitizers have been used in the fabrication of the DSSCs with the ruthenium dye being widely researched on (Zhang *et al.*, 2013), there has been limited study on the use of dyes derived from locally grown plants such as spinach, and blue berries. This study investigated the optical influence of sensitizing TiO_2 thin films with anthocyanin and chlorophyll dyes for the modification of TiO_2 based DSSC. The anthocyanin and chlorophyll dyes were from blueberry fruits and spinach leaves respectively sourced locally. Researches in various aspects are still ongoing with the common goal of improving the efficiency of dye solar cells. Among the

areas of research are on cost effective materials which improve the energy conversion efficiency like alternative sensitizers which this study sets out to perform.

1.2 Statement of the problem

The current photovoltaic solar cells require expensive fabrication techniques and high purity materials. For instance, Ru-complex dye is commercialized in large scale but is disadvantaged due to its inclination to degrade in the presence of water, complicated synthetic routes and it's very costly. Most of the current dyes for example cobalt, pose environmental and health risks. Plant based DSSCs can be good alternative to the current dyes as they are both eco-friendly and cheaper. There is need to do further fundamental research or study with aims of solving the basic properties that affect the overall performance of DSSC such as optical properties of new and alternative sensitizers.

1.3 Objectives

1.3.1 General objective

The main objective of the study was to optically characterize dye-sensitized TiO₂ thin films for solar cell applications.

1.3.2 Specific objectives

- (i) To deposit TiO₂ thin films by screen printing technique.
- (ii) To investigate the optical characteristics of TiO₂ thin films both un-sensitized and sensitized in local dyes
- (iii) To fabricate and study the I-V characteristics of the dye sensitized solar cell employing TiO₂ thin films.

1.4 Justification of the study

Optical properties have shown that dyes determine the absorption of solar energy in different wavelengths. The absorbed energy excites the electrons to move from the valence band to the conduction band. Study of optical properties of new sensitizers may reveal new properties that the sensitizers have. With that knowledge, it may be possible to manipulate and increase the functioning of DSSCs. Improved efficiency of the solar cell may lead to accelerated uptake of commercialization of DSSC which will further lead to availability of cost effective solar modules in the market. Although characterization of DSSC has been intensively done, it is important to perform the characterization of the compounds used in DSSC fabrication as they tend to have different absorption power. This has been fuelled by the desire to know exactly why their overall efficiencies are still low since a major milestone to their discovery was made around 30 years ago (O'regan and Gratzel, 1991). Since the material choice of both the photo-anode and the counter-electrode has implications on the performance of these solar cells, these materials need to be chosen depending on their best optical properties. It is therefore important that material characterization is done to enable the correct choice. Research on natural dyes is ongoing after the realization of their advantages which include; low cost of production, complete biodegradation, non-toxicity ratio and they are easily available. The new materials used in this study are blueberry and spinach dyes.

CHAPTER TWO

LITERATURE REVIEW

2.1 An account of dye sensitized solar cells

The use of dye sensitized solar cells (DSSC) with chlorophyll dye sensitized zinc oxide electrode was first introduced in 1972 (Rawal *et al.*, 2015). The first DSSC using powdered and highly porous multi-crystalline zinc oxide as the dye support was developed at Osaka University (Tsubomura *et al.*, 1976). The use of powdered ZnO significantly improved the efficiency of the photo-electrode and the energy conversion efficiency was 2.5%. Grätzel (1991) at Ecole Polytechnique Federale (EPFL), Switzerland, came up with a DSSC prototype with improved conversion efficiency of 7.12%. Grätzel's DSSC prototype improvement were based on the following characteristics.

- i. He used titanium oxide nanoparticles to increase the dye adsorption area.
- ii. He utilized ruthenium-based dyes having a wider optical absorption.
- iii. Grätzel's prototype also ensured minimal loss on the conversion efficiency.

In 1993, Grätzel and his group developed a new set of DSSC with the objective to produce them at a cheaper cost by utilizing low cost TiO₂ as the semiconductor. These solar cells also had a thin layer organisation of the photo-electrodes with efficiencies of more than 10% (Grätzel, 2003). Their sole aim was to improve the DSSC efficiency at the expense of other optical properties of the compounds used in the solar cell fabrication.

Conversion efficiencies were compared with those of the National Institute of Advanced Industrial Science and Technology (AIST) of Japan as they meet the industrial standards (Matsuoka *et al.*, 2005). The industrial standards dictate that any

product with a conversion efficiency of 8% meets the minimum requirement for market production (Grätzel, 2003).

The United States was the first to come up with dye-sensitized TiO₂ solar cells in 1978 (Deb *et al.*, 1978). The DSSC utilized N-methyl-phenazinium ion so as to expand optical spectrum to the 500 nm region. Despite the wide wavelength of the dye the cells were unstable in terms of light absorption and had a low conversion efficiency of 4%. In addition, the optical properties of the N-methyl-phenazinium ion dye used were not studied. The DSSC was later improved by Grätzel and Kay who came up with DSSC with conversion efficiencies 7.12% and 10% (Kay & Grätzel, 1996). However, for both TiO₂ film and the ruthenium dye used, there were no studies of their transmittance and reflectance. Ruthenium dye is expensive, toxic and non-biodegradable. According to Kay and Grätzel, the previous solar cells used monolithic surfaces as semiconductors which resulted to low absorption of incoming light. Properties of the film thickness were not considered in terms of their relation to electrical output of the solar cell fabricated.

Research has shown that organic dyes have a high ability to improve the efficiency of DSSC due to their elevated molar extinction coefficient as compared to ruthenium complex dyes (Koumura *et al.* 2006). Hara and Arakawa, in 2005 tested the efficiency of different organic dyes that can be used in solar cells and among them, coumarin dyes had good photoelectric conversion properties, unfortunately its high concentration of 4-*tert*-butylpyridine (TBP) meant high power requirement for high conversion efficiency (Hara and Arakawa, 2005). Later, Wongcharee *et al.* (2007) presented a DSSC using organic dyes extracted from blue pea and rosella flowers.

The findings showed that the rosella extracts had higher photo-sensitized efficiency as compared to blue pea dyes. At optimal settings, rosella had an efficiency of 0.7%. In this case, water was a better solvent over alcohol. However, ethanol solvent was noted to have negative effects on the stability of the dye sensitized solar cells. It was also noted that the maximum efficiency of the solar cell fabricated was still very low ranging between 7-10%.

Sun *et al.* (2014) made a DSSC by utilising Co (PY5Me₂) (NMBI)^{2+/3+} (CoII/III) composite electrolyte. Application of this electrolyte together with an available commercial organic sensitizers enabled attainment of 8.4% and 9.2% efficiencies at a simulated light intensity of 100% sun (100 mW cm⁻² AM1.5 G) and at 10% sun, respectively. However, Cobalt is a main source of contact dermatitis as reported by Basketter *et al.* (2003). Chang *et al.* (2010) used chlorophyll from spinach as a dye for DSSC. He compared the solvents which were ethanol and distilled water. Spinach dye extracted with distilled water was found to have a fill factor of 0.49 % and spinach dye extracted with ethanol had 0.36%. The efficiency was 1-2% but there was no study for transmittance and reflectance.

2.2 TiO₂ film optical properties

TiO₂ is extensively used for the fabrication of DSSC as layered electrode for absorption of the dye molecules (Lao *et al.*, 2005). Nano-crystalline particles ensure a higher surface area which is approximated to be 2000 times more compared with a flat-layered electrode (Lao *et al.*, 2005). Among the TiO₂ crystalline structures with conducive environments, i.e. rutile, anatase, srilankite and, brookite, TiO₂ having a wide band gap accompanied with low dielectric constant and, high electron mobility

is the most appropriate. This is because TiO₂ anatase phase strictly takes in radiations within the UV region. The aim of this study was to utilize low cost and locally available dye sensitizers such as blueberry dye and spinach dye so as to cut on the DSSC fabrication cost. In addition, the electrolyte to be used needs to be non-toxic to the user unlike the cobalt-based DSSC and of a medium concentration unlike the 4-*tert*-butylpyridine, which will help in improving the efficiency of the DSSC fabricated. The review highlighted above shows how rich the area of DSSC is in terms of new materials, understanding of the processes that the DSSC goes through and the various impediments in the already researched area. One of the areas that still has the potential for research is the investigation of alternative sensitizers with the view of identifying affordable materials yet efficient sensitizers. This was the main goal of this study.

CHAPTER THREE

THEORETICAL BACKGROUND

3.1 Introduction

Photovoltaic cells are electrical device with the ability to convert the solar energy into electrical energy. These appliances constitutes of Pn junctions as extrinsic semiconductors. The introduction of a dopant element into the intrinsic semiconductors. The introduction of a dopant element into the intrinsic semiconductor determines the formation of a p or n type semiconductor. The types of solar cells related to this study include; the hybrid solar cell and the organic solar cell.

3.2 Physics of solar cells

The standard (non-DSSC) solar cells use semiconductors with photo-induced optical absorption separated with a transition of a band gap. The efficiency of the semiconductors to absorb the solar energy is dictated by a band gap of either 1 or 2 eV, in situations of high sunlight intensity (Smith & Nile, 2010).

Solar cells usually needs to incorporate the charges to “drift” their contacts respective positions.

Figure 3.1a

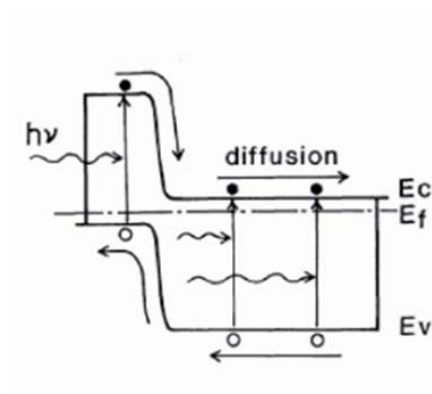


Figure 3.1b

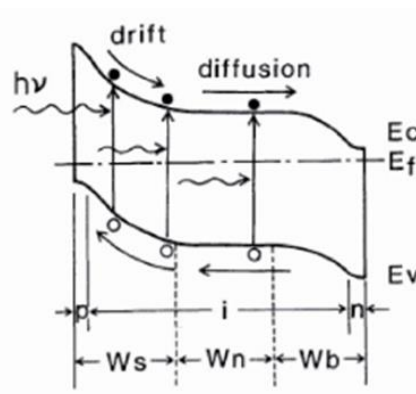


Figure 3.1: A Schematic diagram for photo-generation in a crystalline solar cell (3.1a) and Amorphous silicon solar cell (3.1b) (Takaishi and Yamashita, 2008).

To effectively convert the sun energy, photovoltaic cells have to be kept such that recombination does not occur. This is achieved by placing semiconductors having chemical potential gradients so as to offset the energy bands resulting from the electrical fields (Oh *et al.*, 2012).

A number of factors that determine the photoelectric energy produced are as presented by the formulae below (Werthen *et al.*, 1983).

$$JSC = q \int bs(E)QE(E)\partial E$$

(3.1)

where;

JSC- represents the density of photocurrent.

QE - quantum efficiency

QE (E) is the probability of excitation of an electron by a photon of energy E.

bs (E) is the incident spectral photon flux density.

The EQ.3.1 shows that the photocurrent generated by the solar cell depends on the wavelength as absorption is a coefficient function of wavelength. For instance, high energy coming from short wavelength has relatively wide absorption coefficient.

3.3 Dye sensitized solar cells

Employing sintered nanoparticles rather than using the convoluting interface, dye sensitised solar cells increase the surface area sandwiched by the donor-acceptor layers. The importance of nano-particles is seen in the increase of the amount of solar energy generated by molecular monolayer coating on the acceptor surface (Kay and Gratzel, 1996).

Similarities of both the DSSC and the Photo-electrochemical Solar Cell (PSC) are that they are both have counter electrodes, redox electrolytes and a photo-electrode.

While in the photo-electrochemical solar cell the electrode is highly likely to be

degraded by the electrolyte, DSSCs have corrosion resistance oxide semiconductor materials for example ZnO, TiO₂ and Tin Oxide(SnO₂) fabricated by a dye generating solar energies (Tiwana *et al.*, 2011).

A DSSC has a mesoporous layer of nanoparticles (semiconductor oxide) which establish a great electrical contact between the particles when sintered together. A standard DSSC has a mesoporous of about 10 μm thick and the nano-particle of diameter range between 10 nm and 30 nm with a 50-60 % porosity (Hagfeldt *et al.*, 2018). It also has an electrolyte solution (high ionic strength) surrounding the sensitized film, mostly composing of an organic solvent as shown in Figure 3.2.

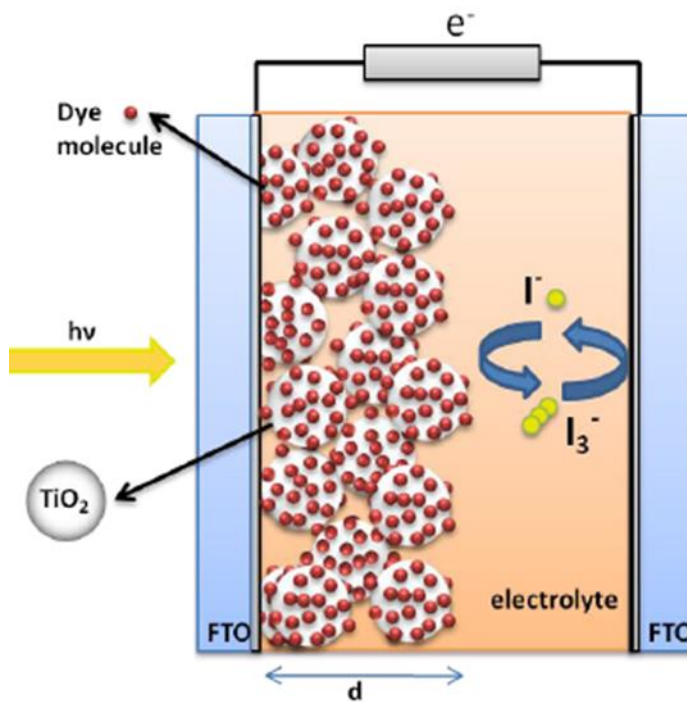


Figure 3. 2: A DSSC cell device schematic view (Grätzel *et al.*, 1991)

The pioneering work by the Grätzel group is considered one of the most successful combination of materials, which further expanded research of DSSCs. Gratzel came up with the basic design of DSSC which consisted of a layer of a semiconductor oxide (electrode) fabricated with organic dyes, electrolyte layer with hole-conducting

capability and a catalytic material layer (recycles oxidized electrolyte) (O'Reagan and Grätzel, 1991).

3.4 DSSC working principle

Solar energy by DSSC, is captured by a dye (Hagfeldt *et al.*, 2018). The photons are absorbed causing an electron to be ejected from the dye after which they are pumped into the transmission band of TiO₂ and passes by diffusion across the electrolyte. The ejected electron is then substituted by another electron from the iodide electrolyte layer below the TiO₂ film.

It is expected that the solar radiations will excite the dye electron causing energy transfer across the electrode to the TiO₂ (Figure 3.3, reaction 1) after which they are returned back to the ground state (reaction 3). According to Kalyanasundaram & Grätzel (1998) the energy of the excited dye electrons is higher compared to the TiO₂ electrolyte forcing the electrons to be injected into the semiconductor at a very high speed (Reaction 2). The backflow of the electrons on the other hand is slow while the electrolyte to oxide dye charge is fast to give room for the oxide dye regeneration. It is for this principle that a dye used should always have a higher excitement energy compared to the TiO₂ Substrate and must have an expanded absorption spectrum for visible light and high energy turnover (Kalyanasundaram and Grätzel, 1998). From the end of the nano-crystalline TiO₂ the electrons diffuse through the conductive glass to the outer circuit of cathode, which is usually made by platinum (Reaction 4). Redox reaction takes place to replenish the electrolyte electrons (Yu, 2011) (Reaction 8). Reaction 7 is regeneration of oxide to ground state. The dye regeneration occurs to its lowest state (reactions 5 and 6).

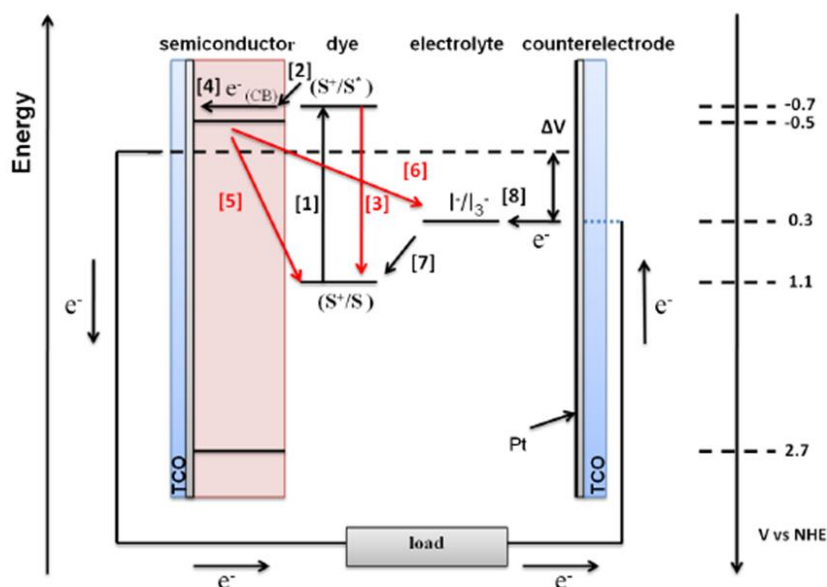


Figure 3.3: Electron movement through a DSSC (Hagfeldt *et al.*, 2010).

3.5 The individual DSSC components

3.5.1 Fluorine doped Tin Oxide glass substrate

It is the basic layer of a DSSC, made of either plastic or glass material. The substrate displays significant transparency due to its broad band-gap. It also has low electrical resistance attributed to its high carrier concentration thus allowing electron flow (Kwak *et al.*, 2011).

Fluorine doped tin oxide glass substrate (FTO) is considered as potential substrate due to its stability under different atmospheric conditions (Kwak *et al.*, 2011). This substrate is used to make photo-anode electrode and counter electrode. The photo-anode electrode forms the anode electrode of the cell whereby deposition of the semiconductor material occurs. The counter-electrode on the other hand, forms the cathode electrode of the cell. It provides the liquid electrolyte electrons for completion of the redox reaction in a short time so as to ensure lifetime stability and prevent electron recapture. Platinum having a high electron mobility that regenerates electrolytes fast is the commonly preferred material for DSSC cells. In this study, the

counter-electrode was prepared from the pencil rod coat because it is inexpensive and has a good catalytic activity (Onwujiuba, 2018).

3.5.2 Titanium Dioxide (TiO₂)

Titanium dioxide (TiO₂) is a common oxide material in use for DSSC. It is a wide band gap semiconductor (3.2 eV) found in nature as rutile crystalline structures, anatase, or brookite (Chen *et al.*, 2015). Its compound, Titania, causes a bright white appearance in most substances like wall paint. Figure 3.4 shows the anatase crystal structure of TiO₂. It is made up of titanium ions located at the centre of an octahedron of six oxide ions. TiO₂ has partly ionic and partly covalent type of bonding which in turn means insulating stoichiometric crystals. Anatase has a lower density than rutile. Rutile has a greater average distance between the titanium ions when compared to anatase making it more stable (Su *et al.*, 2015).

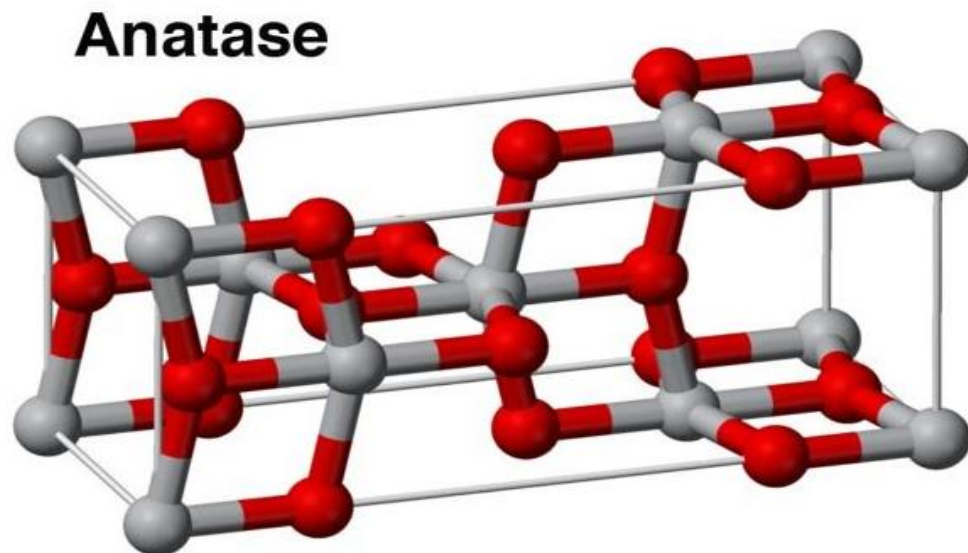


Figure 3. 4: Crystal structure of titania (Kay and Grätzel, 1996)

Substantive thermal activation energy is needed for the phase conversion from anatase to rutile but depends on the amount of impurity and crystal size (Mahdi, 2012). The size of the TiO₂ particles determines the effectiveness of interactive

platform of the cell because its direct contact with TiO₂ surface is by the sensitizer which is only photoactive. Hence the efficiency is improved consequently by reducing particle size.

3.5.3 The Dye Material

Dyes help in light absorption and inject electrons into the semiconductor and replenish themselves with the electrons from the electrolyte (Kitamura *et al.*, 2004). Some of the requirements and characteristics the dye should possess include; a wide absorption spectrum, good interfacial and stability properties. Small band gap materials are used as dye for DSSC since absorption of photons' energy cannot occur if it's smaller than the material's band gap energy. DSSC dyes can either be organic or inorganic in nature (Tvrđy, *et al.*, 2011).

3.5.4 Inorganic/Synthetic Dyes

Ruthenium (II) polypyridyl complexes are usually used in the DSSC because they have good redox properties, wide absorption spectrum as well as good stability (Kalyanasundaram and Grätzel, 1998; Kong *et al.*, 2007). Red dye (N3) and Osmium polypyridyl complexes are some of the effective photosensitizers (Vail *et al.*, 2015; Figure 3.5).

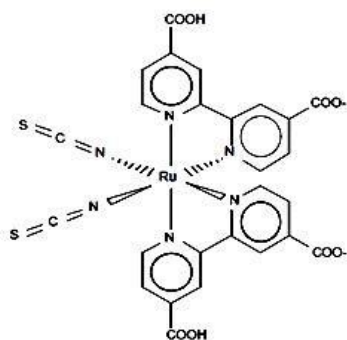


Figure 3. 5 N3 ruthenium complex structure (Grätzel, 2003)

copper (II) co-protoporphyrin-I, coumarin, phthalocyanines, co-protoporphyrin-I and indoline are other components used as sensitizers (Alibabaei *et al.*, 2010; Giribabu *et*

al., 2007; Hara *et al.*, 2003; Chen *et al.*, 2010). Ruthenium (II) polypyridyl complexes have numerous drawbacks e.g. inaccessibility, manufacturer complexity thus high cost of production. It is also a heavy metal thus not eco-friendly (Wongcharee *et al.*, 2007).

3.5.5 Natural Dyes

Natural dyes are considered a great option to inorganic dyes as they are economical for fabrication of the DSSC. This is because they are cheaper, readily available, and also environmentally friendly, non-toxic and biodegradable. Extraction of natural dyes is done using simple methodologies and its usage has no purifications (Fernando and Senadeera, 2008).

3.5.5.1 Chlorophyll

Chlorophyll is a pigment that gives plants their green color. The use of chlorophyll for fabrication of DSSC is due to the alkyl group in the structure of chlorophyll (Arof and Ping, 2017; Kumara *et al.*, 2017). Its weakness is due to the ester keto and carbonyl functional groups which don't tally well to TiO_2 (Calogero *et al.*, 2009).

Figure 3.6 shows spinach leaves from which chlorophyll molecules are extracted;



Figure 3. 6: Spinach leaves; the green pigmentation is caused by the organic dye chlorophyll

The structure of chlorophyll is as shown in Figure 3.7

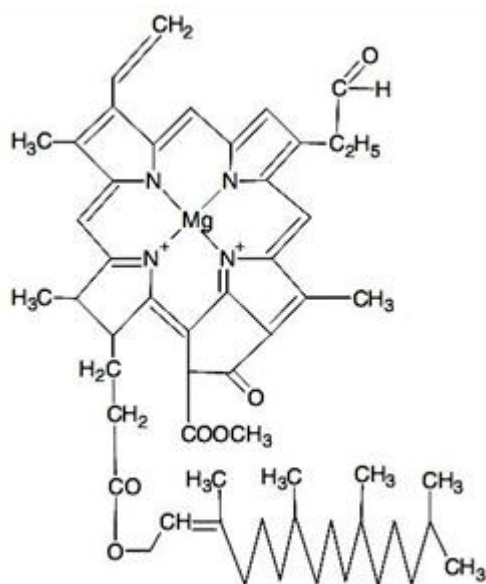


Figure 3. 7: The organic structure of chlorophyll molecule (Hao *et al.*, 2006)

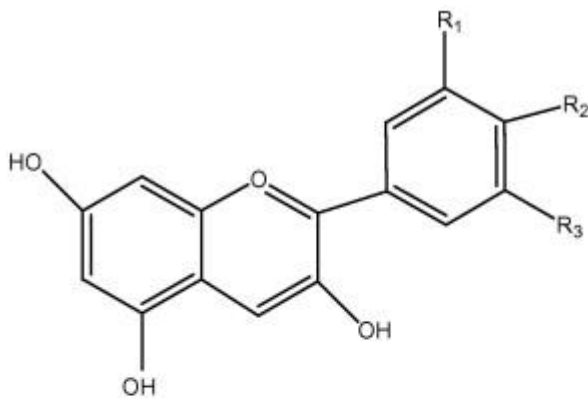
3.5.5.2 Anthocyanins

Anthocyanins are the natural plant pigments that give the red, blue and purple colors to fruits, flowers, leaves, and some vegetables (Lila *et al*, 2016). The anthocyanins structure comprise of carbonyl and hydroxyl functional groups binding to the photo electrode boosting dye sensitizers (Wongcharee *et al.*, 2007). Anthocyanins display red to blue colors in the visible region after interacting with metal ions (Cherepy *et al.*, 1997). Blueberries have one of the highest antioxidant levels of all berry fruits (Castrejón *et al.*, 2008). Figure 3.8 shows a blueberry fruit. Blueberry fruit is a good example of a plant part where anthocyanin molecule can be extracted.



Figure 3. 8: Blueberry fruit. The deep purple color is caused by anthocyanin molecule (www.wholesomekitchen.com).

The structures of anthocyanin pigments from blueberry are depicted in Figure 3.9 below;



Anthocyanidin	R ₁	R ₂	R ₃
Cyanidin	OH	OH	H
Delphinidin	OH	OH	OH
Malvidin	OCH ₃	OH	OCH ₃
Pelargonidin	H	OH	H
Peonidin	OCH ₃	OH	H
Petunidin	OCH ₃	OH	OH

Figure 3.9: Anthocyanin common structure in blueberry (Lohachoopol *et al.*, 2008)

3.5.6 Electrolyte

This is a chemical compound that releases ions capable of transporting electric charges. Its purpose is donating electrons to oxidized sensitizer thus preventing the

recapturing of excited electrons (Sreekala *et al.*, 2012). The most commonly used electrolyte is liquid iodide/tri-iodide redox mixed with organic solvents. Properties of a good electrolyte should meet requirements such as: compatibility with the dye, the redox potential and the dye regeneration. High conductivity is desired and preferred to ensure fast charge transfer, excellent interfacial properties for both photo- and counter electrodes, and good stability (Wu *et al.*, 2008)

3.6 I-V Characteristics of TiO₂ DSSCs

DSSC performance is assessed based on the following parameters:

3.6.1 Open circuit photo-voltage (V_{oc})

Cell voltage taken when current within the cell is equal to zero (Malekshahi Byranvand *et al.*, 2012)

3.6.2 Short circuit photocurrent (I_{sc})

Photo-cell current measured at zero voltage usually expressed as short circuit current density (J_{sc}) which is the ratio of the short circuit photocurrent to the active cell area (Malekshahi Byranvand *et al.*, 2012).

3.6.3 Fill factor (FF)

Maximum power output (P_m) to the product of short circuit photocurrent (I_{sc}) ratio and open circuit photo-voltage (V_{oc}) (Malekshahi Byranvand *et al.*, 2012);

$$FF = \frac{P_m}{I_{sc} \cdot V_{oc}} = \frac{I_m \cdot V_m}{I_{sc} \cdot V_{oc}} \quad (3.2)$$

Where;

I_m and V_m stands for photocurrent and photo-voltage corresponding to the maximum power point, respectively.

A number of interacting parameters influences the fill factor (FF) making it difficult to understand how the FF works.

3.6.4 Energy conversion efficiency

According to Malekshahi Byranvand *et al.* (2012), DSSC conversion efficiency (η) is the ratio of Maximum Power output (P_m) to the incident radiation power (P_{in}) on the solar cell surface. Energy efficiency is produced by the reduction of I^3 with electrons in the electrode circuit as shown by the equation.

$$\eta = \frac{P_m}{P_{in}} = \frac{I_{sc} \cdot V_{oc} \cdot FF}{P_{in}} \quad (3.3)$$

Where;

H is a function of I_{sc} , V_{oc}

FF , enhancement of the DSSC performance is attained by maximization of the three parameters. H greatly rely on the incident irradiation energy and its absorption spectrum, both of which must be correctly defined when η is mentioned.

CHAPTER FOUR

MATERIALS AND METHODS

4.1 Introduction

This chapter outlines the methods used to attain the study results which are; cleaning of apparatus, dye extraction, preparation of organic dyes, sensitization of TiO₂ thin film, Optical characterization of TiO₂ thin film, counter electrode preparation, solar cell assembly and solar cell characterization.

4.2 Cleaning of the apparatus to be used

Fluorine doped Tin oxide (FTO) slides, plastic and glass beakers were used in the experiments. Prior to using these apparatus, they were cleaned using the power sonic 405 ultrasonic bath. The apparatus were ultrasonically cleaned in acetone for 15 minutes, then in alcohol for another 15 minutes, then in distilled water for 15 minutes before being dried under standard room temperature and pressure conditions.

The FTO slides are utilized for the deposition of the TiO₂ layer and the counter electrode, the beakers were used to hold the dyes during sensitisation and the bottles were used to store the dye during the extraction until it was used.

4.3 Titanium dioxide layer preparation

Screen printing method as described by Yu (2011) was used in the deposition of TiO₂-layer. The form of titanium dioxide deposited was the naturally occurring anatase.

4.3.1 Preparation of TiO₂ screen printing paste.

The TiO₂ screen printing paste used in this study was sourced from Solaronics SA Company of Switzerland.

4.3.2 Deposition of the TiO₂ layer using screen printing

The printing cycle followed the described 3 steps method; 1. Deposition of the TiO₂-paste on the FTO-glass substrate, 2. Incubation of the deposited paste at room temperature for 5 mins to reduce the mechanical tension within the layer, 3. Drying of the prepared TiO₂ film at 120°C for 10 mins to eradicate the volatile components of the paste.

The prepared dry TiO₂-layers was then subjected to high heating to dry the organic components of the TiO₂-paste and to increase the mechanical contact of the nanoporous TiO₂ particles. To prevent breaking of the glass substrate, heating was started at 200°C and slowly increased in steps of 50 °C after every 10 minutes to a maximum of 450 °C having in mind that phase transition from anatase to the thermodynamically more stable rutile starts at the temperature of 550 °C. Cooling of the electrode was again done by slowly reducing the temperature to reduce the tension within the glass substrate. At 80 °C the TiO₂ electrode was then immersed in the respective dyes. The overall screen-printing process is as depicted in the figure 4.1.

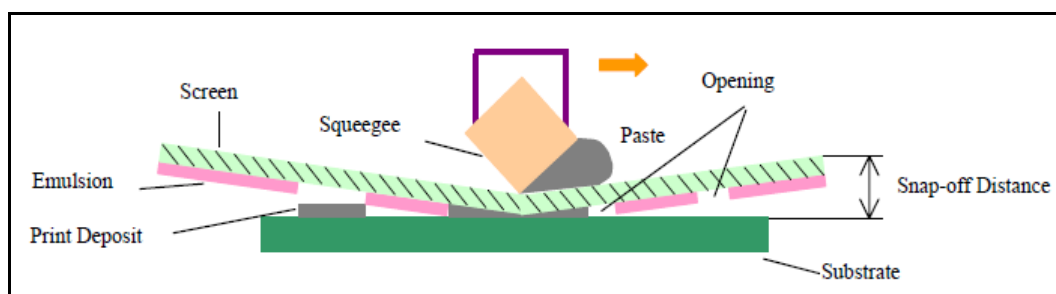


Figure 4.1: A schematic diagram of the screen printing process (Souk up *et al*, 2012)

4.3 Dye extraction

To produce the dyes, fresh blueberry fruits were blended in a mortar, the concentrated blue berry juice produced was then filtered and placed in a clean bottle

and labelled concentrated blueberry dye. For the Spinach dyes the spinach leaves were first sorted and cleaned, some spinach leaves with the stalk were blended in a blender. The juice extracted from these leaves was then filtered and placed in another clean bottle that was labelled Spinach A (with stalk). For other spinach leaves, the stalks were removed and the leaves were then crushed without the stalk and the juice extracted from these leaves was filtered and placed in another clean bottle that was labelled spinach B (without stalk). The ruthenium dye was obtained from the University of Nairobi which had purchased it from Solaronics SA Company, Switzerland.

4.4 Preparation of the organic dyes

The extracted dyes were then segregated into different portions and mixtures. To get the concentrated samples 5 ml of the concentrated dye was measured and placed in a beaker. This was done for all the three extracted dyes (blue berry dye, Spinach A dye and Spinach B dye). To get the 0.5ml diluted dyes another 5ml was then poured from the concentrated dye bottles into another set of beakers and 0.5 ml distilled water added to these beakers. Then to get the 1 ml diluted dyes another 5ml was measured and put into another set of beakers, to this distilled water (1 ml) was added. Finally, to prepare the mixed dye sample 2.5 ml of the spinach A was added to 2.5ml of blue berry dye were mixed to get the spinach A mixed with blue berry dye. The same was repeated for the spinach B and blue berries dye. Ruthenium dye was also used to sensitise some of the samples. It's important to note that some of the samples were not sensitised so as to act as controls in the study.

4.5 Sensitization of the titanium dioxide electrode

Sensitization was done by plunging the TiO₂ films in the different dye solutions once they attained the 80°C on cooling to ensure maximum absorption of the dye to the

TiO₂ semiconductor. The sensitization was done overnight for 24 hours. This was followed by rinsing with distilled water and isopropanol, respectively. Once dry, all the films (sensitized and unsensitized) were then stored in diluted acetic acid (pH 4) under dark condition so as to prevent oxidation as a result of exposure to air and light which make them lose their photosensitivity.

4.6 Optical characterization of TiO₂ thin films

The optical properties of the prepared TiO₂ films were determined by taking their film thickness and reflectance by use of a spectrophotometer (Shimadzu model type DUV3700) at wavelength range 300 nm –800 nm. SCOUT software (Lance, 2018) was utilized in determining the thickness, energy band gap, refractive indices, absorption co-efficient and extinction co-efficient of TiO₂.

The measurement of transmittance was done by directing the a beam of photons of intensity (I_0) and wavelength λ through the thin film sample and the transmittance read by a detector and recorded in the spectrometer with the aid of the UV probe 2.31 software (Figure 4.2).

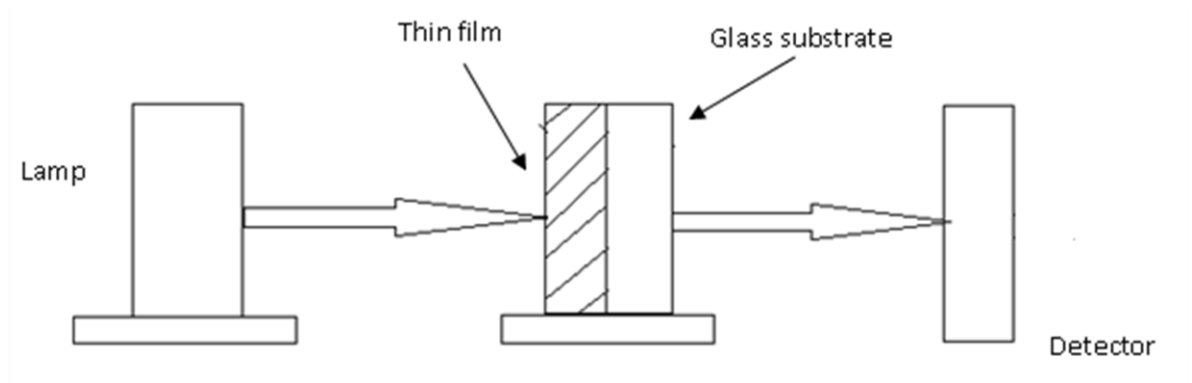


Figure 4. 2: A representation diagram for optical transmission measurements

To accurately calculate band gap energy, transmittance with less energy photons is required. Energy band gap was determined by absorption coefficient values from the equation (4.1):

$$hv\alpha = A(hv - E_g)^n \quad (4.1)$$

where

E_g represents the band gap of the material,

h represents the Planck's constant (6.626×10^{-34} Js),

ν represents the frequency of light,

n represents an exponent with its value depending on the type of transition involved,

α represents the absorption coefficient

A represents a constant defined as the edge width parameter.

The absorption intensity depends on a number of factors which include; the wavelength of light, and film properties. Photons intensity I_t , transmitted through the film thickness l , is given by equation 4.2.

$$I_t = I_0 e^{-\alpha l} \quad (4.2)$$

Where α is the absorption coefficient and was calculated using equation 4.3

$$\alpha = \frac{4\pi k}{\lambda} \quad (4.3)$$

4.7 Counter electrode preparation

The counter electrode was set by drilling and cleaning a small hole in the FTO glass slide. The conducting side of FTO glass was coated with a carbon film using a HB pencil rod.

4.8 Solar cell assembly

The HB pencil rod coated slide was vertically erected on the dye sensitized TiO₂ photo-electrode and held firmly using binder clips and liquid electrolyte (2 drops) were added to the cell.

The DSSC was then sealed using microscope cover slips to prevent the electrolyte from drying and pouring during the I-V measurements. The negative terminal was attached to the TiO₂ coated slide while the positive terminal of the Kiethley Multi-meter attached to the graphite coated slide.

4.9 I-V Solar cell characterization

Measurements were taken using the lab view interfaced with the kiethley meter to determine the dark I-V properties of the DSSC cells. The I-V light characteristics were also measured with the monochromatic light switched on in the I-V set up under standard illumination conditions (AM 1.5). From the I-V characteristics curve the short-circuit current (I_{sc}), open circuit voltage (V_{oc}), maximum current I_{max} and maximum voltage V_{max} were obtained. The performance of the solar cells was then evaluated by computing the fill factor and the efficiency. Fill factor (FF) is a measure of the diode behaviour of the cell and is expressed as shown in equation 4.4 (Zhao *et al.*, 1999).

$$FF = \frac{V_{max} I_{max}}{V_{oc} I_{sc}} \quad (4.4)$$

Global electricity power conversion efficiency was compared with electricity conversion efficiency (η) of a cell with P_{out} electrical power under standard as described by Zhao *et al.* (1999). This was used to determine the best DSSC basing on the dye type.

$$\eta = \frac{V_{max} I_{max}}{P_{in}} = \frac{V_{oc} I_{sc} FF}{P_{in}} \quad (4.5)$$

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 Introduction

This chapter discusses the study results which include reflectance, absorbance and transmittance. It also highlights the I-V characteristics of the prepared dye sensitised solar cell which include open circuit voltage (V_{oc}), short circuit current (I_{sc}), maximum current output (I_m), maximum voltage output (V_m), fill factor (FF) and conversion efficiency (η) of various fabricated solar cells.

5.2 Optical characteristics of un-sensitized and sensitized titanium dioxide thin films

5.2.1 Reflectance

Reflectance is the fraction of incident electromagnetic power that is reflected at an interface. Figure 5.1 shows the measured spectra for reflectance against incident photons of wavelengths in the range 300-800nm for the un-sensitized and sensitized TiO_2 films.

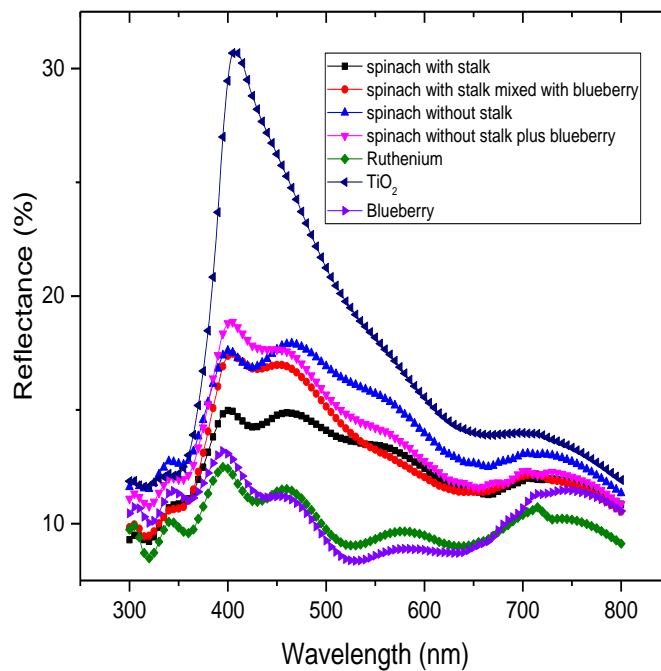


Figure 5.1: Reflectance versus wavelength for sensitized and non-sensitized titanium dioxide film

From figure 5.1, it was observed that all the sensitized films had lower reflectance compared to the un-sensitized TiO₂ films. The reflectance of all the sensitized films decreased compared with the reflectance of the un-sensitized TiO₂ films in the wavelength range between 400nm- 800nm. The reflectance was less than 20% in the visible light region (380nm-750nm) for all sensitized films. Among the organic dyes the film sensitized with blue berry had the least reflectance and compares well with the film sensitized with ruthenium.

The reflectance of spinach dye with stalk mixed with blue berry dye appear second after unsensitised titanium oxide followed by spinach dye without stalk and spinach dye with stalk mixed with blueberry dye. Light energy that is not absorbed or transmitted is reflected at the interface of the thin film. The suppressed reflectance due to sensitization implies that the absorption of the photons is enhanced resulting in a better TiO₂ film for solar cell applications. Blueberry sensitized dye had the lowest reflectance because it contains a lot of anthocyanin which absorbs most of the light energy (Hamid *et al.*, 2018).

5.2.2 Transmittance

Transmittance is described as the part of the incident light occurring at a specific wavelength that passes through the sample. Optical transmittance is a very important parameter to check on photovoltaic (PV) coating materials (Miller *et al.*, 2013). Figure 5.2 shows transmittance of the different TiO₂ samples sensitized with different dyes at wavelengths 300nm-800nm.

For all the samples sensitized and unsensitised transmittance was low between the 300nm-450nm. Transmittance for TiO₂ films sensitized with spinach without stalk dye mixed with blue berry dye, spinach with stalk dye, spinach with stalk plus blueberry dye, spinach without stalk dye, and unsensitised TiO₂ increased between

the 450 nm to 700 nm. The transmittance of blueberry and ruthenium sensitized TiO₂ thin films increased between 550 nm to 700 nm.

The results showed TiO₂ film sensitized with spinach without stalk mixed with blueberry dye had the highest transmittance while TiO₂ sensitized with blue berry alone had the lowest transmittance followed by unsensitised TiO₂ (Figure 5.2).

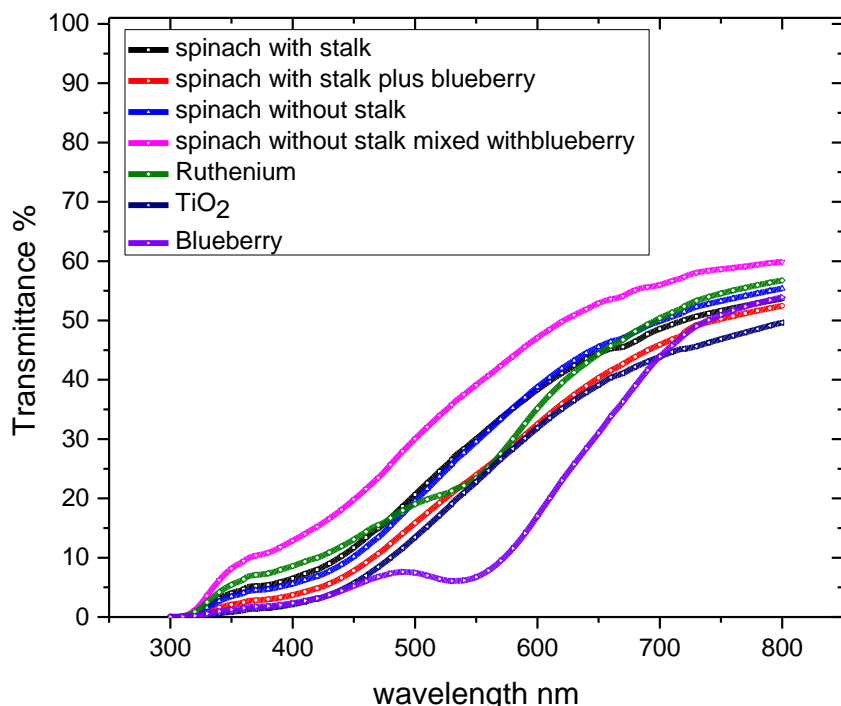


Figure 5. 2: Transmittance against wavelength of different TiO₂ samples sensitized with different dyes

Dye sensitisation of TiO₂ thin films had no effect on the transmittance beyond the visible light region for all the samples. In general, dye sensitisation of the TiO₂ film produced an increase in transmittance between the 300-800 nm wavelength range which is in agreement with the finding by Grätzel, (2003) and Wang *et al.* (2011).

5.2.3 Dye Absorbance Properties

5.2.3.1 Concentrated Dye Absorbance Spectra

The absorption spectra for the different dye types was calculated using equation 5.3

$$(A = 1 - (T + R)) \quad 5.3$$

where;

A- absorbance,

T – transmittance

R- reflectance of the dye used.

The resulting absorbance spectra are shown in figure 5.3 below:

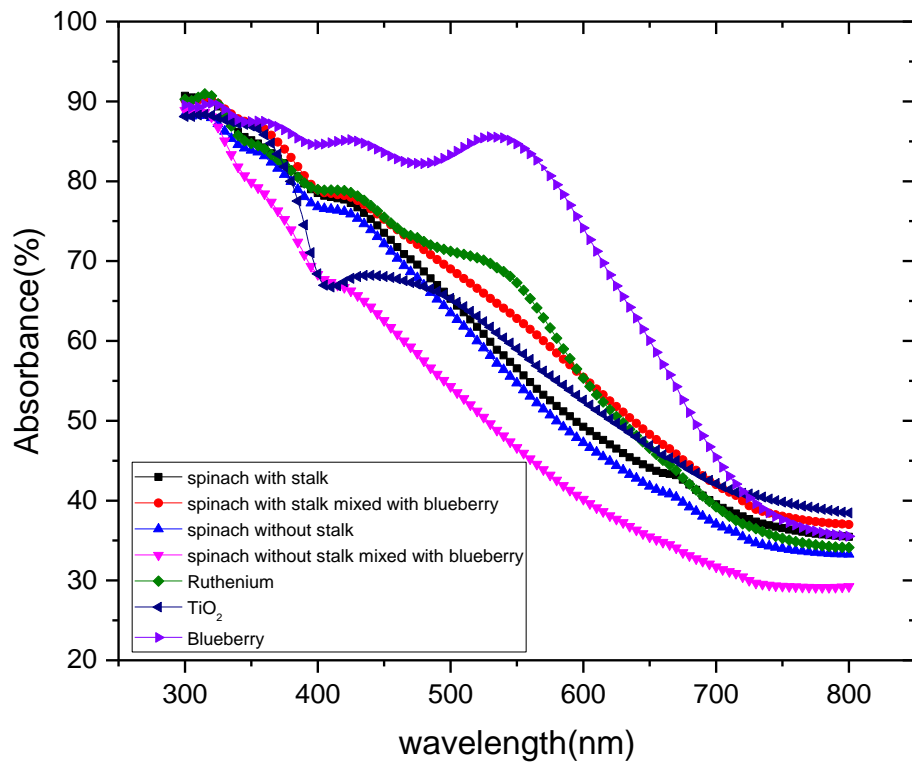


Figure 5.3: Absorbance against wavelength for sensitized and non sensitized TiO_2 films.

From the study results as shown in figure 5.3, the absorbance of all the samples both the sensitized and un-sensitized were high between the 300nm -350 nm wavelengths. The absorbance of blue berry dye sensitized TiO_2 substrate was the highest between 300nm-600 nm where it started decreasing before stabilizing. Ruthenium dye

sensitized TiO₂ thin film was second with absorbance percentage after blueberry dye sensitized TiO₂.

TiO₂ films sensitized with spinach without stalk mixed with blueberry dye had the lowest absorbance percentage while TiO₂ films sensitized with spinach with stalk mixed with blueberry dye, spinach without stalk dye, spinach with stalk dye and un-sensitized TiO₂ were intermediates. For all the samples, absorbance stabilized beyond the visible light ranged (750 nm of wavelength).

The high absorption of blue berry dye sensitized TiO₂ thin film is attributed to its high anthocyanin pigments concentration which comprise of a carbonyl (C=O) and a hydroxyl group (OH) attaching the dye to TiO₂ surface and stabilizing of the excited electrons thus resulting maximizing absorption by having low energy (Hamid *et al.*, 2018). The low absorption percentage of TiO₂ films sensitized with spinach without stalk mixed with blueberry dye was because the chlorophyll pigment in spinach dye has high transmittance and reflectance between the 300-650 nm wavelength thus low absorbance (Chang *et al.*, 2010; Syafinar *et al.*, 2015). The study results concur with the findings by Thiyagu *et al.* (2012) that sensitizing dye reflectance is directly proportional to its transmittance and inversely proportional to absorbance. From the results, blue berry dye sensitized TiO₂ thin film had the lowest reflectance, transmittance and high absorbance compared to all other sensitized and un-sensitized TiO₂ films. On the other hand, TiO₂ films sensitized with spinach without stalk mixed with blueberry dye which had the highest reflectance and transmittance and the lowest absorbance.

5.2.4 Influence of Organic Dye Dilution on the Transmittance and Reflectance of TiO₂ films

5.2.4.1 Transmittance and reflectance of TiO₂ films sensitized with blueberries

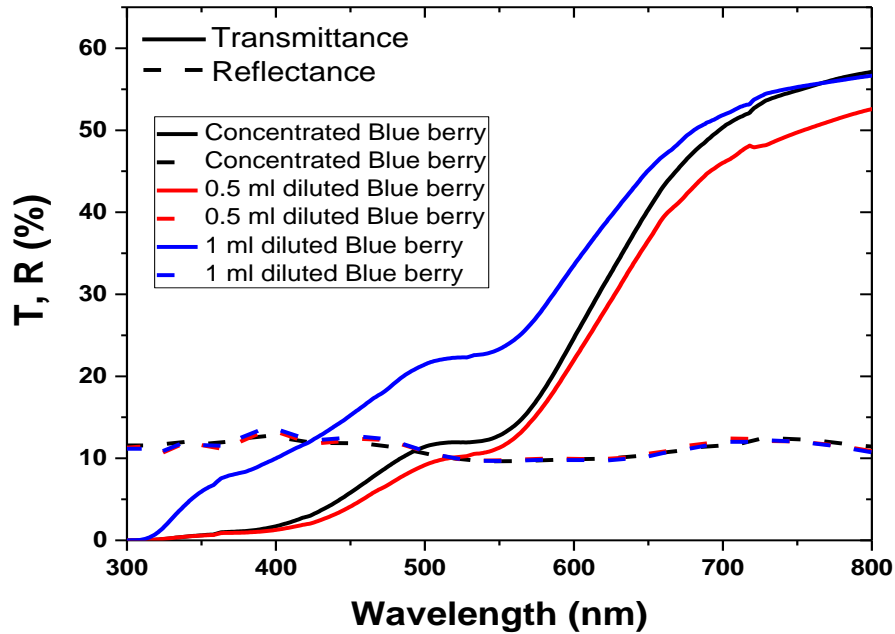


Figure 5.4: Transmittance and reflectance against wavelength of diluted blue berry dye sensitised samples

From figure 5.4, it is noted that when the concentrated blue berry dye was diluted with 0.5 ml of distilled water the film stained with this dye showed the least transmittance, while dilution of the dye with 1 ml increased transmittance by a slight shift of the transmittance curve towards the left (shorter wavelength region) in the visible range. Dilution did not affect transmittance beyond the visible light region towards the infrared region. It is also noted from figure 5.4 that diluting the dye solution did not have any notable influence on the reflectance of the samples in the entire wavelength range. The result was in line with the Beer-Lambert's Law which states that beam light intensity reduces as it passes through an absorbing medium. It also states that lowering of the absorbing species concentration by dilution decreases

absorbance and increases transmittance (Atherton, 1955; Elwell & Gidley *et al.*, 2013)

5.2.4.2 Transmittance and reflectance of TiO₂ films sensitized with spinach with stalk

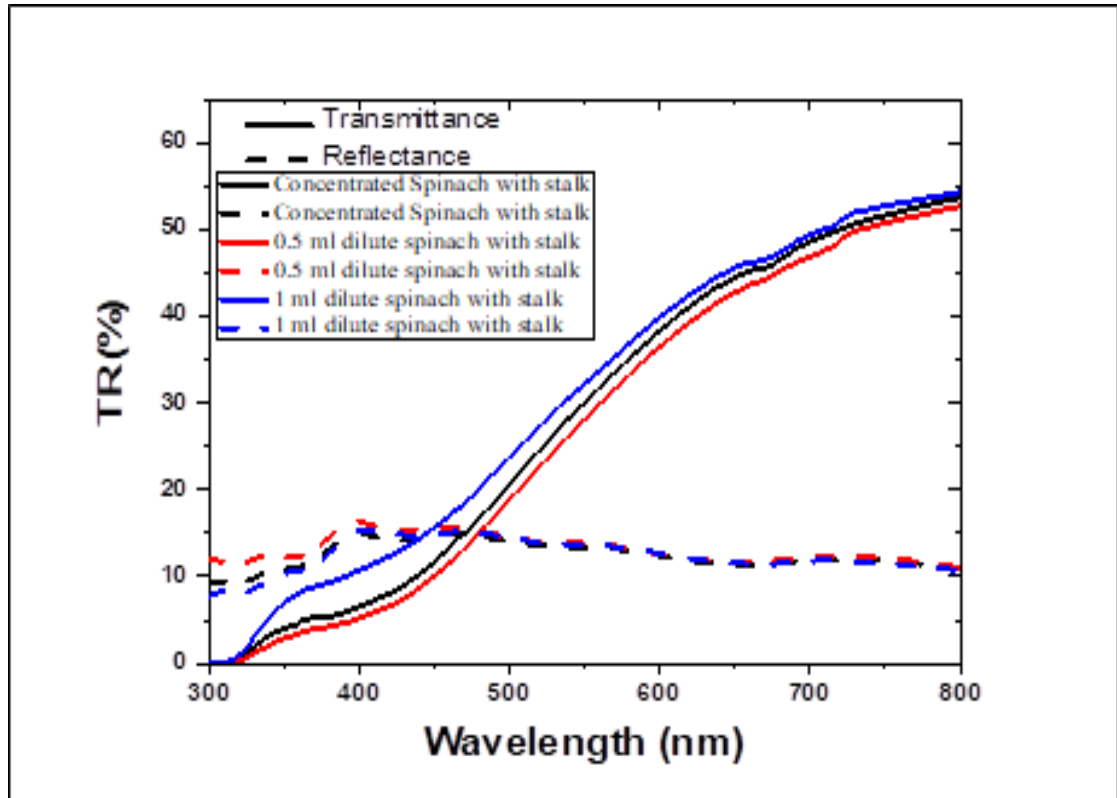


Figure 5.5: Transmittance and reflectance against wavelength of diluted Spinach with stalk dye sensitized samples

Dilution of spinach with stalk dye with 0.5 ml of distilled water led to a slight decrease in transmittance when compared with the undiluted dye. Dilution of the same dye with 1 ml of distilled water led to slight increase in its transmittance when compared with the undiluted dye (Figure 5.5)

Both dilutions didn't have any significant effect on the reflectance of the dye when compared with that of the undiluted dye (Figure 5.5). The un-changed transmittance and reflectance in the experiment may be attributed to the fact that the stalk is composed of over 90 % water due to the large amount of the xylem cells which are

associated with water uptake in the plant, thus an addition of 1ml of distilled water will not produce a significant difference in the transmittance and reflectance curves of both the concentrated and diluted samples of the spinach with stalk dye

5.2.4.3 Transmittance and reflectance of TiO₂ films sensitized with spinach without stalk.

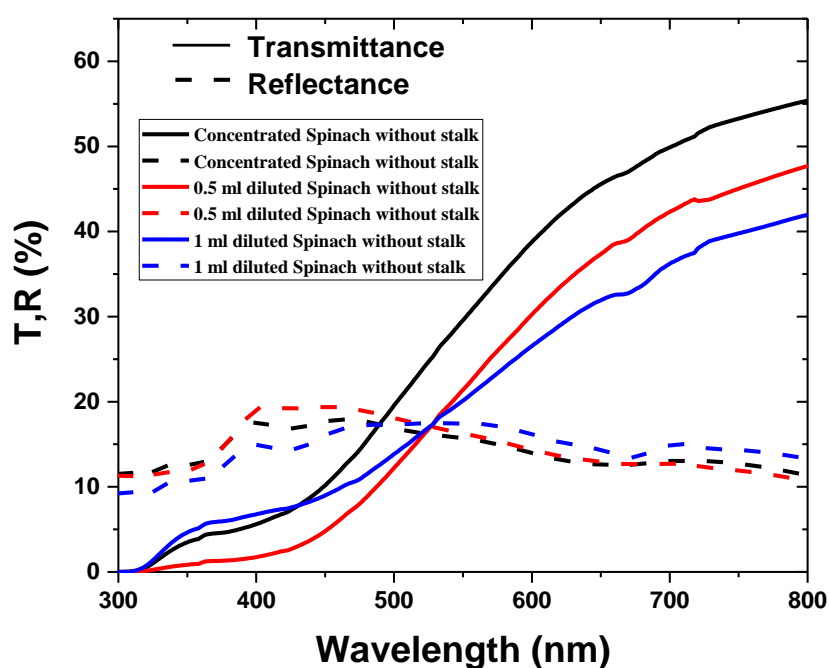


Figure 5. 6: Transmittance and reflectance against wavelength of diluted Spinach without stalk dye sensitised samples

As shown in figure 5.6, dilution of the spinach without stalk dye by 0.5 ml and 1 ml of distilled water led to reduction in the transmittance of the dye when used to sensitize a TiO₂ thin film. Thus the effect of dilution is seen prominently as the transmittance reduces with the addition of distilled water.

There was no significant difference on the reflectance of the samples sensitized with the diluted dyes and the undiluted dye meaning dilution by 0.5 and 1ml of water does not affect reflectance. The decrease in transmittance and reflectance could be

attributed to the fact that water serves as an electrolyte enhancing absorption of the solar light rather than reflectance (Wang *et al.*, 2005).

5.2.5 Optical Band Gap

Optical band gap helps in determining the DSSC efficiency (Snaith, 2010). The optical properties of organic dyes from (Spinach with stalk, spinach without stalk and blueberry), ruthenium and TiO₂ were checked under Fourier transform infrared (FTIR) and UV spectroscopy to determine the efficiency properties. The organic dyes showed the ability to take in photons within the visible spectrum with spinach dyes ranging from 367.3 nm to 451.5 nm in wavelength while blueberry dye absorbed the photons at 400 nm. Spinach dyes had lowest energy band of 2.98 eV, followed by Blue berry dye at 3.10 eV which was slightly lower than those of TiO₂ and ruthenium, 3.20eV and 3.40 eV respectively. Spinach without stalk + blueberry had an optical band energy of 3.38 eV which was almost equal to that of Ruthenium which was 3.40 eV (Figure 5.7, Table 5.1). As reported by Hamid et al. (2018), dyes with the wider energy band have the highest efficiency in improving the DSSCs. The results indicated that organic dyes can be successfully be used in improving the efficiency of the dye-sensitized solar cells (DSSC) (Murphy, 2007).

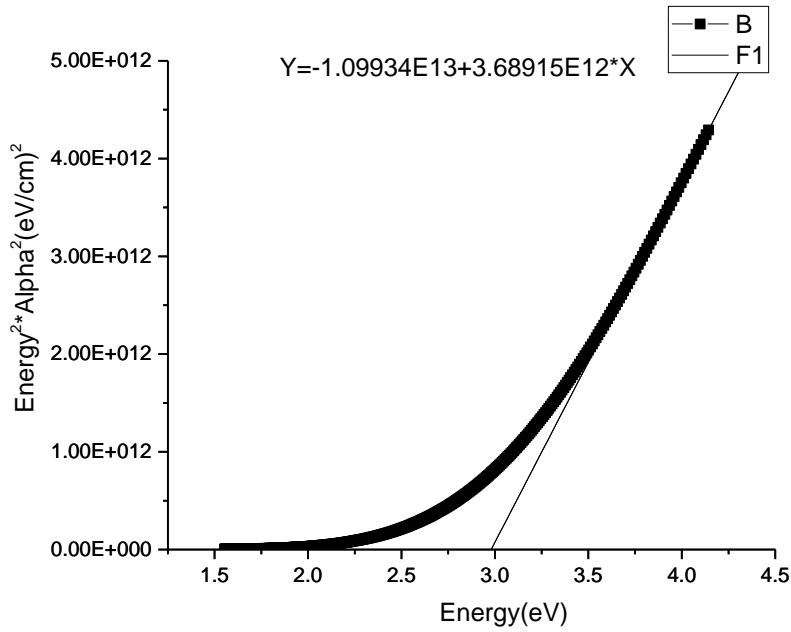


Figure 5. 7: optical band gap for spinach with stalk + blue berry

Table 5.1: Optical band energies for the organic and inorganic dyes

	Spinach with stalk +Blue berry	Spinach with stalk	Spinach without stalk	Spinach without stalk +Blue berry	Ruthenium	TiO2	Blueberry
Bandgap(eV)	2.98	3.30	2.75	3.38	3.40	3.20	3.10
Wavelength(nm)	416.6	376.2	451.5	367.3	365.2	388.0	400.5

5.3 I-V Characterization of the DSSC solar cells

5.3.1 Influence of Dye Sensitisation on the IV characteristics

The I-V characteristics of the prepared dye sensitised solar cells were measured and the influence of organic dye sensitisation on the I-V characteristics is presented in figure 5.8.

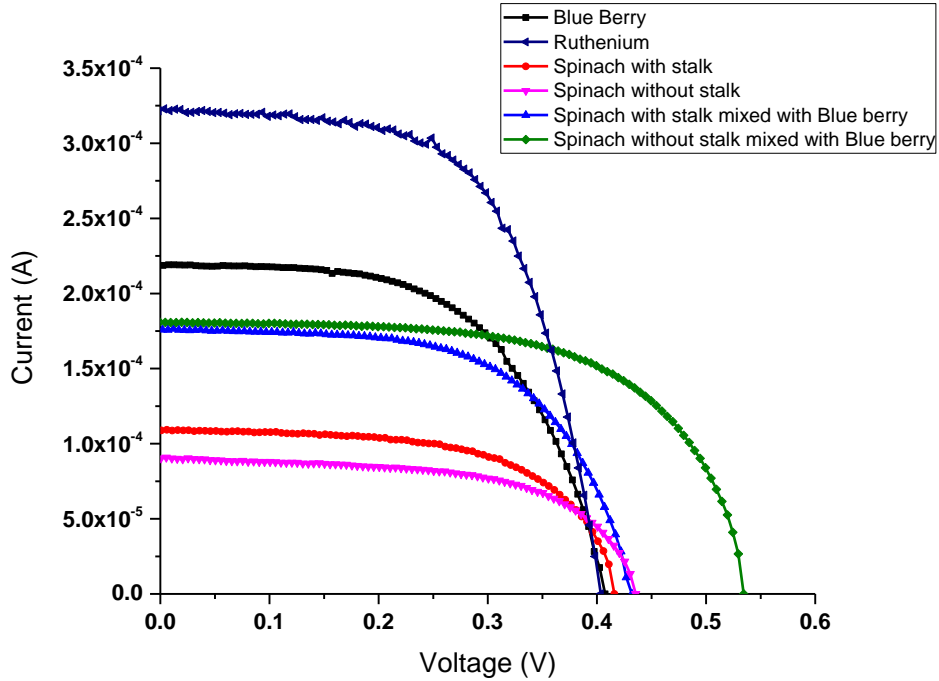


Figure 5. 8: Current against voltage of sensitized I-V characteristics of the DSSC cells

From figure 5.8, it's noticed that the best short circuit current of 0.322 mA was attained when using the Ruthenium dye, the open Circuit Voltage was 0.404 V and the cell had a fill factor of 0.614 and a cell efficiency of 1.992%. The blue berry dye sensitised solar cell had a short circuit current of 0.219 mA with the open circuit voltage of 0.408 V, a fill factor of 0.580 and efficiency of 1.295%. The Spinach with stalk dye sensitised solar cell had a short circuit of 0.109 mA, with an open circuit voltage of 0.416 V, a fill factor of 0.617 and efficiency of 0.698 %.The spinach without stalk dye sensitized solar cell had a short circuit of 0.090 mA, open circuit voltage being 0.436V and a fill factor of 0.605 and efficiency of 0.595%. The DSSC fabricated using spinach with stalk + blueberry mixture dye had a short circuit of 0.176 mA, with an open circuit voltage of 0.436 V, a fill factor of 0.604 and an efficiency of 1.148%. The spinach without stalk + blueberry mixture dye cell was

found to have a short circuit of 0.181 mA, open circuit voltage of 0.535 V, a fill factor of 0.628 and an efficiency of 1.517% (Table 5.2).

Table 5.2: Summary of the I-V characteristics of the different DSSCs

Dye employed	Voc(V)	Isc(mA)	Vmax	Imax (mA)	Fill factor	Efficiency (η) (%)
Ruthenium	0.404	0.322	0.299	0.267	0.614	1.992
Spinach without stalk+ blue berry	0.535	0.181	0.400	0.152	0.628	1.517
Blue berry	0.408	0.219	0.293	0.177	0.580	1.295
Spinach with stalk+ blue berry	0.432	0.176	0.307	0.150	0.604	1.148
Spinach with stalk	0.416	0.109	0.311	0.090	0.617	0.698
Spinach without stalk	0.436	0.090	0.331	0.072	0.605	0.595

From the results obtained in Table 5.2 and Figure 5.8 the DSSC made using Ruthenium dye has the highest solar conversion efficiency compared with cells employing other organic dyes used in this study. This concurs with other studies that ruthenium has higher efficiency conversion especially when used as a complex with other materials because of its stability (Qin and Peng, 2012). It is also noted that the cells produced using organic dyes with blue berry or blue berry complexes have higher conversion efficiency ranging between (1.15-1.5 %). This is attributed to the high anthocyanin in blue berry which has shown the ability to convert about 2.06 % of sunlight into electrical energy (Calogero *et al.*, 2012).

DSSC fabricated using organic dyes from spinach had poor conversion of the sun energy compared to other dyes used and this is attributed to fast degeneration of chlorophyll pigment resulting to high reflectance and transmittance resulting to poor absorption of the light energy (Steidle Neto *et al.*, 2017). The improved efficiency conversion in combined spinach dyes was as a result of increased absorption range of chlorophyll in spinach and anthocyanin in blueberry resulting to the seen high open circuit voltage (Pratiwi *et al.*, 2017 a, b).

5.3.2 Influence of Organic Dye Dilution on the I-V Characteristics

5.3.2.1 For Blue berries

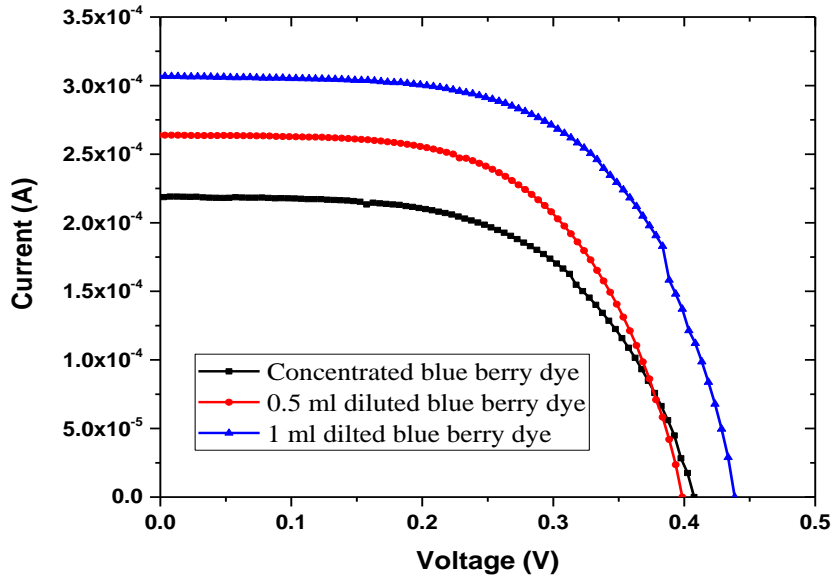


Figure 5. 9: Current against voltage for diluted blue berry dye on the I-V Characteristics

From figure 5.9 it's noticed that the best short circuit current of 0.307 mA was obtained when using the blue berry dye diluted with 1 ml of distilled water, with the cell's open circuit voltage of 0.439 V and the cell had a fill factor of 0.612 and a cell efficiency of 2.059% this was the best performing solar cell. The blue berry dye sensitised solar cell diluted with 0.5 ml of distilled water had a short circuit of 0.264 mA with the open circuit voltage of 0.399 V, a fill factor of 0.595 and efficiency of 1.564%. The concentrated blue berry dye sensitised solar cell had a Short circuit of 0.219 mA, with an open circuit voltage of 0.408 V, a fill factor of 0.580 and efficiency of 1.295%. The summary of the IV characteristics for the dilution of the concentrated blue berry dye is shown in table 5.3;

Table 5.3: Summary of the effect of Blue berry Dye Dilution on the I-V Characteristics

Dye Dilution	Voc(v)	Isc(mA)	Vmax (V)	Imax (mA)	Fill Factor	Efficiency (η) (%)
Concentrated blue berry	0.408	0.219	0.293	0.177	0.580	1.295
0.5 ml diluted blue berry	0.399	0.264	0.284	0.221	0.595	1.564
1 ml diluted blue berry	0.439	0.307	0.324	0.255	0.612	2.059

5.3.2.2 For Spinach with Stalk.

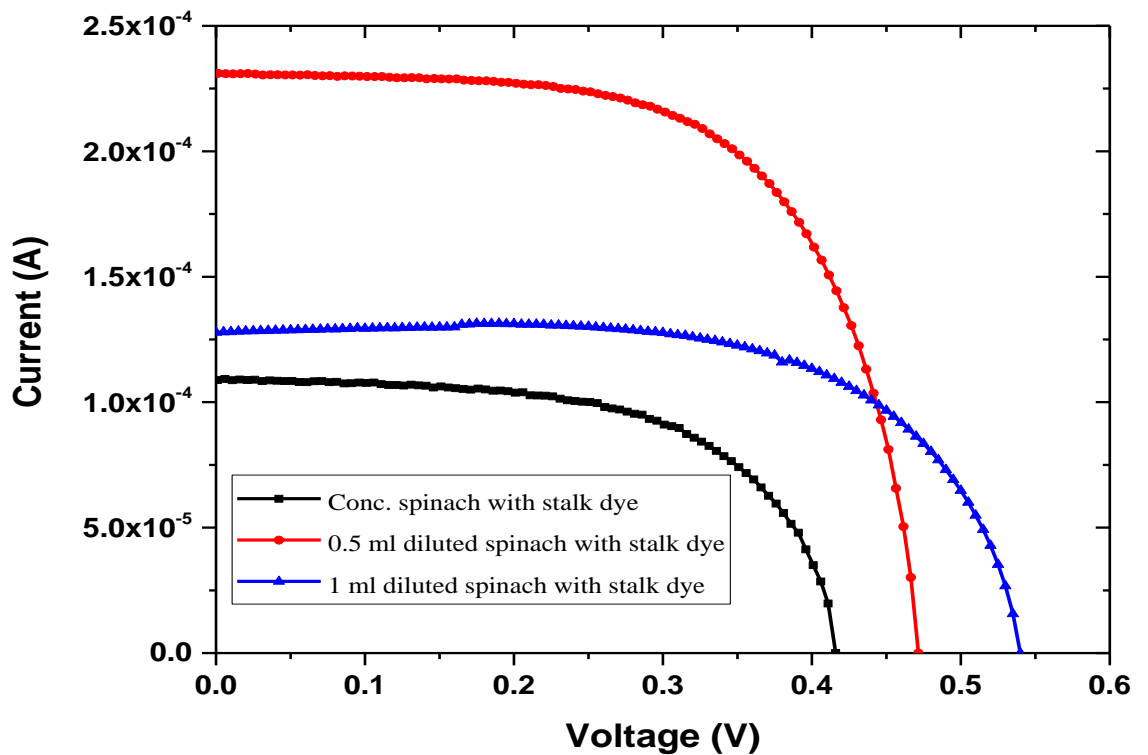


Figure 5. 10: Current against voltage of diluted spinach with stalk Dye on the I-V Characteristics

From figure 5.10, it's noticed that the best short circuit current of 0.231 mA was obtained when using the Spinach with stalk dye diluted with 0.5 ml of distilled water, its open circuit voltage was 0.472 V and the cell had a fill factor of 0.642 and a cell efficiency of 1.747%. The spinach with stalk dye sensitised solar cell diluted with 1

ml of distilled water had a short circuit current of 0.128 mA with the open circuit voltage of 0.540 V, a fill factor of 0.6580 and efficiency of 1.136% when diluted with 0.5ml of distilled water. The concentrated spinach with stalk dye sensitised solar cell had a short circuit current of 0.109 mA, with an open circuit voltage of 0.416 V, a fill factor of 0.617 and efficiency of 0.698%. The summary of the IV characteristics for the dilution of the concentrated spinach with stalk dye is shown in Table 5.4.

Table 5.4: Summary of the DSSC I-V Characteristics on effect of spinach with stalk dye dilution.

Dye	Voc(V)	Isc (mA)	Vmax (V)	Imax (mA)	Fill Factor	Efficiency (η) (%)
Concentrated Spinach with stalk	0.416	0.109	0.311	0.090	0.617	0.698
0.5 ml diluted spinach with stalk	0.472	0.231	0.357	0.196	0.642	1.747
1 ml diluted spinach with stalk	0.540	0.128	0.410	0.111	0.658	1.136

5.3.2.3 For Spinach without stalk dye

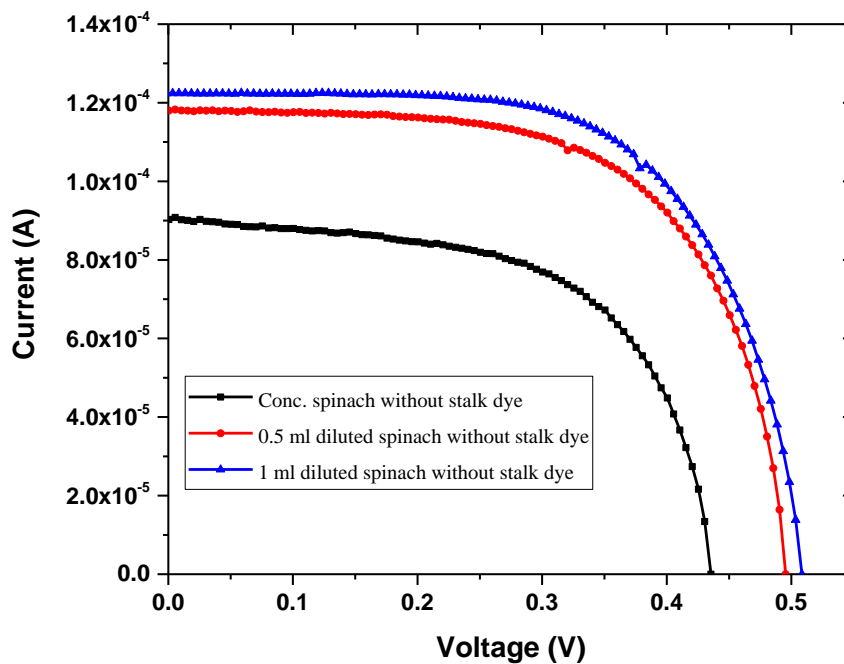


Figure 5. 11: Current against voltage of diluted spinach without stalk dye on the I-V characteristics

From figure 5.11 it's seen that the best short circuit current of 0.122 mA was obtained when using the Spinach without stalk dye diluted with 1 ml of distilled water, with an open circuit voltage of 0.509 V and the cell had a fill factor of 0.642 and a cell efficiency of 0.999%. The spinach without stalk dye sensitised solar cell diluted with 0.5 ml of distilled water had a short circuit of 0.118 mA with the open circuit voltage of 0.496 V, a fill factor of 0.639 and efficiency of 0.934%. The concentrated spinach without stalk dye sensitised solar cell had a short circuit of 0.090 mA, with an open circuit voltage of 0.436 V, a fill factor of 0.605 and efficiency of 0.595%.

Table 5.5: Summary of the DSSC I-V Characteristics on Effect of spinach without stalk Dye Dilution.

Dye	V_{oc} (V)	I_{sc} (mA)	V_{max} (V)	I_{max} (mA)	Fill Factor	Efficiency (η) (%)
Concentrated Spinach without stalk	0.436	0.090	0.331	0.072	0.605	0.595
0.5 ml diluted Spinach without stalk	0.496	0.118	0.376	0.099	0.639	0.934
1 ml diluted Spinach without stalk	0.509	0.122	0.384	0.104	0.642	0.999

Generally, dilution results of both the blue berry dye and spinach dyes, used for sensitization of TiO₂ improved the short circuit photo-current (I_{sc}), open circuit photovoltage (V_{oc}) and conversion efficiency (η) of the light energy from the sun. The improved efficiency on dilution is because the water serves as electrolyte to the dye ensuring efficient electron diffusion (Law *et al.*, 2010). Electrolyte also serves to reinstate the dye after the redox activity hence improving its longevity and conversion efficiency (Gu *et al.*, 2017). According to Cho *et al.* (2014), efficiency of the DSSC increases when the dye solution is diluted since there is an increase in the amount of dye absorbed by TiO₂ as well as enhance interaction between TiO₂ nanoparticles and the dyes extract which gives the DSSCs a better charge transfer performance. Conversion efficiency of spinach with stalk dye reduced with 1 ml dilution. This was attributed to the succulence of the stalk which is about 90% water

resulting in over dilution. This concurred with the study by Law *et al.* (2010) where over dilution of the electrolyte led to the reduced conversion efficiency of the dye.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

This research work aimed at determining the optical properties of dye sensitized TiO₂ thin films, fabrication and characterization of plant based TiO₂ DSSCs. The plant extracted dyes from blue berries and spinach were employed to sensitize TiO₂ thin films. The plant based dyes were classified into 5 groups blue berry dye, spinach without stalk dye, spinach with stalk dye, spinach without stalk mixed with blue berry and spinach with stalk mixed with blue berry. The performance of the DSSCs fabricated using the plant based dyes were compared to solar cells fabricated using ruthenium a commercial synthetic dye.

In terms of optical properties, TiO₂ film sensitized by blue berry dye had low reflectance, low transmittance and high absorption followed by ruthenium sensitized TiO₂ thin film. TiO₂ film sensitized with spinach dye mixed with blue berry dye had the highest reflectance, transmittance and the lowest absorbance. All the sensitized TiO₂ thin films had reflectance below 20% as compared to the unsensitized TiO₂ which had a reflectance above 30%.

As for solar cells I-V characteristics and energy conversion efficiency (η), ruthenium dye had the highest conversion of ~2% closely followed by blue berry dyes at ~1.5% and lastly spinach dye with the conversion efficiency of ~0.7%. Dilution of the dye with 1 ml of distilled water improved the conversion efficiency of the DSSC as compared to the 0.5 ml dilution and the undiluted dyes (1ml dilution, (η) Blue berry- 2.059%, (η) Spinach with stalk- 1.747%, (η) spinach without stalk-0.999%; 0.5ml

dilution, (η) Blue berry-1.564%, (η) Spinach with stalk- 1.136%, (η) spinach without stalk-0.934%).

This research results, depicted blue berry as a favourable substitute to the synthetic dyes used in the sensitization of the TiO₂ solar cells as compared to other plant based dyes. The dye exhibited better optical properties than other plant dyes in regard to solar cell applications. This is further confirmed by the resulting conversion efficiency of DSSC fabricated employing the said dye.

6.2 Recommendations for further studies

The following recommendations are deduced from the study:

- i. The concentration of the dyes was found to be a key parameter which affects the performance of DSSC and thus this study recommends that more work is required to optimize this parameter for optimal output.
- ii. The appropriate thickness of the active layer TiO₂ should be investigated to eliminate energy loss through transmission of photons.
- iii. There is also a need to investigate the use of dense electrolytes in DSSC as it was not tackled in this study.

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