

Fabrication and Optimization of Dye Sensitized Solar Cell Using *Carissa Carandas* Dye

M.S. THESIS



Institute of Energy
University of Dhaka

A thesis on

**Fabrication and Optimization of Dye
Sensitized Solar Cell Using Carissa Carandas
Dye**

A thesis is submitted to the Institute of Energy at the University of Dhaka in partial fulfillment of the requirements for the Degree of Masters of Science in Renewable Energy Technology

By

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Dedication

To my beloved parents Syed Kamrul Huda and Afroza Huda

And

All my respected Teachers

Declaration

It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma as per my knowledge.

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➤ Abstract

This study presents an approach on the development of DSSC and the photo-electrochemical effect with natural *Carissa Carandas* dye sensitized Titanium Dioxide anode. To find the optimal performance of the dye *Carissa Carandas* was soaked in different solvent for varying time and the optimum time to soak anode in dye is measured by soaking anode in the dye for varying time. The optimum condition was soaking *Carissa Carandas* in ethanol solvent for 48 hours and soaking Titanium Dioxide anode in dye for one hour. The light conversion efficiency of the Dye-sensitized solar cell reached 0.10271% with short circuit density .8566 mA/cm² ,open circuit voltage 478mV and a fill factor of .2546.The UV-visible absorption characteristics of natural dye solution were shown to absorb in visible region at $\lambda_{\max} = 535\text{nm}$.

1.0 Introduction

1.1 Prologue

This modern technologically advanced era runs by energy. From morning to night everything people need is operated by energy. Past day the supply of energy is coming from non-renewable sources like fuel, gas, coal which has limited supply. Nuclear energy which is a promising supply of vast amount of electricity has a very high risk potential. So researchers are working on finding sustainable sources that are safe and can mitigate this energy crisis. The Sun emits 3.8×10^{33} ergs/sec or 3.8×10^{26} watts of power, an amount of energy each second equal to 3.8×10^{26} joules. [1] Whereas the total energy demand of the earth is 12.3×10^{12} watts [2]. So if 50% of the energy produced by sun can be converted the world energy scarcity will be mitigated.

Photovoltaic cells, for generation of electricity, was initially developed in the early 20th century while commercially viable model made its appearance using silicon technology in the mid 20th century. The energy crisis of the 1970s brought about an increased interest in the technology to help try and mitigate energy crisis. Researchers dedicated their attention to bring in changes with the help of technology to the silicone industries of photovoltaic cells. With the microchip industry also rising demand for silicon increased making photovoltaic cells expensive, in achieving purity of silicon for production, compared to the efficiency obtained.

A second option to obtain electricity directly from solar energy is the organic solar cells which imitates the photosynthetic process for energy conversion. The ease of procuring while a low need for purity of the raw materials makes these cells affordable and largely demanding. The new class of organic solar cell developed by Michael Gratzel and Brian O'Regean in 1991 using titanium dioxide as comparatively inexpensive semiconductors and organic or synthetic dyes as synthesizers was another breakthrough. Although the commercial viability is still in question owing to the still low efficiency and a few other factors.

The beginning of the organic cells have been slow however there has been a significant increase in efficiency and durability in the lab. On the other hand silicon based cells has had an increase in cost because of the worldwide increase in the consumption of hyper-pure silicon. Soon organic solar cells can be expected to replace the silicon based solar cell industry owing to the cost issue.

In context of Bangladesh the energy demand is increasing with the development of industrialization. Being overly populated it is hard to find more places to establish power plants. Moreover the fuels required to run the power plants are mostly imported which is costly. But Bangladesh is blessed with very high solar radiation most of the time of the year. So installing solar cells is an easy solution of land scarcity and costly fuel supply. Moreover organic cells are easier to produce eco-friendly. While conventional silicone photovoltaic cells cause environmental hazard after dumping, Dye-sensitized solar cell is much more environment friendly as natural dye is used. The materials required to produce DSSC are easily available and viable in this country. So after proper development Dye-sensitized solar cell can play a vital role to meet the energy demand in Bangladesh.

➤ 1.2 Objectives of Study

This study focuses on finding the optimal condition to use *Carissa Carandas* dye in Dye Sensitized Solar Cell. This is done by varying the solvent and *Carissa Carandas* soaking time. The optimal time for soaking the anode is also obtained. So the objectives of this study are-

- Finding the best solvent to prepare *Carissa Carandas* dye that will give highest efficiency in DSSC
- Finding the best soaking time of *Carissa Carandas* in solvent
- Identifying optimal condition to soak anode in *Carissa Carandas* dye
- Fabrication of DSSC with the best *Carissa Carandas* dye and optimal anode soaking condition.
- Characterization of the prepared cell and dye.

1.3 Motivation of Thesis

Dye-sensitized solar cell (DSSC), known as a third generation solar cell may be the alternative of the conventional silicon solar cell. No silicon is needed in the manufacturing of DSSC. The DSSC is a device for the conversion of visible light into electricity. DSSC represents a cheap and clean technology that harnesses solar energy efficiently and have been intensively studied. How to further decrease the production cost and how to enhance device performance becomes the subject for large scale application and commercialization of DSSC.

DSSC being easy to fabricate can be produced easily in Bangladesh. Moreover the materials are less costly and easily available from natural resources. With proper research and development DSSC can be used to mitigate the energy crisis in Bangladesh. *Carissa Carandas* is a common fruit in Bangladesh which produced largely in tropical area. The ripe berries are very rich in anthocyanin which is responsible for the color of the cranberries. The uses of natural bio-pigments, such as anthocyanin is an excellent alternative to synthetic colors. They are non-toxic and from renewable resources. They have very good light absorption capacity and turns out very good dye for DSSC. So it is highly beneficial to use this easily available fruit to produce DSSC in Bangladesh.

1.4 Thesis Outline

The remainder of this thesis is organized as follows:

Chapter 2: In this chapter detailed literature review on Dye Sensitized Solar Cell is carried on. At first the world energy consumption scenario is included. It also presents the energy consumption situation in Bangladesh. Then the history of development of Solar cells and DSSC is described. Afterwards the advantages, main components, materials and principle of DSSC is described. The description of machine and procedure used in the study is also included.

Chapter 3: Includes a description of the raw materials and the general procedures for the fabrication of DSSC. It also presents the details of experimental procedure and experimental data.

Chapter 4: Presents the results of each experiment and their explanation.

Chapter 5: Provides summary of the findings of this research work and suggests ideas and directions for future research.

2.0 Literature Review

2.1 Introduction

In this chapter energy demand and consumption of the present world is described. Afterwards the energy consumption and production scenario in Bangladesh is included. The history of solar cell from first generation solar cell to third generation is deduced. Then focus is given on Dye-sensitized solar cells. The history, advantages, working principle and mechanism of Dye-sensitized solar cell is illustrated in the chapter. Later all the process, chemical and materials used are described briefly.

2.2 World Energy Consumption Statistics

Around the globe the major methods used for generation of electricity are production of electricity by turbine, reciprocating engine, photovoltaic cells. In the year 2012 the total generation was 22504TWh¹ [1]The majority of electricity is produced from fossil fuel like oil, natural gas , coal . The amount of electricity generated from different fuel is shown in a pi chart

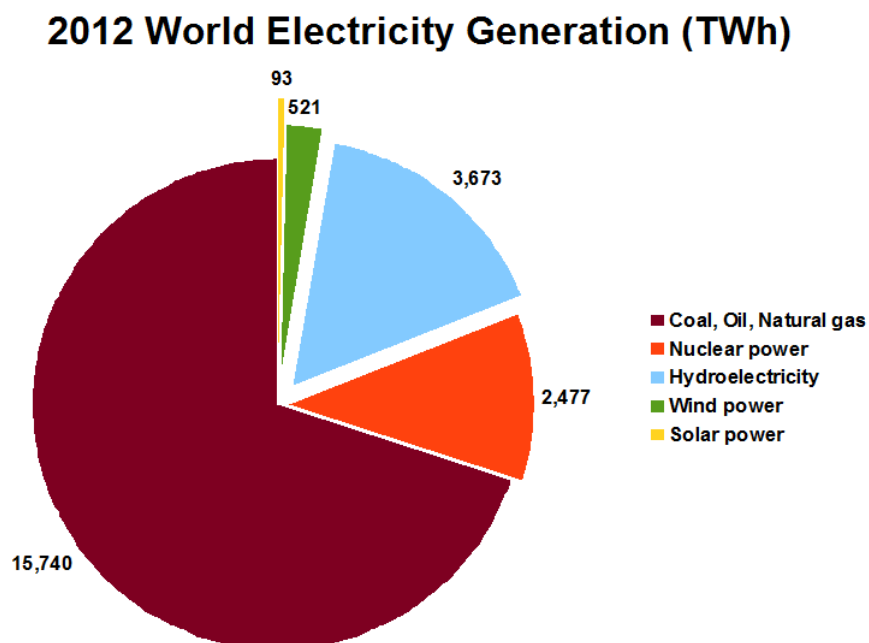







Figure 1 World Electricity Generation [1]

The List showing the generation capacity in kwh,billion with the percentage of use of different sources of different countries is given bellow :

Table 1 Electricity Production and Sources [2]

Country	Electricity production (kWh, billion)	% Coal	% Natural gas	% Oil	% Hydropower	% Other renewable	% Nuclear power
 <u>Albania</u>	4.2	0	0	0	100	0	0
 Argentina	129.6	2.5	51.4	15.1	24.4	1.7	4.9
 Austria	62.2	11.8	19.9	1.6	55	10.7	0
 <u>Australia</u>	252.6	68.6	19.7	1.6	6.6	3.5	0
 <u>Brazil</u>	531.8	2.3	4.7	2.8	80.6	6.6	2.9

Country	Electricity production (kWh, billion)	% Coal	% Natural gas	% Oil	% Hydropower	% Other renewable	% Nuclear power
 United States	4,326.6	43.3	24.2	0.9	7.4	4.8	19
 India	1,052.3	67.9	10.3	1.2	12.4	5	3.2
 Japan	1,042.7	27	35.9	10.1	8	4.2	9.8
China	4,715.7	79	1.8	0.2	14.8	2.2	1.8
 Sweden	150.3	0.9	1	0.5	44.2	11.7	40.2
 Germany	602.4	45.1	13.9	1.1	2.9	17.6	17.9

[3]

If focus is given to individual country it is seen that, in USA (United States of America) the total generation capacity is 4326.6kwh, billion. There the main sources of electricity are Fossil fuel, Nuclear energy, Hydropower and wind. 12.2% of total electricity comes from renewable sources [3]. In USA 80% of electricity generated by private companies, the rest is produced by Federal agencies. [4]

In 2011 the gross electric power generation in Germany totaled 602.46kwh, billion. A major proportion of the electricity supply is based on lignite and hard coal (45.1 %) and nuclear energy (17.9 %). Natural gas has a share of 13.9 %. The renewable sources (wind, water, biomass, photovoltaic) account for 20.5%. Key to Germany's energy policies and politics is "Energiewende", meaning "energy turnaround" or "energy transformation". Germany intends to eliminate current use of nuclear power in 2022

[3].Germany is known as one of the largest consumers of electricity around the world. The country also imports 10% of its generated electricity from other countries. In China, the highest electricity producer in the globe, by the end of 2011, its total production capacity is 4715.7kwh, billion¹. At present, China's hydropower output amounts to 14.8 percent of the national total, nuclear power output accounts for 2.2 percent and wind power output amounts to 0.26 percent, while coal-fired power output amounts to at least 79% of the national total [5]

The electricity sector in India had an installed capacity of 237.742 GW¹ as of February 2014, the world's fourth largest. Captive power plants generate an additional 39.375 GW. [6] Non Renewable Power Plants constitute 87.55% of the installed capacity, and Renewable Power Plants constitute the remaining 12.45% of total installed Capacity.

2.3 Energy Generation and Consumption Scenario in Bangladesh

In Bangladesh most of its electricity is produced by non-renewable means. The fuels used are gas, coal, heavy fuel oil. Steam turbine, reciprocating engine and hydro power plant are used for electricity generation. A very few amount of electricity is generated by renewable sources like solar. Bangladesh not being an industrially developed most electricity demand is for household, office, agriculture or markets. With the rise of industrial development more electricity demand will increase.

2.3.1 Electricity Generation by Non-renewable Sources

In Bangladesh most (99%) of the electricity is used by different power plants situated throughout the country. These plants use steam, gas, combined cycle turbine, reciprocating engine for production of electricity. Bangladesh has only one hydroelectric power plant in Chittagong. The fuels used in the power plants are coal, gas, fossil oil, high speed diesel. As Bangladesh has a high reserve of natural gas the mostly used fuel is natural gas (64.59%) The amount of electricity generated by different fuels in April 2014 is given in the chart below :

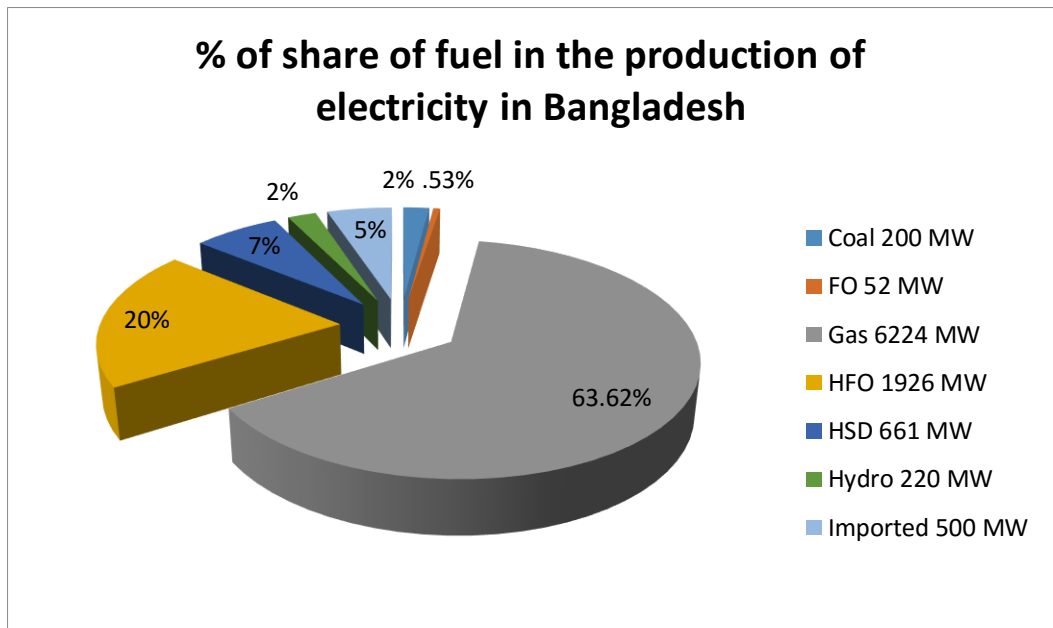


Figure 2 Sharing of fuel in electricity generation [7]

In Bangladesh the main type of contrivance used for electricity generation are steam turbin, hydraulic turbine ,reciprocating engine . Among them reciprocating engine is used most as it requires less space to install and the operation and maintenance is easy The share of different contrivance in production of electricity with their installed capacity is shown in the figure bellow :

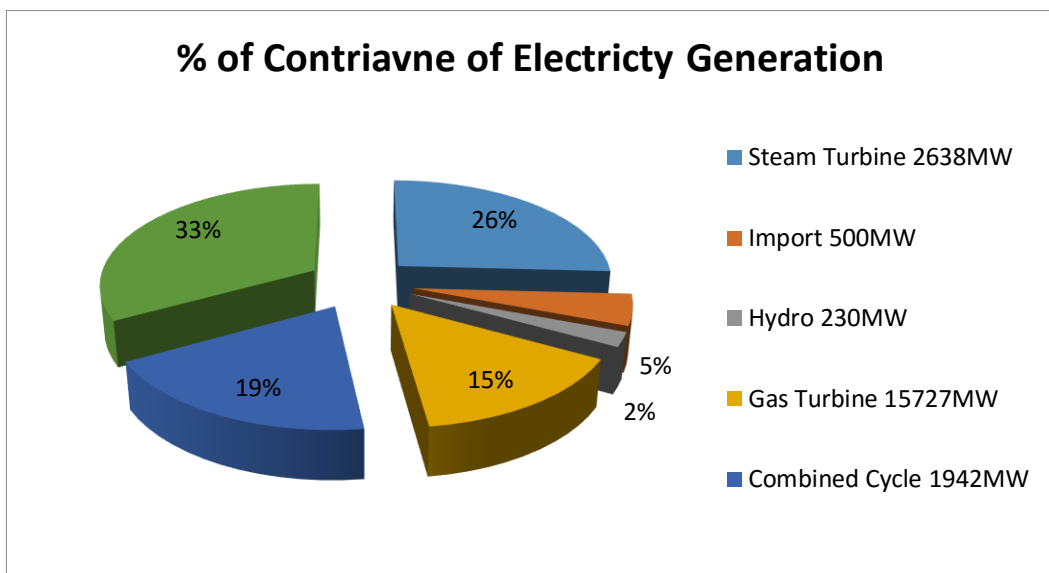


Figure 3 Sharing of contrivance in the production of electricity in Bangladesh [7]

2.3.2 Electricity Generation by Renewable Sources

Bangladesh is endowed with plentiful supply of renewable sources of energy. Out of various renewable sources solar, biomass, peat, and hydro-power can be effectively used in Bangladesh. With the help of renewable energy Bangladesh is producing 364.7MW electricity. [8]

Solar Energy is inexhaustible and pollution free. It is available everywhere; but the greatest amount is available between two broad bands encircling the earth between 15° and 35° latitude north and south. Fortunately Bangladesh is situated between 20°43' north and 26°38' north latitude and as such Bangladesh is in a very favorable position in respect of the utilization of solar energy. Annual amount of radiation varies from 1840 to 1575 kwh/m² which is 50-100% higher than in Europe. Taking an average solar radiation of 1900 kwh per square meter, total annual solar radiation in Bangladesh is equivalent to 1010 X 10¹⁸ J. present total yearly consumption of energy is about 700 X 10¹⁸ J. this shows even if 0.07% of the incident radiation can be utilized, total requirement of energy in the country can be met. At present energy utilization in Bangladesh is about 0.15 watt/sq. meter land area, whereas the availability is above 208 watt/sq. meter. This shows the enormity of the potentiality of this source in this country. The government has taken various projects to use solar energy in the production of electricity. Like with the help of IDCOL the Bangladesh government is producing 130MW electricity form solar energy. Other projects are also going on to use the maximum of solar energy radiated in the country. [8]

Wind energy has the potential to provide mechanical energy or electricity without generating pollutants. Bangladesh is situated between 20°34'-26°38' North Latitude and 88°01'-92°41' East Longitude. The country has a 724 km long coast line and many small islands in the Bay of Bengal, where strong south-westerly tradewind and sea-breeze blow in the summer months and there is gentle north-easterly trade wind and breeze in winter months. From wind energy the government is getting 2MW electricity. [8]

Biomass energy is the important source of energy in many countries of the world. Biomass is biological material derived from living, or recently living organisms. It most often refers to plants or plant-based materials which are specifically called lignocelluloses biomass. As an energy source, biomass can either be used directly via combustion to produce heat, or indirectly after converting it to various forms of biofuel. In Bangladesh, commonly known Biomass fuels are: fuel wood, agricultural residues and animal dung. The country has naturally high potential for production of Biomass resources; but because of

high growth rate of population (2.4%) forest cover is being reduced in an alarming proportion. Now-a-days 2MW electricity is producing by Biomass energy .

2.4 Evolution of Photovoltaic (PV) Technology

2.4.1 First Generation PV

The first generation photovoltaic, consists of a large-area, single layer p-n junction diode, which is capable of generating decent electrical energy from light sources with all possible wavelengths of solar light. These cells are typically made using silicon wafer. First generation photovoltaic cells (also known as silicon wafer based solar cells) are the products in the commercial production of solar cells, accounting for more than 86% of the solar cell market. [9]

2.4.2 Second Generation PV

The second generation of photovoltaic materials is based on the use of thin-film deposits of direct band gap semiconductors such as CdTe, CdS, CdSe etc ., These devices were initially designed to be high efficiency, multiple junction photovoltaic cells. Later, the advantage of using a thin-film of material was noted, reducing the mass of material required for cell design. This contributed to a prediction of greatly reduced costs for thin film solar cells. However, most of the assembly costs for depositing thin film solar cells are still significantly higher than for bulk silicon technologies. Another advantage of the reduced mass is that less support is needed when placing panels on rooftops and it allows fitting panels on light materials, even textile. [8]

2.4.3 Third Generation PV

Third generation photovoltaics are very different from the other two, broadly defined as semiconductor devices which do not rely on a traditional p-n junction to separate photogenerated charge carriers. Two fundamental mechanisms that greatly limit the performances of solar cells are: thermalization of hot carriers and transmission of sub band gap photons. Thermalization is the tendency of energetic charge carriers to lose their kinetic energy through collisions with crystalline lattices (phonon creation) as the carriers move towards the band edge. These devices have two fundamental limiting mechanisms such as transmissivity and thermalization. Transmissivity of sub band gap photons is the inability of the semiconductor to absorb photons with wavelengths greater than the band gap. [10] These less energetic photons pass through the material. Thermalization is particularly degrading the open circuit voltage and transmissivity degrades the short circuit current. Structures using special band gap engineered materials (e.g., materials with intermediate

bands to absorb sub band gap photons, materials incorporating quantum dots or quantum wells to slow down thermalization dynamics) like ZnO , TiO₂ based Dye Sensitized Solar Cells are promising topics of academic research in third generation PV. [11]

2.5 Dye Sensitized Solar Cell

A dye-sensitized solar cell is a low-cost solar cell belonging to the group of thin film solar cells It is based on a semiconductor formed between a photo-sensitized anode and an electrolyte, a *photoelectrochemical* system.

2.5.1 History

Although the electricity generation capability of organic dyes has been known since late 1960s, the first attempt to generate electricity from dye sensitized semiconductor film was from ZnO sensitized with Chlorophylls⁸ and that's why they are sometimes referred as 'Artificial Photosynthesis'. [12] The first embodiment of modern day Dye-sensitized Solar Cell (DSC) dates back to late 1980s.⁹ However, not until the fundamental work of Grätzel and O'Regan in 1991,¹⁰ it was proven that DSCs can be a feasible alternative energy source. [13] The highest reported efficiency for DSCs with conventional Ru-based dyes is around 11.5%.^{11,12} Recently, a Zn-based dye and Co-based electrolyte pair have been developed and their efficiency has exceeded 12%

2.5.2 Advantages of DSC

Although the power conversion efficiency of DSC is not as good as compared to other inorganic 1st and 2nd generation solar cells, it has an edge over them at some points. In the normal operating temperature range of 25–65⁰C, DSC efficiency is nearly temperature-independent. For the same range, the efficiency of Si solar cells declines by 20%. [14]¹⁴ In diffuse sunlight or cloudy conditions, DSC shows even better efficiency than polycrystalline Si solar cell. Performance is less sensitive to the incident angle of the light radiation; hence a solar tracking mechanism is less necessary. Although a mass commercial production of DSC is still not available, it can be expected that it has a cost advantage over all thin film devices. Only low cost and abundantly available materials are needed. Unlike amorphous silicon, CdTe or CIGS cells, DSC can avoid the costly and energy-demanding high vacuum as well as materials purification steps. DSC materials are biocompatible and abundantly available. The technology can be expanded up to the terawatt scale without facing material supply problems. This gives organic-based solar cells an edge over the 2 major competing thin-film photovoltaic technologies - CdTe and CuIn(As)Se; which use

highly toxic materials of small natural abundance. A key requirement for all types of solar cells is long-term stability. From

different extensive studies, it has been confirmed that the DSCs can satisfy the stability requirements for commercial solar cells to endure outdoor operation for 20 plus years. Considering these advantages, DSC has the potential to be a feasible candidate for the race of large-scale solar energy conversion systems.

2.5.3 Components of Dye Sensitized Solar Cell

The current DSSC design involves a set of different layers of components stacked in serial, including glass substrate, transparent conducting layer, TiO₂ nanoparticles, dyes, electrolyte, and counter electrode covered with sealing gasket [15]. The typical configuration is shown in following figure

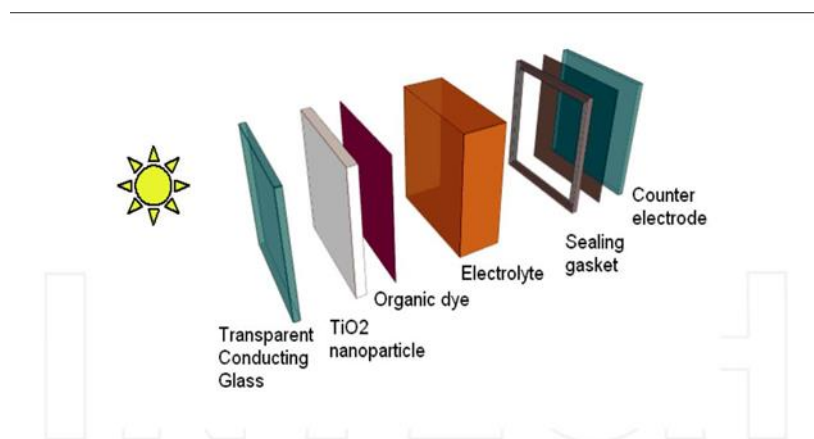


Figure 4 Components of Dye-sensitized Solar cell

2.5.3.1 Transparent Conducting Glass

In the front of the DSSC there is a layer of glass substrate, on top of which covers a thin layer of transparent conducting layer. This layer is crucial since it allows sunlight penetrating into the cell while conducting electron carriers to outer circuit. Transparent Conductive Oxide (TCO) substrates are adopted, including F-doped or In-doped tin oxide (FTO or ITO) and Aluminum-doped zinc oxide (AZO), which satisfy both requirements. ITO performs best among all TCO substrates. However, because ITO contains rare, toxic and expensive metal materials, some research groups replace ITO with FTO. AZO thin films are also widely studied because the materials are cheap, nontoxic and easy to obtain.

The properties of typical types of ITO and FTO from some renowned manufacturers are shown in Table

Table 2 Properties of a few types of commercial ITO and FTO materials

Conductive glass	Company	Light transmittance	Conductivity (Ohm/sq)	Thickness (mm)	Size (cm×cm)
ITO	Nanocs	>85%	5	1.1	1×3
ITO	PG&O	85%	4.5	1.1	2×3
FTO	NSG	>84%	<7	3	100×100

2.5.3.2 TiO₂ nanoparticles

DSSC has a low efficiency less than 1% until Professor Grätzel employs porous TiO₂ as the anode material. Usually a layer of negatively doped TiO₂ (n-TiO₂) nanoparticles is used. The advantages of TiO₂ include high photosensitivity, high structure stability under solar irradiation and in solutions, and low cost. The typical particle size is 8-30 nm in diameter, and the TiO₂ films thickness is 2-20 μm, with the maximum efficiency located at a thickness of 12-14 μm depending on dyes and electrolyte chosen [16]. However, as a wide bandgap semiconductor (~3.2 eV), TiO₂ absorbs only UV light, which comprises only a small fraction (~5%) of solar spectrum. As a result, dye molecules are employed for visible light capture. Only nanocrystalline TiO₂ provides high light capture efficiency, with external quantum efficiency (incident photon-to-charge efficiency) typically in the range of 60-90% using nanocrystal forms in comparison with <0.13% using the monocrystal form [17]. The reason lies in the high surface-to-volume ratios for porous nanocrystal materials.

2.5.3.3 Dyes

Dye molecules are the key component of a DSSC to have an increased efficiency through their abilities to absorb visible light photons. Early DSSC designs involved transition metal coordinated compounds (e.g., ruthenium polypyridyl complexes) as sensitizers because of their strong visible absorption, long excitation lifetime and efficient metal-to-ligand charge transfer. However, high cost of Ru dyes (>\$1,000/g) is one important factor hindering the large-scale implementation of DSSC. [18] Although highly effective, with current maximum efficiency of 11% the costly synthesis and undesired environmental impact of those prototypes call for cheaper, simpler, and safer dyes as alternatives.

Organic dyes, including natural pigments and synthetic organic dyes, have a donor-acceptor structure called as push-pull architecture, thus improving short circuit current

density by improving the absorption in red and infrared region. Natural pigments, like chlorophyll, carotene, and anthocyanin, are freely available in plant leaves, flowers, and fruits and fulfill these requirements. Experimentally, natural-dye sensitized TiO₂ solar cells have reached an efficiency of 7.1% and high stability [19]

Even more promising is the synthetic organic dyes. Various types have recently been developed, including indolic dyes [20]), and cyanoacrylic acids (JK, C209). The same as some natural dyes, they are not associated with any metal ions, being environmental benign and easily synthesized from abundant resources on a large scale. The efficiency has reached a high level of 10.0-10.3% [21] They are relatively cheap, at the cost of one-tenth of corresponding Ru dyes. Light soaking experiments have confirmed they possess long-time stability: 80% efficiency has been maintained after 1,200 hours of light-soaking at 60 °C (~5 million turnovers). The commercialized production of these synthetic dyes has been established in China this year. A single dye usually has a limited adsorption spectrum, so some research groups use several kinds of dyes to relay energy transfer and compensate each other and have achieved good results. [22]

2.5.3.4 Electrolyte

Currently three different kinds of electrolytes have been used in real DSSCs with pros and cons of each kind: (i) the most common electrolyte is I⁻/I₃⁻ in organic solvents, such as acetonitrile. Sometimes lithium ion is added to facilitate electron transport. This kind of electrolyte is good for ion diffusion and infiltrate well with TiO₂ film, keeping highest efficiency of all DSSCs. But limited long-term stability due to volatilization of liquid hinders its wide use. (ii) Inorganic ionic liquids made of salts or salt mixture. It looks like solid while it has properties of liquid and it performs well in conductivity. But after a long period of time, its efficiency declines. (iii) Solid electrolyte, such as spiro-MeOTAD or CuI [23] For CuI, its instability and crystallization makes it hard to fill in the porous TiO₂ films. The problem can be solved by adding ionic liquid into the electrolyte. Spiro-MeOTAD is a typical kind of organic hole conductor, which has been developed for years and the DSSC based on this kind of electrolyte has reached the efficiency of 5%.

2.5.3.5 Counter electrode

On the back of the DSSC there presents another glass substrate covered with a thin layer of Pt used as the catalyst to regenerate I⁻ and as the cathode material. Pt is the best material to make efficient devices technically. But considering high expenses, carbon cathode has

been an ideal substitute, such as carbon black, carbon nanotubes etc. In 2006, Grätzel's group employs carbon black as the material of counter electrode, and reaches an efficiency of 9.1%, which is 83% of that using Pt [24]

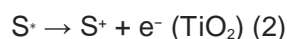
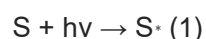
Conducting polymers can also be used. Polyaniline film on stainless steel by electrochemical polymerization has been reported as a counter electrode of DSSC [25] It is cheap and non-fragile.

2.5.4 Basic Operating Principle

The Dye Sensitized Solar Cell (DSC) uses the same basic principle as plant photosynthesis to generate electricity from sunlight. Each plant leaf is a photo-chemical cell that converts solar energy into biological material. Although only 0.02-0.05% of the incident solar energy is converted by the photosynthesis process, the food being produced is 100 times more than what is needed for mankind. [26] The chlorophyll in green leaves generate electrons using the photon energy, which triggers the subsequent reactions to complete the photosynthesis process. The DSC (a typical configuration is shown in Fig. 2.1) is the only photovoltaic device that utilizes separate mediums for light absorption/carrier generation (dye) and carrier transport (TiO₂ nano-particles). The operation steps are the following.

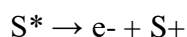
2.5.4.1 Excitation

The light is absorbed by a sensitizer dye molecule, it goes over an electronic state change from the ground (S) to the excited state (S*). For most dyes the absorption onset is in the range of 720nm corresponding to a photon energy of 1.72eV. [27] The lifetime of the excited state is in the order of nanoseconds.



2.5.4.2 Injection

The sensitizing dye molecules are adsorbed on the surface of a wide band gap semiconductor (typically TiO₂). Upon absorption of a photon (excitation), the dye gains the ability to transfer an electron to the conduction band of the semiconductor. [28] The internal electric field of the nanoparticles causes the electron extraction and the dye becomes oxidized (S⁺). For efficient electron injection the lowest unoccupied molecular orbital (LUMO) of the dye has to be about 0.3 eV above the TiO₂ conduction band. The injection rate constant is in the femtosecond range for singlet state.

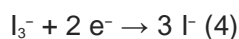


2.5.4.3 Diffusion in TiO₂

The nonporous TiO₂ film consists of spherical anatase particles of diameter ~20 nm. The presence of oxygen vacancies in the lattice makes it a weakly n-doped material (equivalent carrier concentration 10¹⁶ cm⁻³).¹⁶ As the TiO₂ particle diameter is too small for electric field to build up, the dominant electron transport mechanism is diffusion via trapping and de-trapping.

2.5.4.4 Iodine Reduction

The electron travels through the outer circuit performing work, reaches the back FTO electrode, and reduces the iodine in the electrolyte. The platinum layer on the FTO acts as a catalyst for the reduction. The dark cathode reaction:



The iodine reduction can also occur at the excited dye molecules causing recombination of the photo-generated electrons. [29] For efficient charge transfer, the rate of iodine reduction at the counter electrode has to be orders of magnitude faster than the recombination at the TiO₂/electrolyte interface.

2.5.4.5 Dye Regeneration

The reduced iodide ion replenishes the highest occupied molecular orbital (HOMO) of the dye - regenerating its original form, and makes it ready for electron generation again.

This prevents buildup of S⁺, which could lead to the conduction band electrons going back to the dye molecules. The maximum output voltage equals to the difference between the Fermi level of the semiconductor and the redox potential of the mediator. Thus, the device is can produce electricity from light without undergoing any permanent physical and chemical change.

2.6 Solar Cell Terminologies

2.6.1 The IV Curve

The IV curve of a solar cell is the superposition of the IV curve of the solar cell diode in the dark with the light-generated current. The light has the effect of shifting the IV curve down into the fourth quadrant where power can be extracted from the diode.

[30] Illuminating a cell adds to the normal "dark" currents in the diode so that the diode law becomes:

$$I = I_0 \left[\exp \left(\frac{qV}{nkT} \right) - 1 \right] - I_L$$

where I_L = light generated current.

2.6.2 Open-Circuit Voltage

The open-circuit voltage, V_{OC} , is the maximum voltage available from a solar cell, and this occurs at zero current. [31] The open-circuit voltage corresponds to the amount of forward bias on the solar cell due to the bias of the solar cell junction with the light-generated current. The open-circuit voltage is shown on the IV curve below.

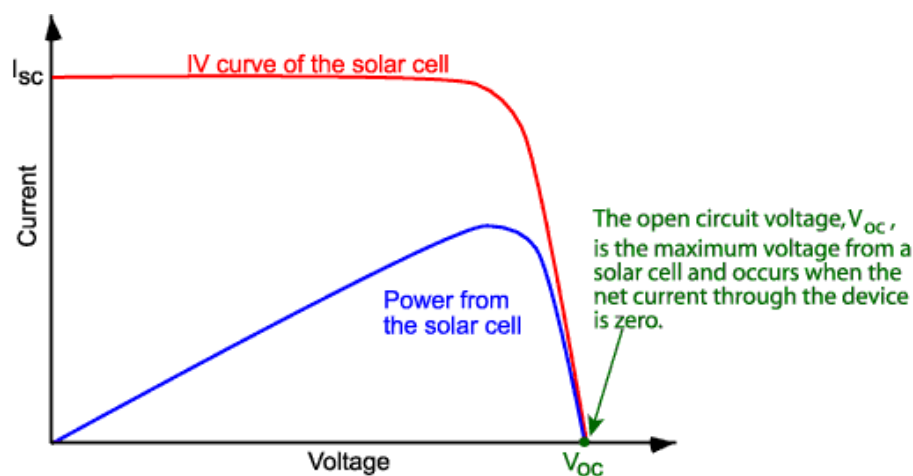


Figure 5 I-V Curve Showing Open Circuit Voltage

An equation for V_{oc} is found by setting the net current equal to zero in the solar cell equation to give:

$$V_{OC} = \frac{nkT}{q} \ln \left(\frac{I_L}{I_0} + 1 \right)$$

2.6.3 Short Circuit Current

The short-circuit current is the current through the solar cell when the voltage across the solar cell is zero (i.e., when the solar cell is short circuited). Usually written as I_{SC} , the short-circuit current is shown on the IV curve below.

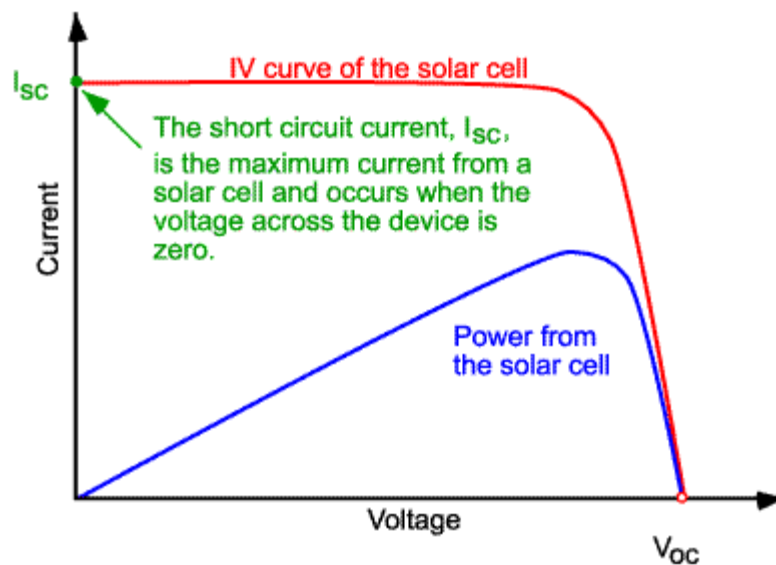


Figure 6 IV curve of a solar cell showing the short-circuit current.

2.6.4 Fill Factor

The short-circuit current and the open-circuit voltage are the maximum current and voltage respectively from a solar cell. However, at both of these operating points, the power from the solar cell is zero. The "fill factor", more commonly known by its abbreviation "FF", is a parameter which, in conjunction with V_{oc} and I_{sc} , determines the maximum power from a solar cell. The FF is defined as the ratio of the maximum power from the solar cell to the product of V_{oc} and I_{sc} . Graphically, the FF is a measure of the "squareness" of the solar cell and is also the area of the largest rectangle which will fit in the IV curve. The FF is illustrated below

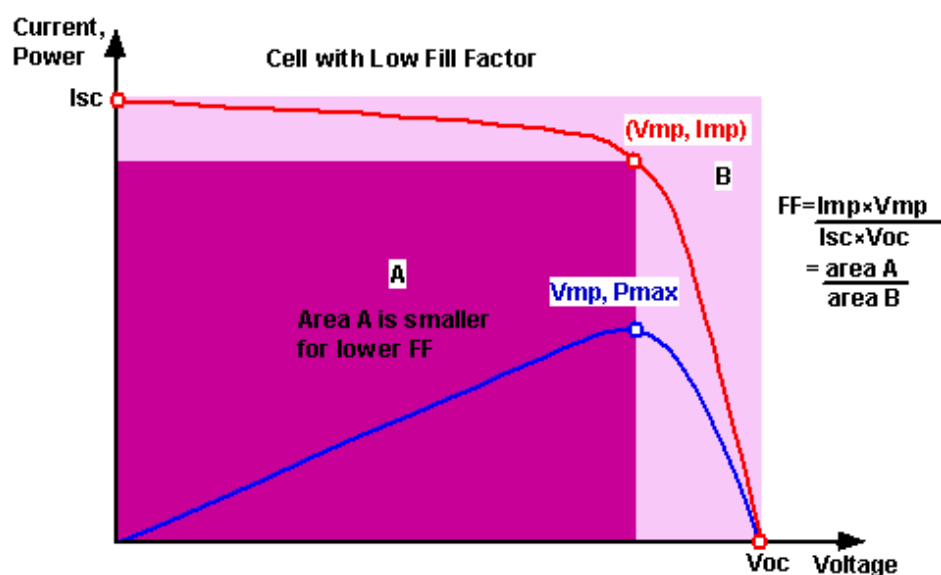


Figure 7 Fill Factor in I-V Curve of Solar Cell

2.6.5 Efficiency

The efficiency is the most commonly used parameter to compare the performance of one solar cell to another. Efficiency is defined as the ratio of energy output from the solar cell to input energy from the sun. In addition to reflecting the performance of the solar cell itself, the efficiency depends on the spectrum and intensity of the incident sunlight and the temperature of the solar cell.

The efficiency of a solar cell is determined as the fraction of incident power which is converted to electricity and is defined as:

$$P_{max} = V_{OC}I_{SC}FF$$

$$\eta = \frac{V_{OC}I_{SC}FF}{P_{in}}$$

Where:

V_{oc} is the open-circuit voltage;

I_{sc} is the short-circuit current;

FF is the fill factor and

η is the efficiency.

2.7 Methods, Materials and Machines Used in DSSC Fabrication

2.7.1 Doctor Blade Method

Doctor blade (or tape casting) is one of the widely used techniques for producing thin films on large area surfaces. In the doctor blading process, a well-mixed slurry consisting of a suspension of ceramic particles along with other additives (such as binders, dispersants or plasticizers) is placed on a substrate beyond the doctor blade. When a constant relative movement is established between the blade and the substrate, the slurry spreads on the substrate to form a thin sheet which results in a gel-layer upon drying. [32]

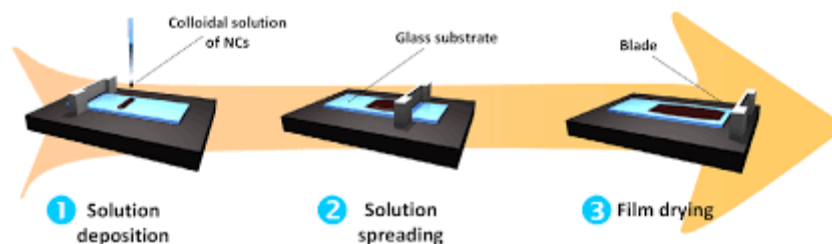


Figure 8 Doctor Blade Method

The doctor blading can operate at speed up to several meters per minute and it is suitable to coat substrate with a very wide range of wet film thicknesses ranging from 20 to several hundred microns.

2.7.2 Degussa P25(Titanium Dioxide)

Degussa P25 is a titania photocatalyst that is used widely because of its relatively high levels of activity in many photocatalytic reaction systems. [33]Actually, it is not easy to find a photocatalyst showing activity higher than that of P25, and it has therefore been used as a de-facto standard titania photocatalyst. Photocatalytic reactions of P25 have been reported in more than thousand papers since 1990..



Figure 9 Degussa P25

It is well known that P25 is composed of anatase and rutile crystallites, the reported ratio being typically 70:30 or 80:20, but it seems that nobody knows the exact crystalline composition presumably due to a lack of methodology for determination of crystalline contents in nanometer-sized particulate samples .Another myth, a hypothesis not proved scientifically, regarding P25 is that the co presence of anatase and rutile crystallites induces the high level of photocatalytic activity; transfer of photoexcited electrons and positive holes between interconnecting anatase and rutile particles may enhance charge separation and hence improve the efficiency of utilization of electron–hole pairs .However, as far as

know, there have been no reports showing enhancement of activity compared with pure anatase and rutile parts of P25 or with the anatase and rutile particles without any electrical contact: no data have been shown for expected lower activity of pure anatase and rutile particles alone. [34] Thus, despite the long history of photocatalysis studies, it seems that we have not yet known what P25 is from the standpoints of structural and photocatalytic characteristics

2.7.3 *Carissa Carandas*

Carissa carandas Linn. its local name is Carandas. The caranda, is a shrub which produces berry-sized fruits. The caranda has attracted more interest as a source of fruit and as a medicinal plant. It is a fruit of dry area. The karanda or karanda cranberry (*Carissa carandas*) is a climbing shrub or small tree usually reaching 5 meters tall.



Figure 10 *Carissa Carandas* (Koromcha)

The numerous and spreading branches form dense masses and are set with sharp thorns, simple or forked, up to 5 cm long, in pairs in the axils of the leaves. It is cultivated for its edible fruit, which can be eaten raw, made into jam and jelly, or used for pies. *Carissa carandas*, a perennial plant, is a hardy shrub that is easily maintained, Pruning of the plant is said to enhance the cultivation of its berries. Harvesting cranberries is not labor intensive. The ripe berries are very rich in anthocyanins. [35] [36] These anthocyanins are responsible for the color of the karanda cranberries. The uses of natural bio-pigments, such as anthocyanins from fruit and food products, are an excellent alternative to synthetic colors. They are non-toxic and from renewable resources. Little has been known, however, of the karanda cranberry's dyeing capability, especially on fabric. Decorators and fashion houses of today have adopted the color of cranberries synthetically for dresses, lipsticks, walls,

and many other things, but they were not the first to appreciate the color. Some early Indians and Asians made use of this fruit as a coloring agent smeared on their skin or clothing

2.7.4 Muffle Furnace

A muffle furnace (sometimes, retort furnace) in historical usage is a furnace in which the subject material is isolated from the fuel and all of the products of combustion, including gases and flying ash. After the development of high temperature heating element and widespread electrification in developed countries, new muffle furnaces quickly moved to electric designs.



Figure 11 Muffle Furnace

Today, a muffle furnace is (usually) a front-loading box-type oven or kiln for high-temperature applications such as fusing glass, creating enamel coatings, ceramics and soldering and brazing articles. They are also used in many research facilities, for example by chemists in order to determine what proportion of a sample is non-combustible and non-volatile (i.e., ash). Some digital controllers allow RS232 interface and permit the operator to program up to 126 segments, such as ramping, soaking, sintering, and more. Also, advances in materials for heating elements, such as molybdenum disilicide, can now produce working temperatures up to 1,800 degrees Celsius (3,272 degrees Fahrenheit), which facilitate more sophisticated metallurgical applications.

2.7.5 Sonicator

Sonication is the act of applying sound energy to agitate particles in a sample, for various purposes. Ultrasonic frequencies (>20 kHz) are usually used, leading to the process also

being known as ultrasonication or ultra-sonication. In the laboratory, it is usually applied using an ultrasonic bath or an ultrasonic probe, colloquially known as a sonicator. [37] In a paper machine, an ultrasonic foil can distribute cellulose fibres more uniformly and strengthen the paper.

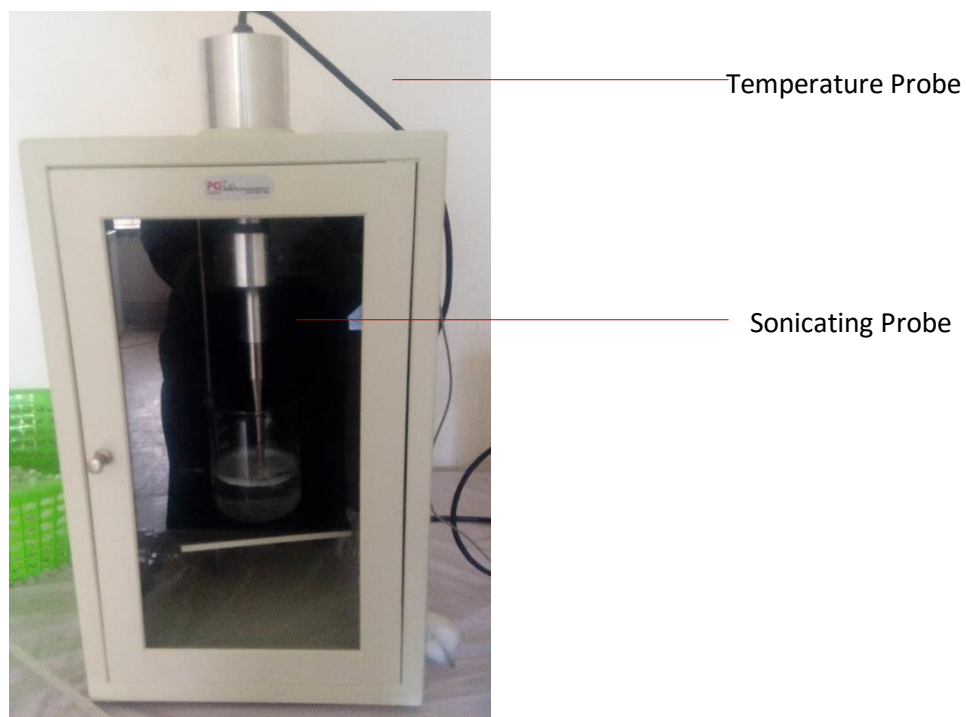


Figure 12 Sonicator

Substantial intensity of ultrasound and high ultrasonic vibration amplitudes are required for many processing applications, such as nano-crystallization, nano-emulsification, deagglomeration, extraction, cell disruption, as well as many others. Commonly, a process is first tested on a laboratory scale to prove feasibility and establish some of the required ultrasonic exposure parameters [38]. After this phase is complete, the process is transferred to a pilot (bench) scale for flow-through pre-production optimization and then to an industrial scale for continuous production. During these scale-up steps, it is essential to make sure that all local exposure conditions (ultrasonic amplitude, cavitation intensity, time spent in the active cavitation zone, etc.) stay the same. If this condition is met, the quality of the final product remains at the optimized level, while the productivity is increased by a predictable "scale-up factor". The productivity increase results from the fact that laboratory, bench and industrial-scale ultrasonic processor systems incorporate progressively larger ultrasonic horns, able to generate progressively larger high-intensity cavitation zones and, therefore, to process more material per unit of time. This is called

"direct scalability". It is important to point out that increasing the power capacity of the ultrasonic processor alone does not result in direct scalability, since it may be (and frequently is) accompanied by a reduction in the ultrasonic amplitude and cavitation intensity. During direct scale-up, all processing conditions must be maintained, while the power rating of the equipment is increased in order to enable the operation of a larger ultrasonic horn. Finding the optimum operation condition for this equipment is a challenge for process engineers and needs deep knowledge about side effects of ultrasonic processors.

2.7.6 UV-visible Spectrophotometer

The instrument used in ultraviolet-visible spectroscopy is called a UV/Vis spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_0). The ratio I/I_0 is called the transmittance, and is usually expressed as a percentage (%T). The absorbance,



Control pane

Sample Cont

Figure 13 UV-visible spectrophotometer

The UV-visible spectrophotometer can also be configured to measure reflectance. In this case, the spectrophotometer measures the intensity of light reflected from a sample (I), and compares it to the intensity of light reflected from a reference material (I_0) (such as a white tile). The ratio I/I_0 is called the reflectance, and is usually expressed as a percentage (%R).

The basic parts of a spectrophotometer are a light source, a holder for the sample, a diffraction grating in a monochromator or a prism to separate the different wavelengths of

light, and a detector. The radiation source is often a Tungsten filament (300-2500 nm), a deuterium arc lamp, which is continuous over the ultraviolet region (190-400 nm), Xenon arc lamp, which is continuous from 160-2,000 nm; or more recently, light emitting diodes (LED)[1] for the visible wavelengths. The detector is typically a photomultiplier tube, a photodiode, a photodiode array or a charge-coupled device (CCD). Single photodiode detectors and photomultiplier tubes are used with scanning monochromators, which filter the light so that only light of a single wavelength reaches the detector at one time. The scanning monochromator moves the diffraction grating to "step-through" each wavelength so that its intensity may be measured as a function of wavelength. Fixed monochromators are used with CCDs and photodiode arrays [39]. As both of these devices consist of many detectors grouped into one or two dimensional arrays, they are able to collect light of different wavelengths on different pixels or groups of pixels simultaneously.

2.7.7 FTIR / Fourier Transform Infra-Red Spectrophotometer

FTIR (Fourier Transform Infra-red Spectroscopy) is a sensitive technique particularly for identifying organic chemicals in a whole range of applications although it can also characterise some inorganics. [40] Examples include paints, adhesives, resins, polymers, coatings and drugs. It is a particularly useful tool in isolating and characterising organic contamination.

FTIR relies on the fact that the most molecules absorb light in the infra-red region of the electromagnetic spectrum. This absorption corresponds specifically to the bonds present in the molecule. The frequency range are measured as wave numbers typically over the range 4000 – 600 cm^{-1} .

The background emission spectrum of the IR source is first recorded, followed by the emission spectrum of the IR source with the sample in place. The ratio of the sample spectrum to the background spectrum is directly related to the sample's absorption spectrum. The resultant absorption spectrum from the bond natural vibration frequencies indicates the presence of various chemical bonds and functional groups present in the sample. FTIR is particularly useful



Sample Contain

Figure 14 FTIR / Fourier Transform Infra-Red Spectrophotometer

for identification of organic molecular groups and compounds due to the range of functional groups, side chains and cross-links involved, all of which will have characteristic vibrational frequencies in the infra-red range.

2.8 Conclusion

This chapter included all the theory work studied for the development of Dye-sensitized Solar cell. In the starting of the chapter energy demand and consumption of the present world is described. Afterwards the energy consumption and production scenario in Bangladesh is included. The history of solar cell from first generation solar cell to third generation is deduced. Afterwards focus is given on Dye-sensitized solar cells. The history, advantages, working principle and mechanism of Dye-sensitized solar cell is illustrated in the chapter. Later all the process, chemical and materials used are described briefly.

3.0 Experimental Procedure and Data

3.1 Introduction

This chapter includes all the necessary chemical, machine and instrument required to fabricate Dye-sensitized Solar cell. The details of working procedure is also described. Later all the experimental data is included.

3.2 Materials

- Indium Tin Oxide (ITO) coated glass plate (Dyesol, Australia)
- Dyes from *Crissa Carandas*
- Carbon (tip of candle flame)
- Binder clips
- Alligator clips
- Hookup wire (black and red)
- Mortar and pestle
- Absorbent tissue paper
- Filter paper
- Safety goggles
- Protective gloves
- Pipets
- Tweezers
- Spatulas
- Scotch tape

3.3 Chemicals

- Titanium Dioxide (TiO₂)
- Degussa P25 (USA)
- Potassium Iodide (KI), and Iodine (I₂)
- Nitric acid (HNO₃), (Merck, Germany)
- Citric acid (C₆H₈O₇), (Merck, Germany)
- Acetic acid (CH₃COOH), (Merck, Germany)
- Hydrochloric acid (HCl), (Merck, Germany)
- Polyethylene Glycol (PEG-400US/NF, Merck, Germany)
- Triton X-100 (Merck, Germany)

- Acetone (BDH, UK),
- Ethanol (BDH, UK),
- Methanol (BDH, UK)
- Isopropanol (BDH, UK)

3.4 Instruments

- Ultrasonic Bath. (Unilab, UBT – 580)
- MultiMate (AGILENT 34401 A)
- UV-Visible Spectrophotometer (PG electronics, U.K)
- Variable resistance (up to 10,000 Ω)
- Light source (55-W Xenon lamp)
- Hot plate
- Muffle furnace (India)
- FTIR Spectrophotometer

3.5 Experimental Procedure

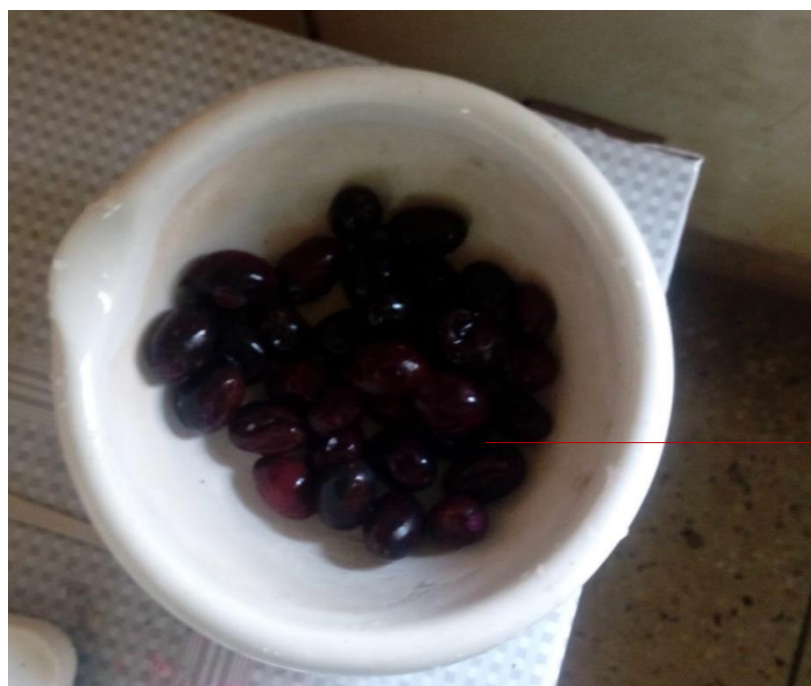
3.5.1 Preparation of *Crissa Carandas* Dye

For dye extraction the *Crissa Carandas* were washed properly with clean water to remove and dirt particles hence removing impurities before they were crushed. In a clean dry mortar the fruits were crushed using a pestle. Care was then that the juices is not spilled while crushing the fruits and the seeds are removed from the pulp.

In this study the dye was extracted by soaking the crushed *Crissa Carandas* in four different solvents-

- Ethanol
- Methanol
- Acetone
- Isopropanol

The mixing proportion for the solvent and fruit was 1gm *Crissa Carandas*:10ml solvent



Washed Crane Berries

Figure 15 Cleaned *Crissa Carandas* taken in Mortar for crushing
 During the use of solvents for extraction the *Crissa Carandas* were immersed in the respective solvents for 24 hours and 48 hours in a dark place to prevent sunlight affecting the dye



Figure 16 *Crissa Carandas* Dye in Isopropanol, Acetone, Ethanol, Methanol Solvent

In each case the dyes were filtered using a “Whatman Filter” before using the dye for staining the TiO₂ electrodes. The for dyes were very carefully handled so that they do not get mixed up.

3.5.2 Preparation of TiO₂ paste

TiO₂ sol-gel paste was produced in the laboratory using nanocrystalline grade TiO₂ powder, anatase. Polyethylene glycol, dilute acid, triton X-100, distill water are the requirements for preparing the solvent for the paste.



Figure 17 Preparation of Titanium Dioxide Paste
TiO₂ (Anatase) = 2.0gm.

HNO₃ (0.4M) = 2 ml

PEG = 1.4 ml

Triton X-100 = 0.5 ml

In a mortar 2.5ml of the prepared solution on 1gm of anatase was mixed thoroughly using a pestle to prepare the paste. The mixing was done over 5 minutes of continuous grinding of the paste to ensure the titanium dioxide nanoparticles are evenly mixed and dissolves completely in the solvent producing a fine paste. A fine paste is acknowledged when no particles are visible during the coating.

3.5.3 Preparation of TiO₂ electrode

Indium doped tin oxide (ITO) glass slides (2cm x 2cm) were used in this research, which were cleaned using detergent and washed with clean water followed by distilled water. The clean ITO glasses were then washed using ethanol solution in a sonicator for further cleaning and removal of impurities such that organic particles like skin cells and oil depositions that may have been deposited are removed. Conductive side of the ITO glass is identified and the ITO is taped to the table top by scotch tape with conductive side up. The slides are taped by 1mm from two edges. Using a glass rod the paste was coated onto the slides following the Doctor Blade technique.

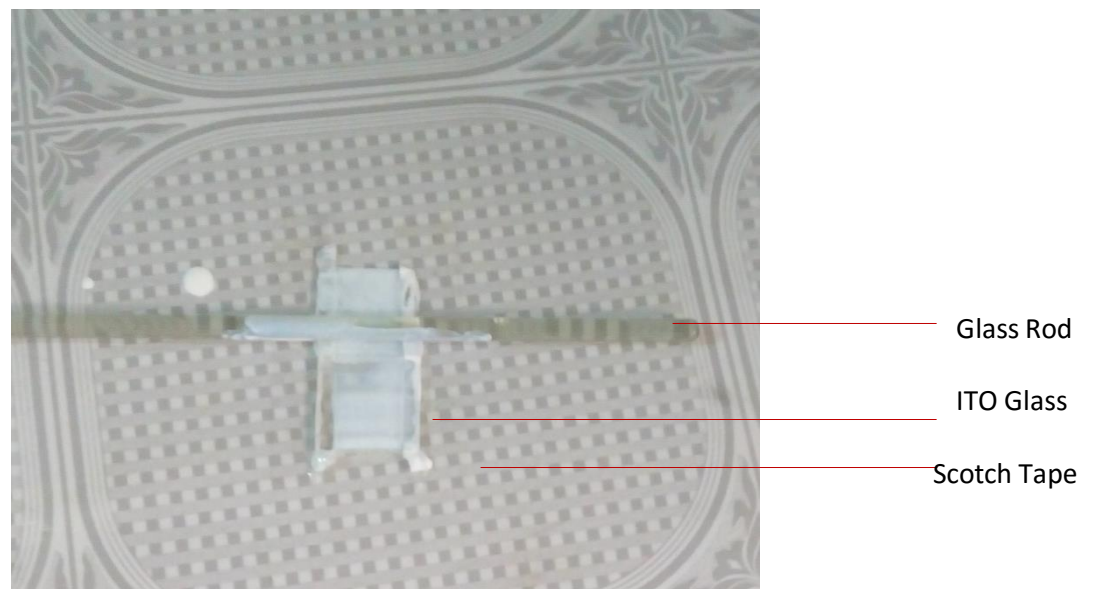


Figure 18 Doctor Blade Method to Deposit Titanium Dioxide Paste

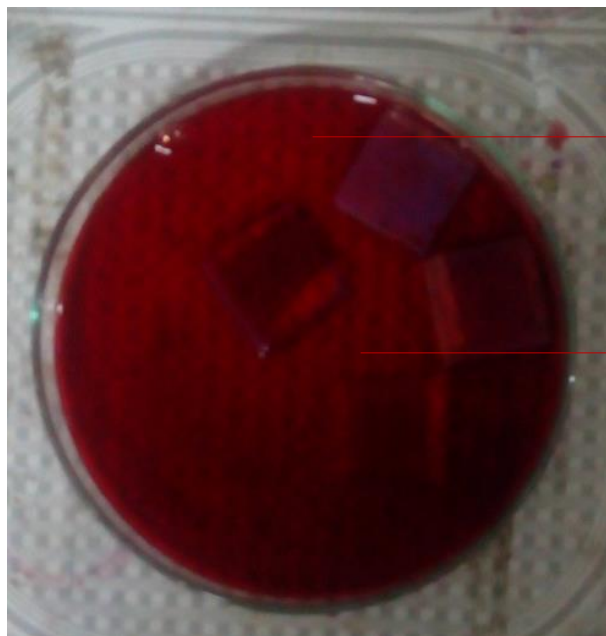
The coated slides are then left on the counter top for a few minutes to allow the paste to dry. Care is taken while removing the tape from the edges before placing the electrode in the muffle furnace for 1 hour at 450°C.



Anode after Annealing

Figure 19 ITO Glass after Annealing in Muffle Furnace

The electrode is provided time to cool down to room temperature slowly to prevent cracking of the titanium coating. This electrode is then placed into the extracted dye solution for different time variation to find the optimum soaking timing.



Anode Soaked in Crane Berry Dye

Crane Berry Dye

Figure 20 Anode Soaked in Dye

The TiO₂/dye electrode is then removed from the dye solution and washed fresh respective solvent to remove excess liquid. Distill water is used for raw dye. The final step is to allow the electrodes to dry at room temperature.

3.5.4 Preparation of Electrolyte

The electrolyte used in the DSSCs consists of iodine (I⁻) and triiodide (I₃⁻) as a redox couple in a solvent with chemicals added to improve the properties of the electrolyte and the performance of the operating DSSC.

For the preparation of Iodide electrolyte solution, 0.05M 0.064g Iodine (I₂) was dissolved in 10 mL of ethylene glycol followed by 0.5M 0.83 g Potassium Iodide (KI). The solution is then stirred and stores in a dark container away from light.

3.5.5 Preparation of Counter Electrode

The counter electrode is prepared by exposing the conductive side of an ITO coated glass on the tip of candle flame for about 30 sec which leaves a dark shade of carbon on the glass. The slide is moved back and forth to produce a thin, uniform coating. Care is given not to miss any spots.

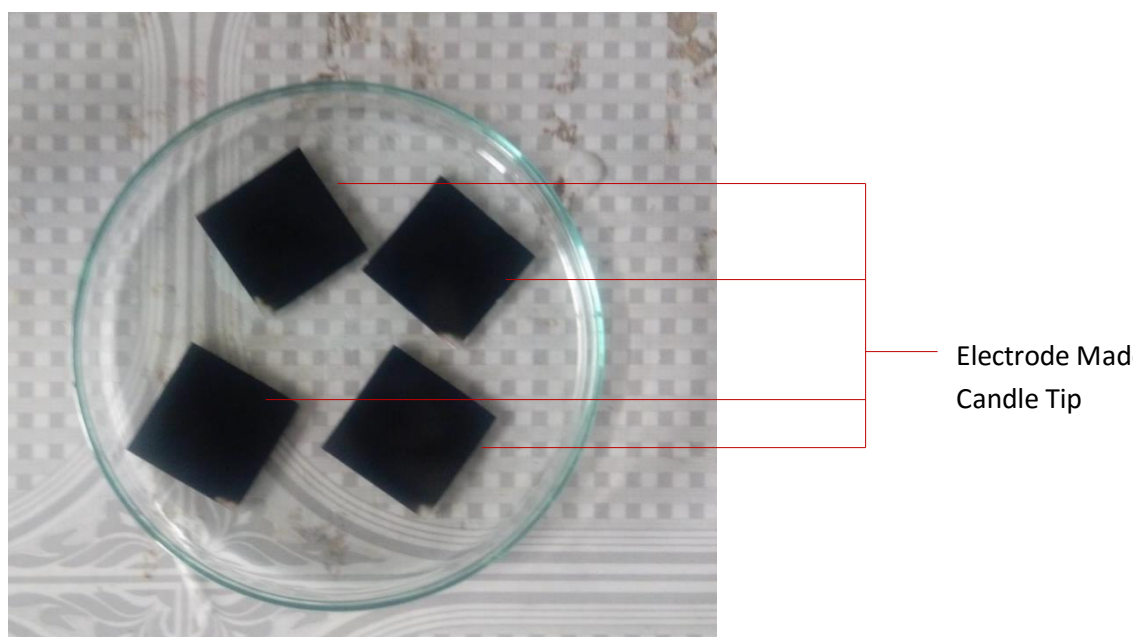


Figure 21 Counter Electrode

The black soot-coated glass is then allowed to cool, and soot is removed from a 5 mm strip at one end of the slide and the edges using a cotton swab. This thin carbon layer serves as a catalyst for the triiodide to iodide regeneration reaction. The catalyst coating on the counter electrode should not be touched. It should not be rubbed or slide against the TiO₂

electrode or any other surface. The counter electrode should be picked up at the edges and carefully placed where it is desired.

3.5.6 Assemble of Cell

Earlier electrode and counter electrode have been made. Now electrode and counter electrode are placed face to face so that the TiO₂ film side of the electrode and catalyst-coated side of the counter electrode are in contact. Electrode and counter electrode were placed such a way that 5 mm strip of each glass slide was exposed. The two exposed sides of the device will later serve the contact points for the negative and positive electrodes. Now two binder clips were placed on the longer edges to hold the slides together. One or two drops of iodide electrolyte solution is put at one edge of the slides. Alternately each side of the solar cell is opened and closed by releasing and returning the binder clips. The liquid is drawn into the space between the electrodes by capillary action, and wets the stained TiO₂ film. It is ensured that all of the stained area is contacted by the electrolyte. Wipe off the excess electrolyte from the exposed areas of the glass using cotton swabs and tissues dampened with ethanol. It is important that the electrolyte is completely removed from the two

exposed sides of the cell. Alligator clips are fastened to the two exposed sides of the solar cell to make electrical contact to the finished device.

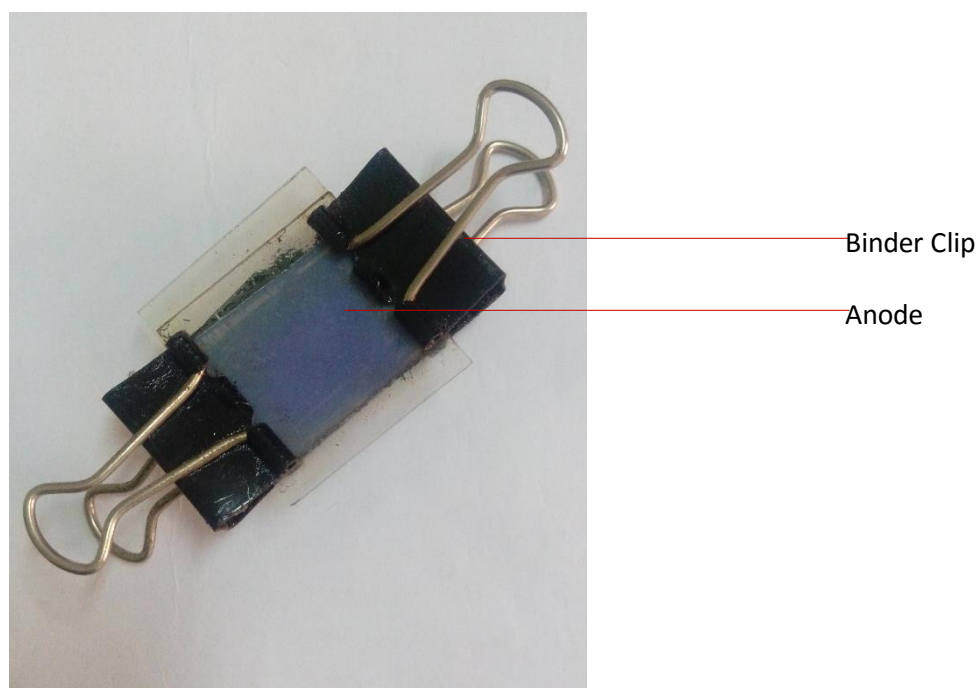


Figure 22 Complete Dye-Sensitized Solar Cell

3.5.7 Measuring Electrical Output Characteristics

The completed solar cell was taken outside under approximately $100\text{mW}/\text{cm}^2$ illumination by sunlight. If sunlight is not available than the cell can be illuminated by the beam of halogen lamp of a solar simulator. Two terminals of the multimeter is connected with two bare edges of the cell. The negative electrode is the TiO_2 coated glass and positive electrode is the catalyst coated glass. So black (-) wire of the multimeter was connected to the TiO_2 coated glass and the red, positive (+) wire to the counter electrode. Maximum voltage (open circuit voltage, V_{oc}) was measured by connecting the solar cell directly to a multimeter set to V (Volt). Maximum current (short circuit current, I_{sc}) was measured by connecting the solar cell directly to a multimeter set to mA (milliampere)

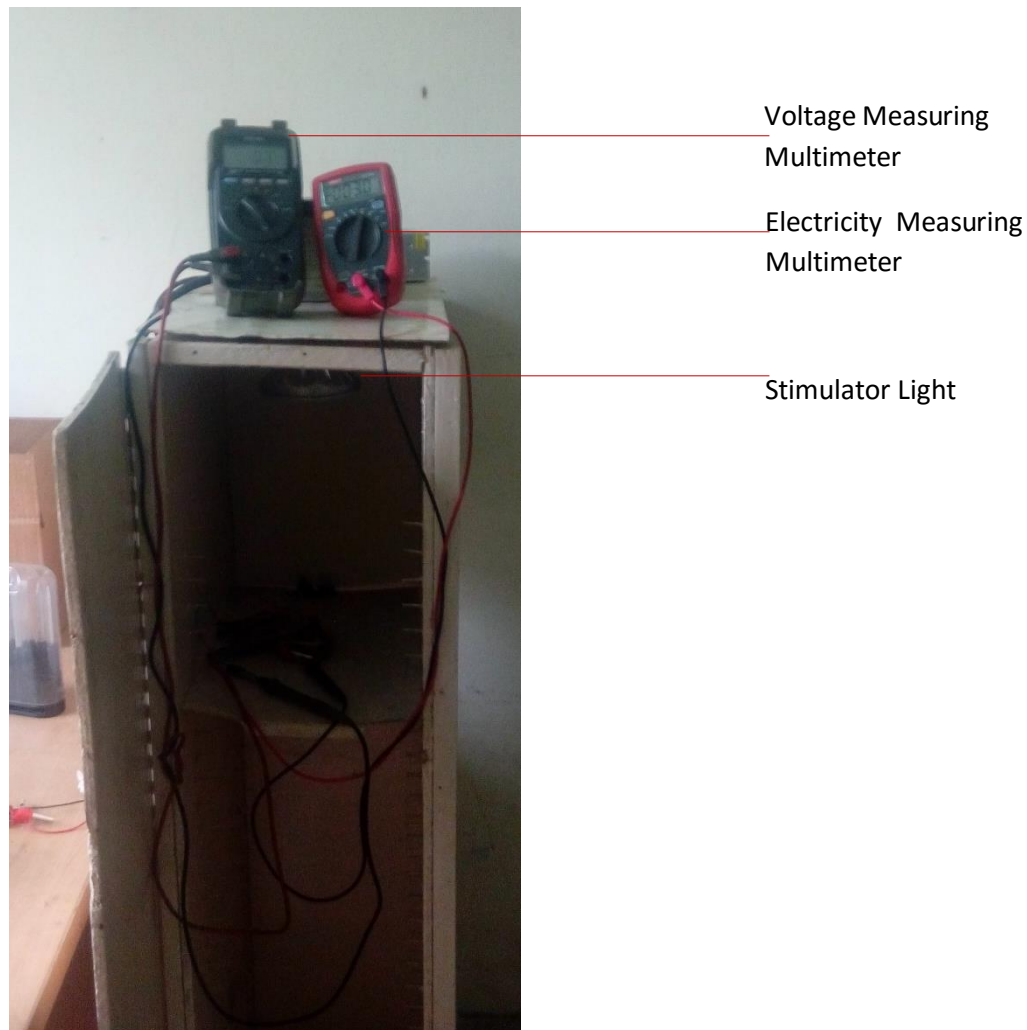


Figure 23 Set-up to Measure Voltage and Current of DSSC

3.6 Experiment Data

Table 3 Voltage and Current for Acetone Solvent(Carissa Carandas Soaked for 48 Hours)

No.	V(mV)	I(mA)
Isc	0	0.54
1	158.3	0.93
2	158.9	0.924
3	354.5	0.482
4	354.5	0.482
5	356.2	0.483
6	401	0.336
7	419	0.282
8	432	0.1971
9	444	0.1462
10	444	0.1462
11	461	0.1171
12	462	0.1082
13	467	0.0885
14	470	0.08
15	473	0.0704
16	474	0.0696
17	476	0.0568
18	478	0.0516
19	479	0.0469
20	480	0.0437
21	480	0.0437
Voc	522	0
No.	V(mV)	I(mA)

Table 4 Voltage and Current for Acetone Solvent (Carissa Carandas Soaked for 24 Hours)

No.	V(mV)	I(mA)
<i>I_{sc}</i>	0	0.54
1	158.3	0.93
2	158.9	0.924
3	354.5	0.482
4	354.5	0.482
5	356.2	0.483
6	401	0.336
7	419	0.282
8	432	0.1971
9	444	0.1462
10	444	0.1462
11	461	0.1171
12	462	0.1082
13	467	0.0885
14	470	0.08
15	473	0.0704
16	474	0.0696
17	476	0.0568
18	478	0.0516
19	479	0.0469
20	480	0.0437
<i>V_{oc}</i>	522	0

Table 5 Voltage and Current for Ethanol Solvent(Carissa Carandas Soaked for 48 Hours)

No.	V(mV)	I(mA)
<i>Isc</i>	0	2.43
1	220.9	1.331
2	222.8	1.233
3	230.7	1.2
4	232.7	1.216
5	234.9	1.227
6	240.3	1.231
7	336.7	0.621
8	380	0.3855
9	383	0.3039
10	388	0.2655
11	396	0.1931
12	400	0.1526
13	403	0.1345
14	406	0.0967
15	410	0.0904
16	414	0.0707
17	416	0.0645
18	423	0.0427
19	424	0.0408
20	425	0.0378
<i>Voc</i>	478	0

Table 6 Voltage and Current for Ethanol Solvent(Carissa Carandas Soaked for 24 Hours).

No.	V(mV)	I(mA)
<i>Isc</i>	0	2.33
1	215.6	1.195
2	216.1	1.196
3	216.9	1.2
4	217	1.201
5	364	0.2775
6	365	0.2734
7	378	0.1486
8	381	0.1133
9	385	0.07
10	388	0.0418
11	406	0.0358
12	410	0.0325
13	401	0.0325
14	415	0.0461
15	418	0.0418
16	422	0.0407
17	424	0.0409
18	427	0.0411
19	430	0.0412
20	431	0.0415
21	432	0.0415
<i>Voc</i>	405	0

Table 7 Voltage and Current for Isopropanol Solvent (Carissa Carandas Soaked for 48 Hours)

No.	V(mV)	I(mA)
<i>Isc</i>	0	0.9
1	452	0.169
2	453	0.135
3	454	0.12
4	455	0.0758
5	456	0.0643
6	457	0.0599
7	458	0.0497
8	459	0.0481
9	461	0.0455
10	462	0.0413
11	464	0.0402
12	465	0.0378
13	466	0.0347
14	467	0.0319
15	468	0.0319
<i>Voc</i>	480	0

Table 8 Voltage and Current for Isopropanol Solvent(Carissa Carandas Soaked for 24 Hours)

No.	V(mV)	I(mA)
<i>Isc</i>	0	1.15
1	195.3	1.116
2	195	1.113
3	194.4	1.11
4	192.6	1.105
5	198.7	1.084
6	199.9	1.085
7	200.4	1.086
8	202.2	1.096
9	362	0.2864
10	376	0.1779
11	381	0.1391
12	386	0.1112
13	389	0.0905
14	391	0.0761
15	393	0.0695
16	397	0.0505
17	399	0.0457
18	400	0.0385
19	401	0.037
20	403	0.0371
21	406	0.0372
<i>Voc</i>	467	0

Table 9 Voltage and Current for Methanol Solvent(Carissa Carandas Soaked for 48 Hours)

No.	V(mV)	I(mA)
<i>Isc</i>	0	1.09
1	156	0.978
2	156	0.978
3	156	0.978
4	156	0.978
5	156	0.978
6	156	0.978
7	156	0.978
8	156	0.978
9	156	0.978
10	156	0.978
11	168	0.984
12	171	0.986
13	185	0.99
14	193	0.991
15	197	0.999
16	225	1.001
17	229	1.018
18	330	1.011
19	353	0.999
20	361	0.94
21	369	0.94
<i>Voc</i>	508	0

Table 10 Voltage and Current for Methanol Solvent(Carissa Carandas Soaked for 24 Hours)

No.	V(mV)	I(mA)
<i>Isc</i>	0	0.9
1	167	0.455
2	171	0.457
3	174.3	0.459
4	174.4	0.46
5	201	0.364
6	211.1	0.3323
7	214.6	0.2884
8	231.1	0.2736
9	236.4	0.2144
10	249.9	0.1685
11	258.6	0.167
12	264.1	0.1008
13	277.3	0.1009
14	334	0.0669
15	330.1	0.066
16	341	0.0576
17	350	0.0453
18	350	0.0453
19	350	0.0453
20	350	0.0453
21	350	0.0453
<i>Voc</i>	467	0

Table 11 Voltage and Current for Anode Soaked in Carissa Carandas Dye (Ethanol Solvent) for 30 minutes

No.	V(mV)	I(mA)
<i>Isc</i>	0	0.9
1	151	0.888
2	152	0.876
3	153	0.874
4	155.1	0.891
5	157	0.882
6	160.4	0.908
7	161.4	0.903
8	163.2	0.899
9	164	0.88
10	177	0.882
11	170	0.881
12	171.5	0.868
13	172.1	0.88
14	174.3	0.879
15	176.9	0.882
16	181	0.88
17	181	0.88
18	181	0.88
19	181	0.88
20	181	0.88
21	181	0.88
<i>Voc</i>	540	0

Table 12 Voltage and Current for Anode Soaked in Carissa Carandas Dye (Ethanol Solvent) for 1 hour

No.	V(mV)	I(mA)
<i>Isc</i>	0	2.33
1	215.6	1.195
2	216.1	1.196
3	216.9	1.2
4	217	1.201
5	364	0.2775
6	365	0.2734
7	378	0.1486
8	381	0.1133
9	385	0.07
10	388	0.0418
11	406	0.0358
12	410	0.0325
13	401	0.0325
14	415	0.0461
15	418	0.0418
16	422	0.0407
17	424	0.0409
18	427	0.0411
19	430	0.0412
20	431	0.0415
21	432	0.0415
<i>Voc</i>	405	0

Table 13 Voltage and Current for Anode Soaked in Carissa Carandas Dye (Ethanol Solvent) for 2 hour

No.	V(mV)	I(mA)
<i>Isc</i>	0	0.78
1	146.4	0.683
2	145.7	0.679
3	153.2	0.672
4	154.6	0.678
5	167.4	0.685
6	327.6	0.397
7	340.1	0.327
8	341.9	0.3274
9	371	0.2305
10	379	0.1948
11	388	0.1944
12	396	0.1294
13	399	0.11149
14	401	0.1056
15	406	0.0965
16	408	0.0756
17	409	0.069
18	411	0.0378
19	411	0.0378
20	411	0.0978
21	411	0.0378
<i>Voc</i>	436	0

Table 14 Voltage and Current for Anode Soaked in Carissa Carandas Dye (Ethanol Solvent) for 2.5 hour

No.	V(mV)	I(mA)
<i>Isc</i>	0	0.9
1	151	0.888
2	152	0.876
3	153	0.874
4	155.1	0.891
5	157	0.882
6	160.4	0.908
7	161.4	0.903
8	163.2	0.899
9	164	0.88
10	177	0.882
11	170	0.881
12	171.5	0.868
13	172.1	0.88
14	174.3	0.879
15	176.9	0.882
16	181	0.88
17	181	0.88
18	181	0.88
19	181	0.88
20	181	0.88
21	181	0.88
<i>Voc</i>	540	0

3.7 Conclusion

This chapter all the necessary chemical, machine and instrument required to fabricate Dye-sensitized Solar cell is listed. Later the details of working procedure is included. All the data of voltage and current is also added here.

4.0 Result and Discussion

4.1 Introduction

In this chapter all the results from the experiments are included. I-V and P-V curve of DSSC for each solvent is described. Afterwards comparison between various parameter like open circuit voltage, fill factor, short circuit current is conducted.

4.2 Comparison between Different Parameters Varying Soaking Time of *Carissa Carandas* in Different Solvent

4.2.1 Ethanol Solvent

Table 15 Comparison Between Different Parameters Varying Soaking Time of *Carissa Carandas* in Ethanol Solvent

	Isc(mA)	Voc(mV)	I _{max} (mA)	V _{max} (mV)	P _{max} (μ W)	FF	η (%)
24h	2.33	405	1.201	217	260.617	0.2761	0.09582
48h	2.43	478	1.231	240.3	295.809	0.2546	0.10271

Figure 5 shows the I-V characteristics of a DSSC operating under normal conditions. The power delivered by a solar cell is the product of current and voltage ($I \times V$). If the multiplication is done, point for point, for all voltages from short-circuit to open-circuit conditions, the power curve above is obtained for a given radiation level.

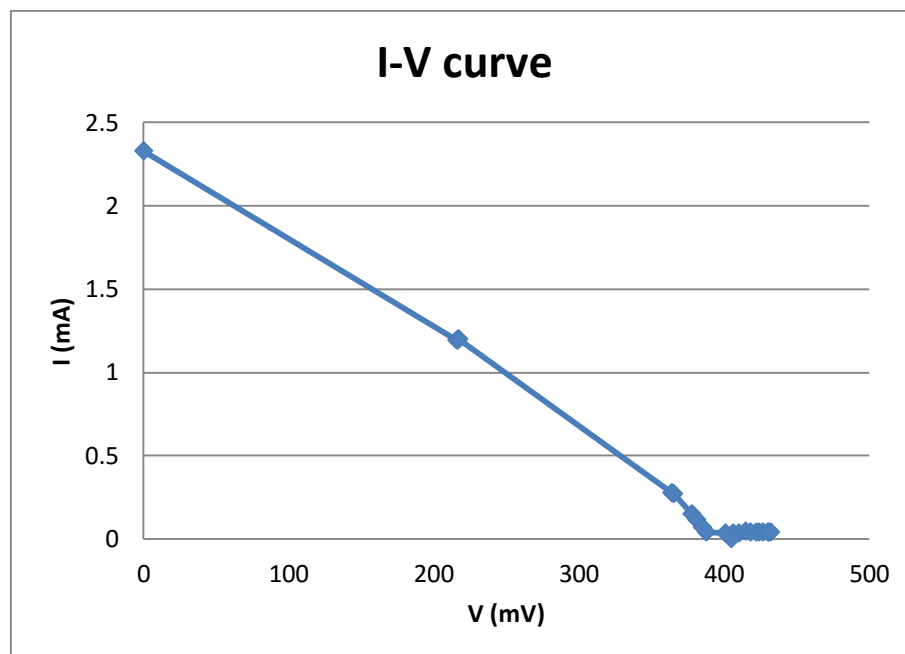


Figure 24 I-V curve of DSSC in *Carissa Carandas* dye (Soaked for 24 Hours)

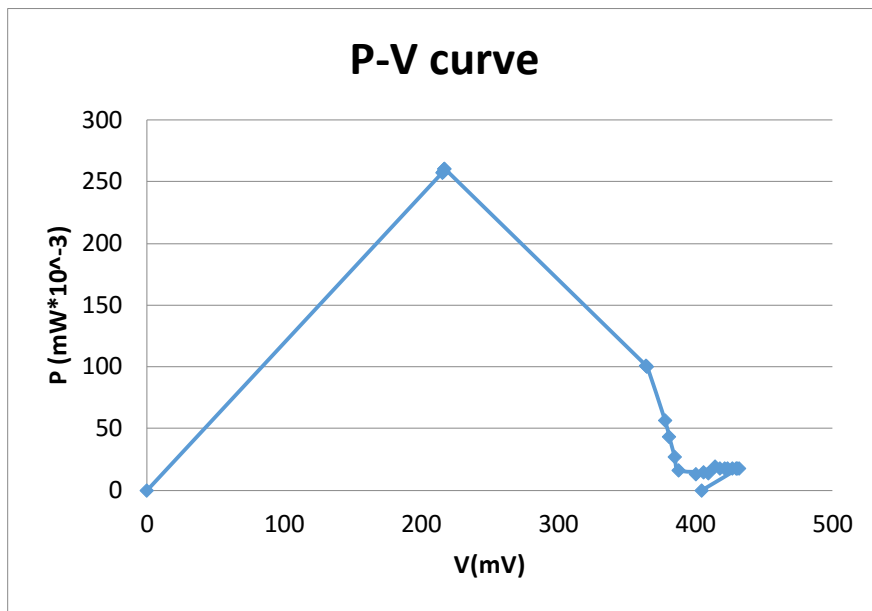


Figure 25 P-V curve of DSSC in Carissa Carandas dye(Soaked for 24 Hours)

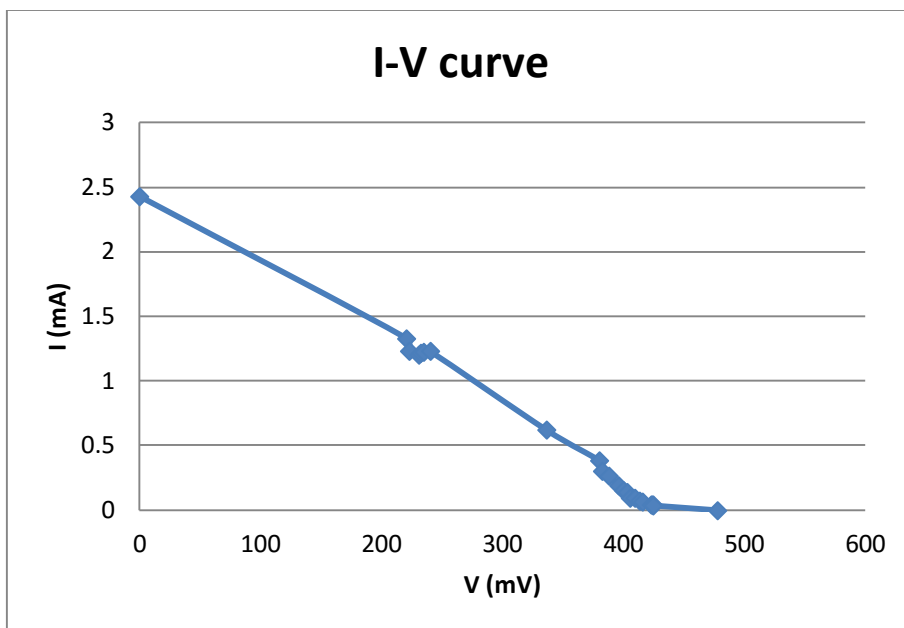


Figure 26 I-V curve of DSSC in Carissa Carandas dye(Soaked for 48 Hours)

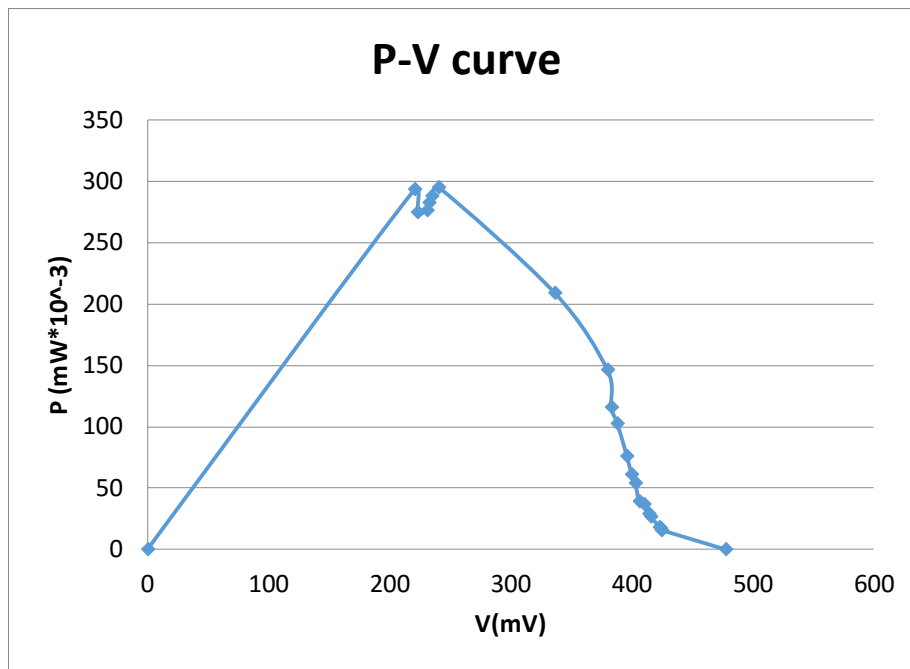


Figure 27 P-V curve of DSSC in Carissa Carandas dye (Soaked for 48 Hours). With the solar cell open-circuited, that is no load, the current will be at its minimum (zero) and the voltage across the cell is at its maximum, known as the solar cells open circuit voltage, or V_{oc} . For 24h & 48h soaking time the open circuit voltage is 405mV & 478mV. On the other hand, when the solar cell is short circuited, that is the positive and negative leads connected together, the voltage across the cell is at its minimum (zero) but the current flowing out of the cell reaches its maximum, known as the solar cells short circuit current, or I_{sc} . Here the short circuit current is 2.33mA and 2.43mA. This current amount is very high.

However, there is one particular combination of current and voltage for which the power reaches its maximum value, at I_{mp} and V_{mp} . In other words, the point at which the cell generates maximum electrical power which is the “maximum power point” or MPP. For 24h & 48h soaking time the maximum power for this particular sample is 260.617 μ W & 295.809 μ W. Therefore the ideal operation of a photovoltaic cell is defined to be at the maximum power point. The maximum power point (MPP) of a solar cell is positioned near the bend in the I-V characteristics curve.

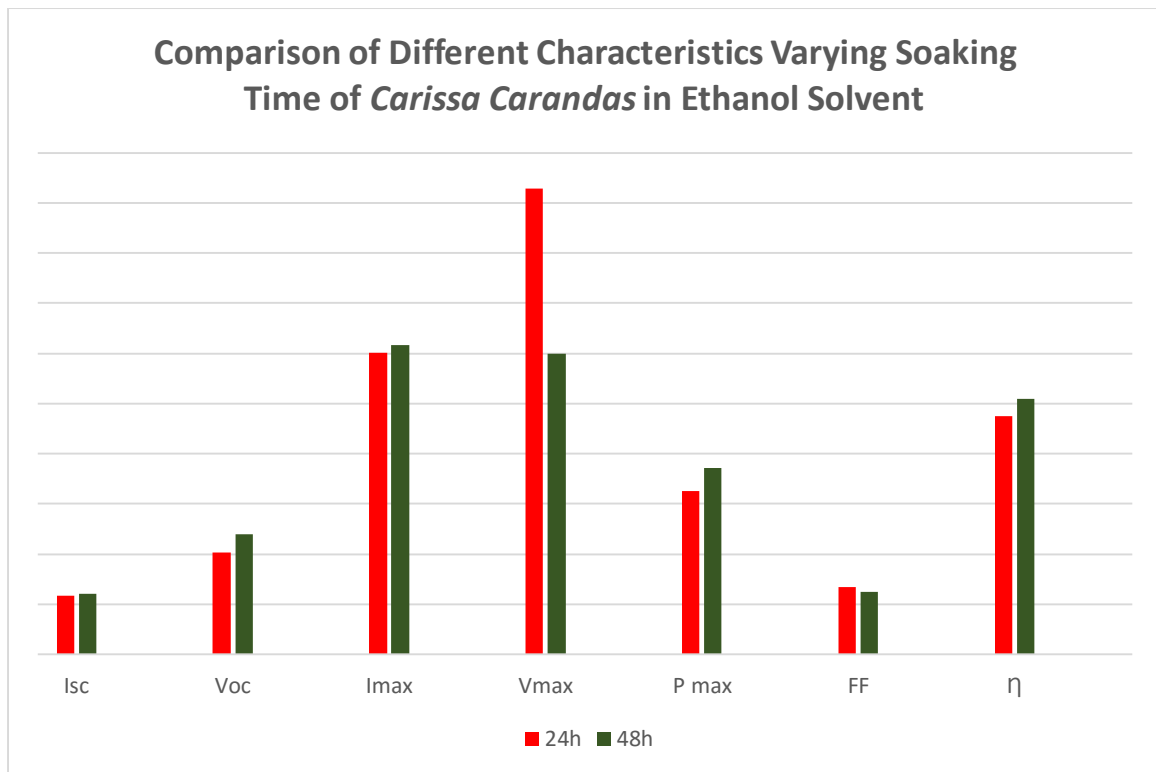


Figure 28 Comparison of Different Characteristics Varying Soaking Time of *Carissa Carandas* in Ethanol Solvent

In Figure 28 the various parameter of DSSC for two different soaking condition is compared. From the bar chart it is seen that short circuit current, open circuit current, maximum power is high when kromcha is soaked for 48 hours. Most parameter even efficiency is increased when kromcha is soaked for 48 hours.

4.2.2 Methanol Solvent

Table 16 Comparison Between Different Parameters Varying Soaking Time of *Carissa Carandas* in Methanol Solvent

	Isc(mA)	Voc(mV)	Imax(mA)	Vmax(mV)	Pmax(μ W)	FF	η(%)
24h	.9	467	.46	174.4	80.224	.19	.02786
48h	1.09	508	.999	197	196.803	.3559	.0724

Figure 5 shows the I-V characteristics of a DSSC operating under normal conditions. The power delivered by a solar cell is the product of current and voltage ($I \times V$). If the multiplication is done, point for point, for all voltages from short-circuit to open-circuit conditions, the power curve above is obtained for a given radiation level.

With the solar cell open-circuited, that is no load, the current will be at its minimum (zero) and the voltage across the cell is at its maximum, known as the solar cells open circuit voltage, or V_{oc} . For 24h & 48h soaking time the open circuit voltage is 466mV & 508mV. On the other hand, when the solar cell is short circuited, that is the positive and negative leads connected together, the voltage across the cell is at its minimum (zero) but the current flowing out of the cell reaches its maximum, known as the solar cells short circuit current, or I_{sc} . Here the short circuit current is 0.9mA and 1.09mA. This current amount is very high.

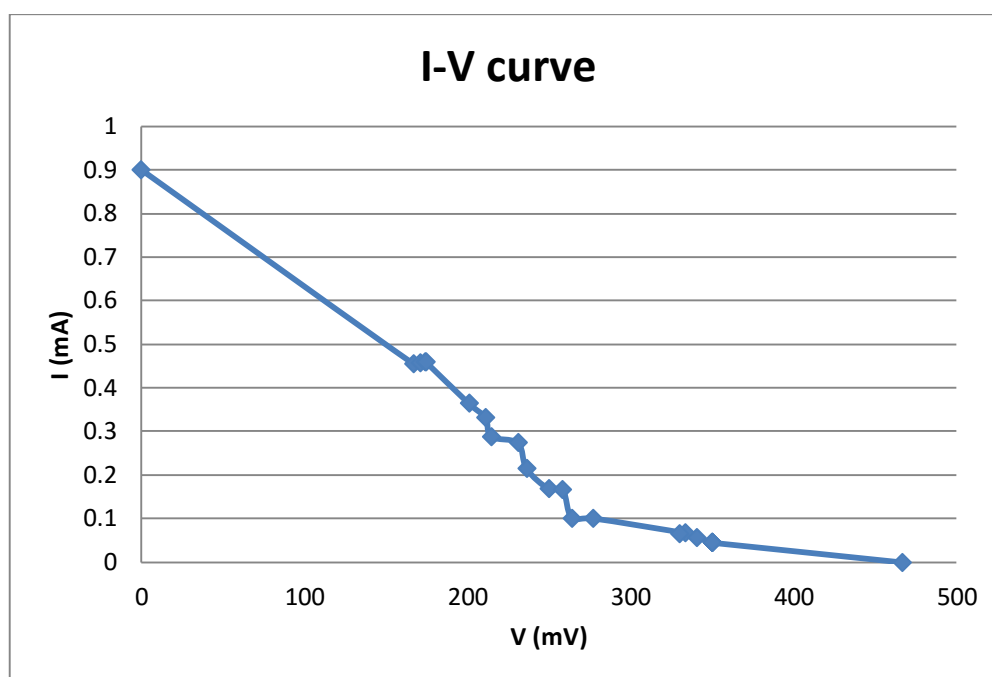


Figure 29 I-V curve of DSSC in Carissa Carandas dye (Soaked for 24 Hours)

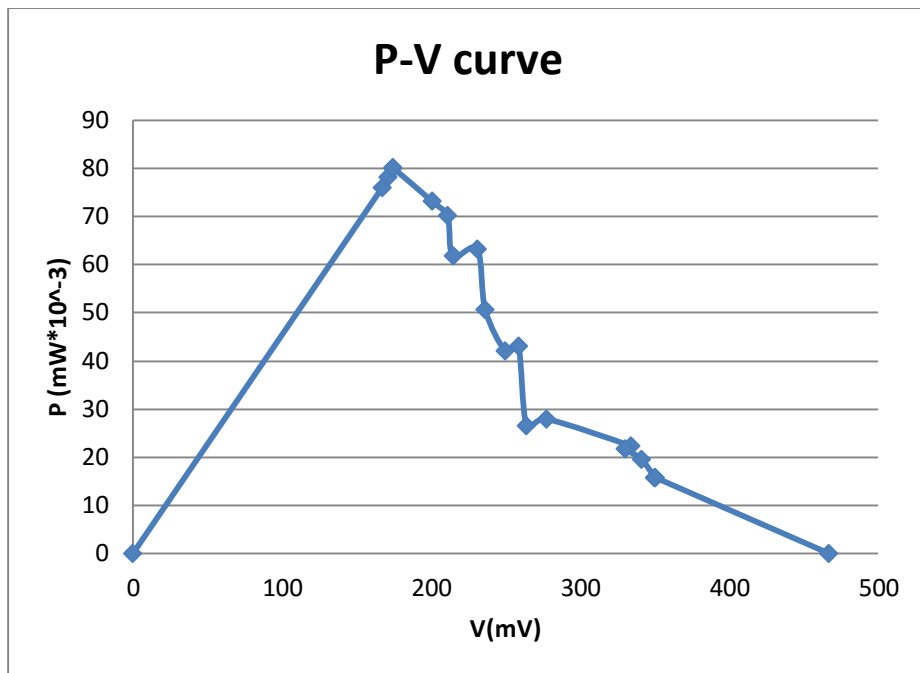


Figure 30 P -V curve of DSSC in Carissa Carandas dye (Soaked for 24 Hours)

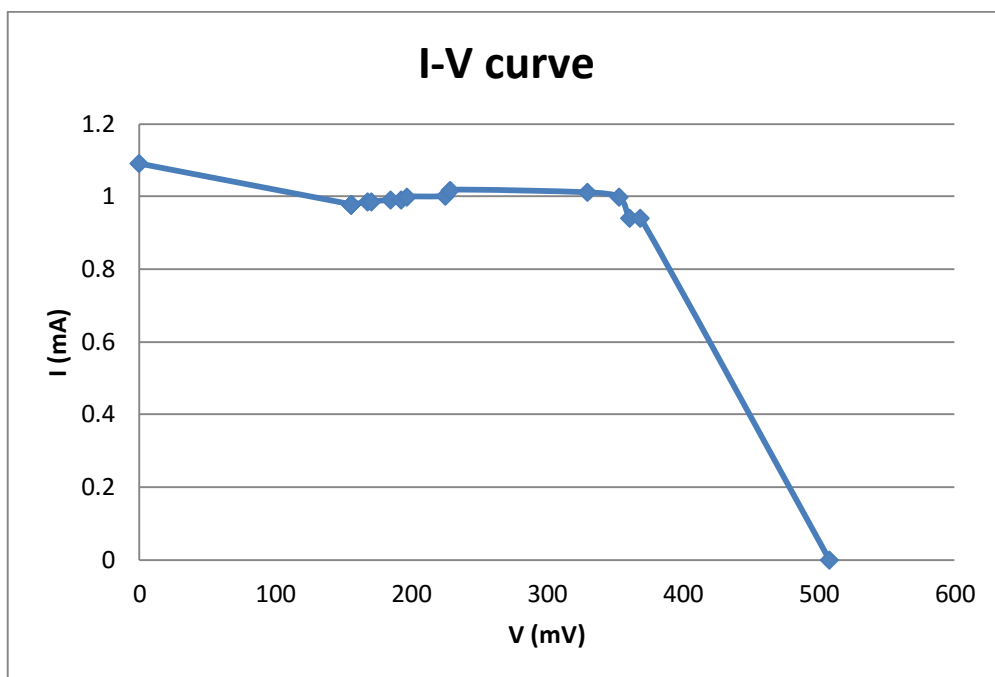


Figure 31 I-V curve of DSSC in Carissa Carandas dye (Soaked for 48 Hours)

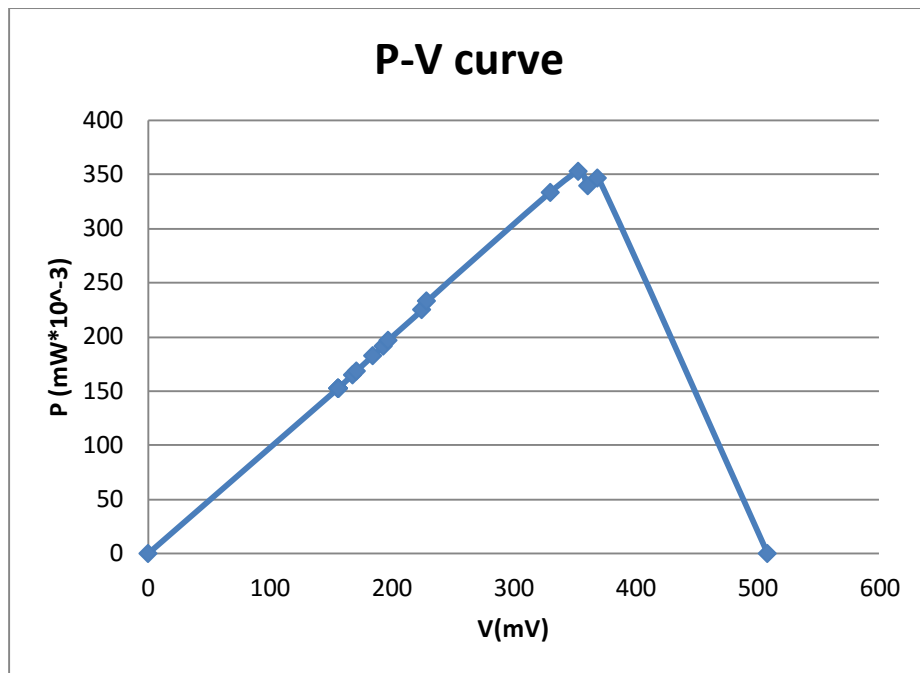


Figure 32 P-V curve of DSSC in Carissa Carandas dye (Soaked for 48 Hours)

However, there is one particular combination of current and voltage for which the power reaches its maximum value, at I_{mp} and V_{mp} . In other words, the point at which the cell generates maximum electrical power which is the “maximum power point” or MPP. For For 24h & 48h soaking time the maximum power for this particular sample is $80.224\mu\text{W}$ & $195.809\mu\text{W}$. Therefore the ideal operation of a photovoltaic cell is defined to be at the maximum power point. The maximum power point (MPP) of a solar cell is positioned near the bend in the I-V characteristics curve

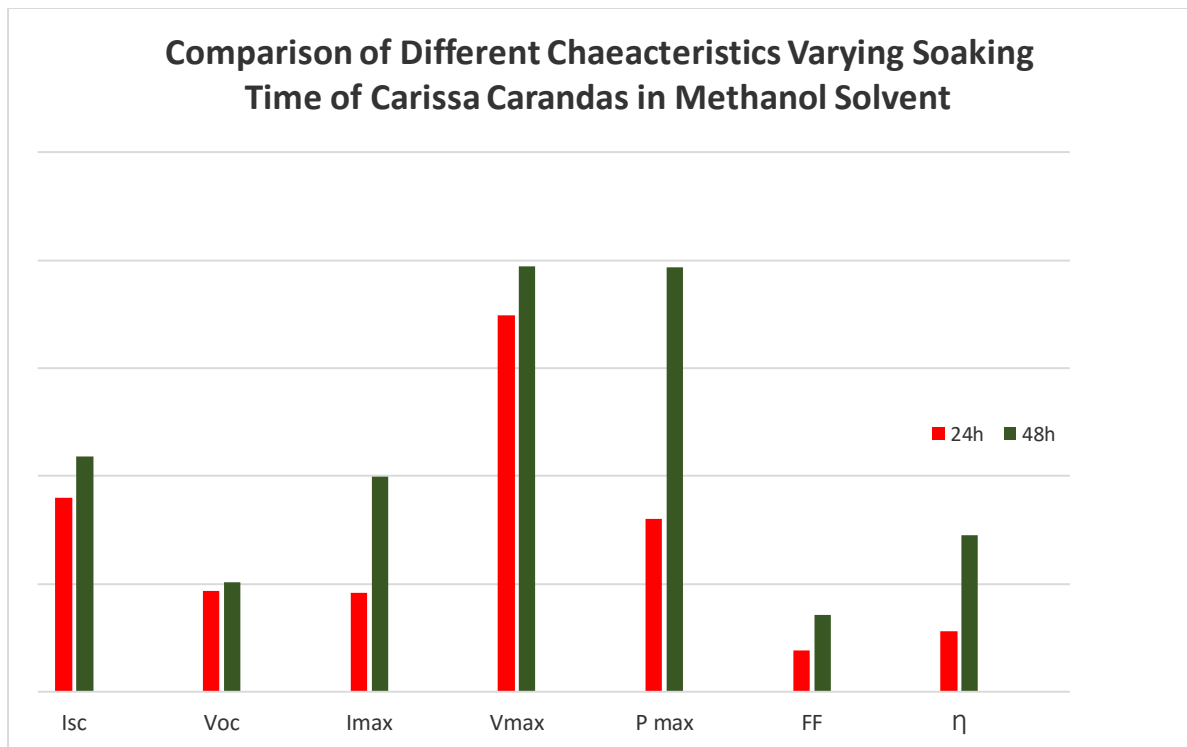


Figure 33 Comparison of Different Characteristics Varying Soaking Time of Carissa Carandas in Methanol Solvent

From figure 33 it is seen that every parameter like short circuit current, open circuit voltage, fill factor, efficiency everything is high when cranberry is soaked for 48 hours. So for methanol solvent the fruit should be soaked for 48 hours

4.2.3 Acetone Solvent

Table 17 Comparison Between Different Parameters Varying Soaking Time of Carissa Carandas in Acetone Solvent

	Isc(mA)	Voc(mV)	I _{max} (mA)	V _{max} (mV)	P _{max} (μ W)	FF	η (%)
24h	.9	540	.882	177	156.114	.3212	.04337
48h	.54	522	.483	336.2	172.0446	.6103	.04779

With the solar cell open-circuited, that is no load, the current will be at its minimum (zero) and the voltage across the cell is at its maximum, known as the solar cells open circuit voltage, or Voc. For 24h & 48h soaking time the open circuit voltage is 540mV & 522mV. On the other hand, when the solar cell is short circuited, that is the positive and negative leads connected together, the voltage across the cell is at its minimum (zero) but the current flowing out of the cell reaches its maximum, known as the solar cells short circuit current, or Isc. Here the short circuit current is 0.9mA and 0.54mA. The I-V curve is almost similar to ideal curve.

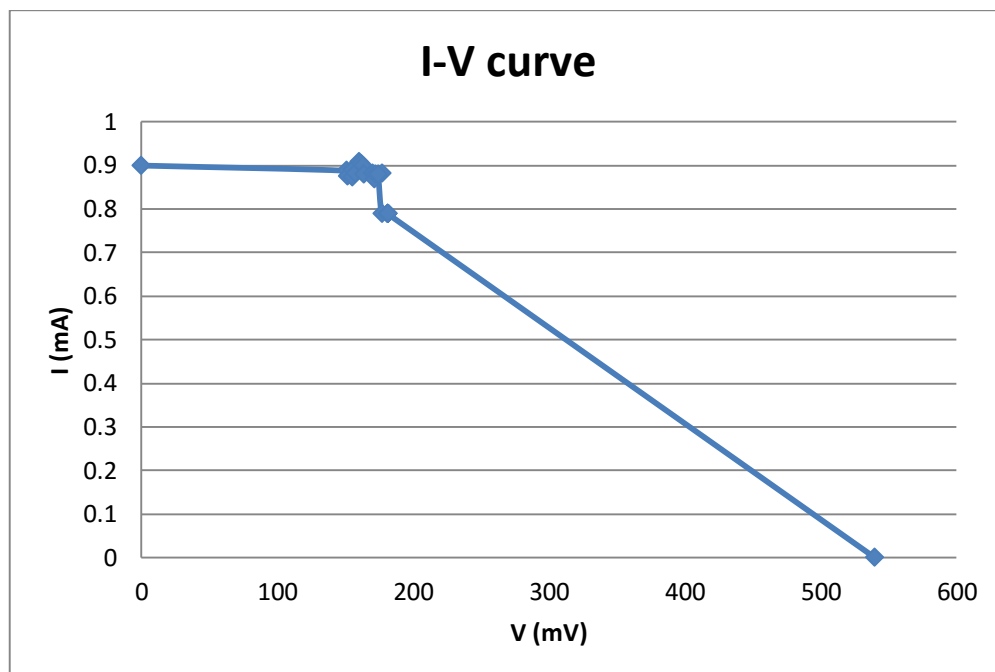


Figure 34 I-V curve of DSSC in Carissa Carandas dye (Soaked for 24 Hours)

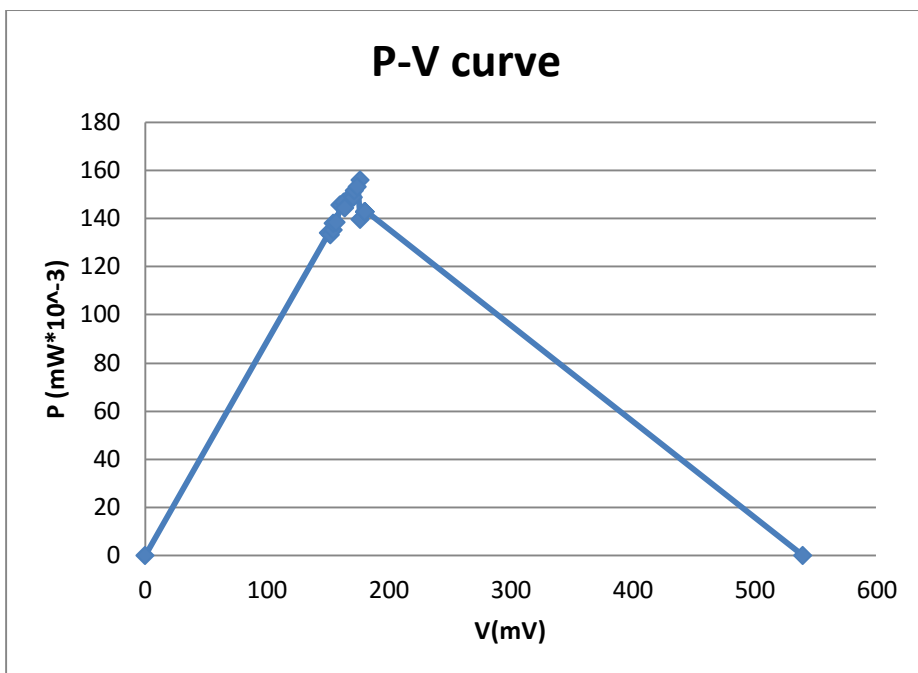


Figure 35 P-V curve of DSSC in Carissa Carandas dye (Soaked for 24 Hours)

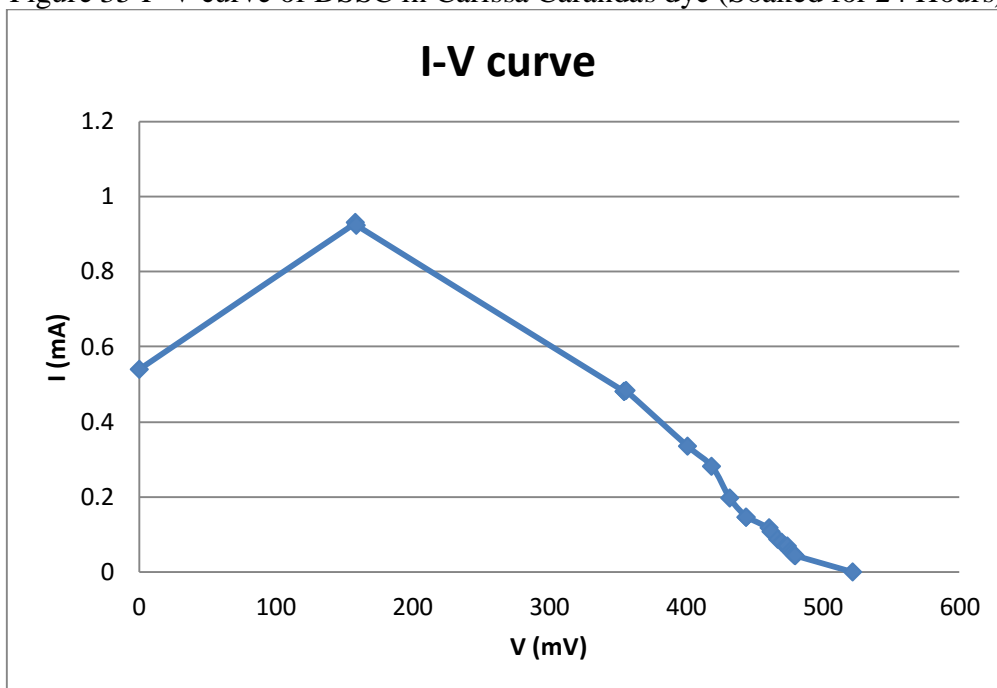


Figure 36 I-V curve of DSSC in Carissa Carandas dye (Soaked for 48 Hours)

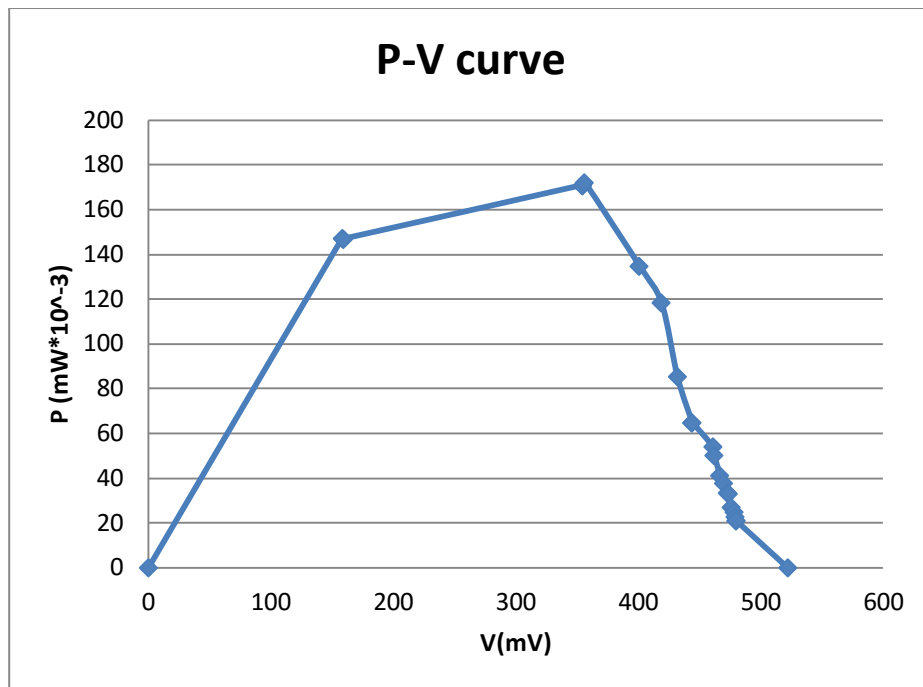


Figure 37 P-V curve of DSSC in Carissa Carandas dye (Soaked for 48 Hours)

However, there is one particular combination of current and voltage for which the power reaches its maximum value, at I_{mp} and V_{mp} . In other words, the point at which the cell generates maximum electrical power which is the “maximum power point” or MPP. For For 24h & 48h soaking time the maximum power for this particular sample is $156.617\mu W$ & $172.809\mu W$. Therefore the ideal operation of a photovoltaic cell is defined to be at the maximum power point. The maximum power point (MPP) of a solar cell is positioned near the bend in the I-V characteristics curve

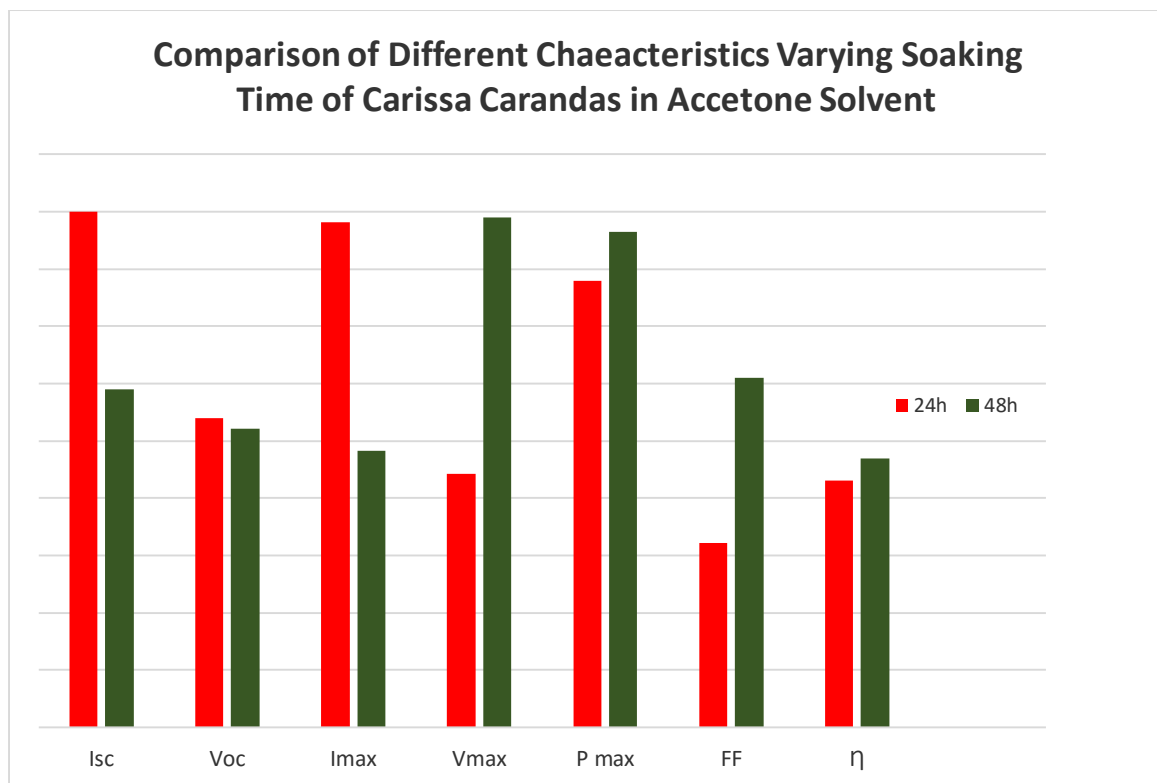


Figure 38 Comparison of Different Characteristics Varying Soaking Time of Carissa Carandas in Acetone Solvent

In Figure 38 the various parameter of DSSC for two different soaking condition is compared. From the bar chart it is seen that short circuit current, open circuit current, maximum power is high when kromcha is soaked for 24 hours. But efficiency, fill factor, maximum power is high when the fruit is soaked for 48 hour. So best result is found when *Carissa Carandas* is soaked for 48 hours/

4.2.4 Isopropanol Solvent

Table 18 Comparison Between Different Parameters Varying Soaking Time of Carissa Carandas in Isopropanol Solvent

	Isc(mA)	Voc(mV)	Imax(mA)	Vmax(mV)	Pmax(μ W)	FF	η (%)
24h	1.16	467	1.096	202.2	221.6112	.413	.062
48h	.9	480	.169	452	76.388	.1768	.02652

With the solar cell open-circuited, that is no load, the current will be at its minimum (zero) and the voltage across the cell is at its maximum, known as the solar cells open circuit voltage, or Voc. For 24h & 48h soaking time the open circuit voltage is 467mV & 480mV.

On the other hand, when the solar cell is short circuited, that is the positive and negative leads connected together, the voltage across the cell is at its minimum (zero) but the current flowing out of the cell reaches its maximum, known as the solar cells short circuit current, or I_{sc} . Here the short circuit current is 1.1 mA and 0.9 mA. This current amount is very high

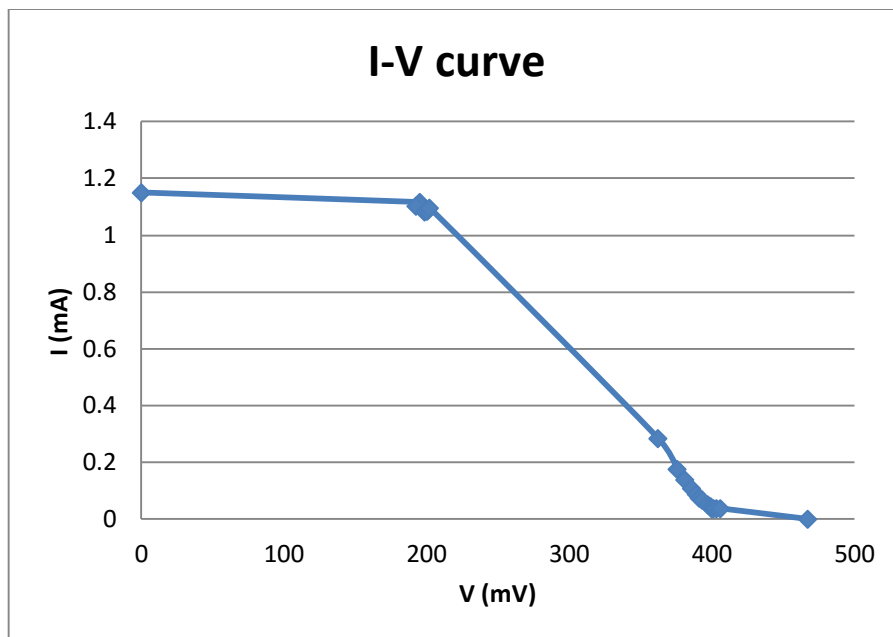


Figure 39 I-V curve of DSSC in Carissa Carandas dye (Soaked for 24 Hours)

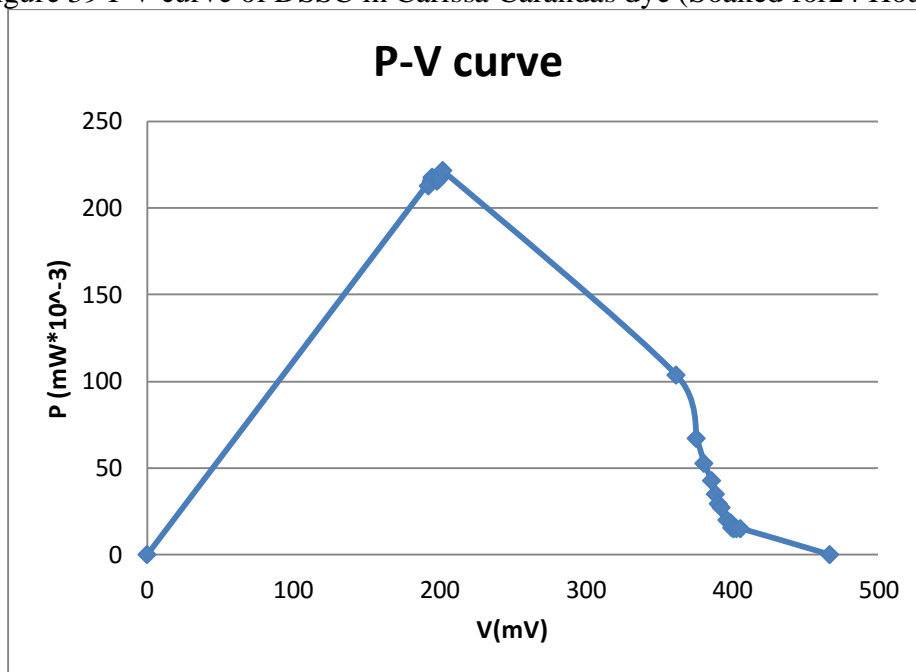


Figure 40 P-V curve of DSSC in Carissa Carandas dye (Soaked for 24 Hours)

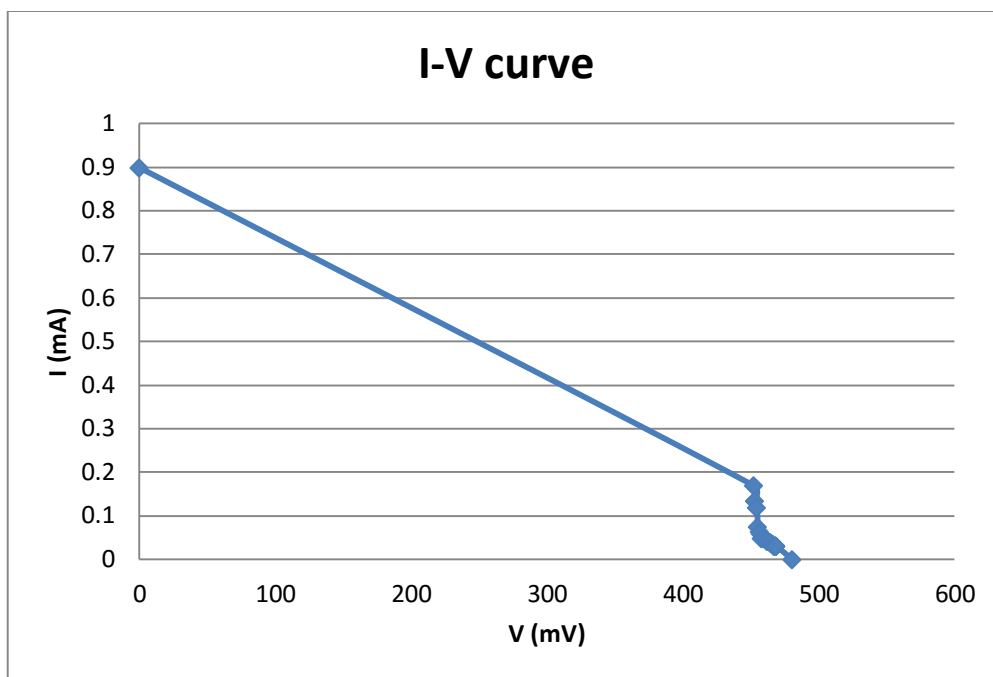


Figure 41 I-V curve of DSSC in Carissa Carandas dye (Soaked for 48 Hours)

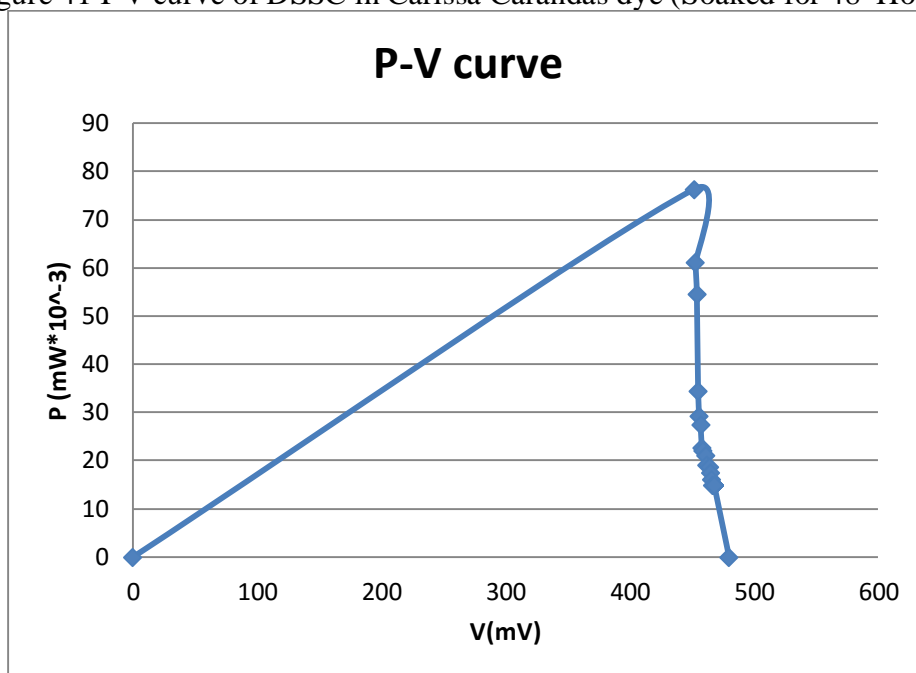


Figure 42 P-V curve of DSSC in Carissa Carandas dye (Soaked for 48 Hours)

However, there is one particular combination of current and voltage for which the power reaches its maximum value, at I_{mp} and V_{mp} . In other words, the point at which the cell generates maximum electrical power which is the “maximum power point” or MPP. For For 24h & 48h soaking time the maximum power for this particular sample is $221.617\mu W$ & $76.55\mu W$. Therefore the ideal operation of a photovoltaic cell is defined to be at the maximum power point. The maximum power point (MPP) of a solar cell is positioned near the bend in the I-V characteristics curve

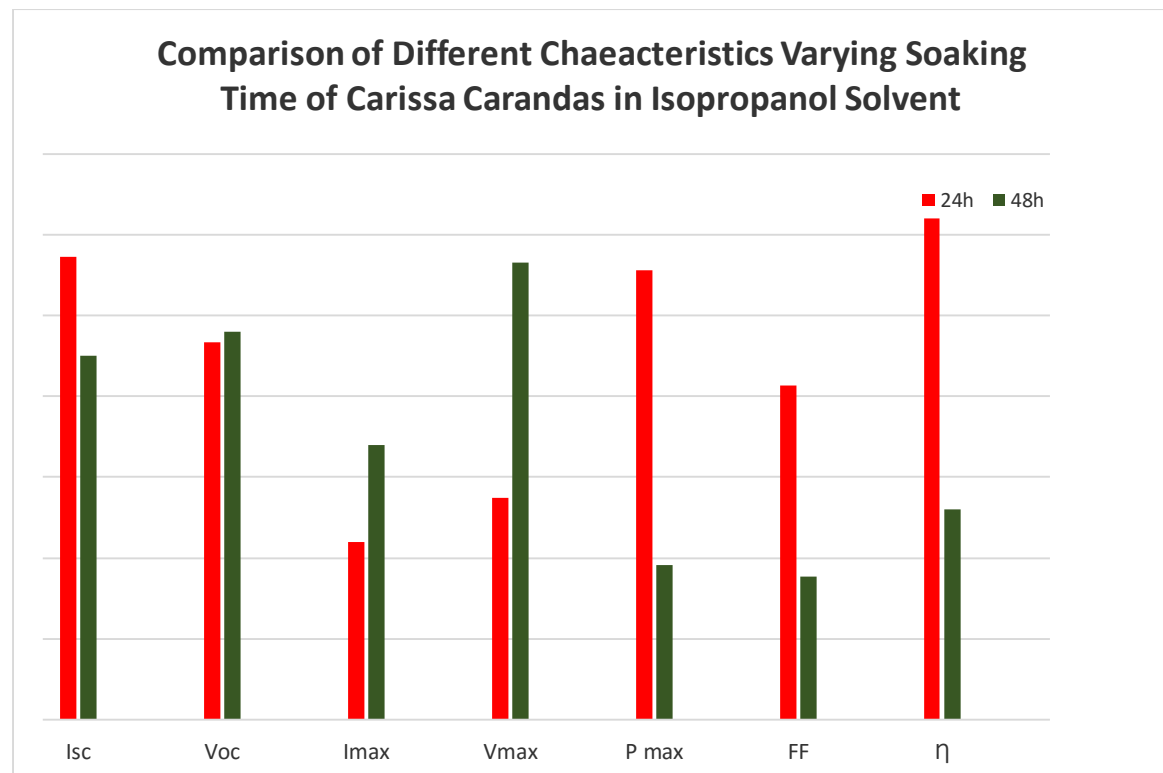


Figure 43 Comparison of Different Characteristics Varying Soaking Time of Carissa Carandas in Isopropanol Solvent

In Figure 43 the various parameter of DSSC for two different soaking condition is compared. From the bar chart it is seen that short circuit current, open circuit current, maximum power is high when kromcha is soaked for 48 hours. But as the fill factor

is high for 24 hours soaking time best result is found when *Carissa Carandas* is soaked for 24 hours.

4.3 UV-Visible Absorption Spectra For *Carissa Carandas* Dye

It is found that dyes extracted by water of room temperature and boiling water both have absorption peak at 680 nm (Fig. 5.23 A, B) corresponds to the energy of 1.83 eV and another higher absorption peak is 520 nm corresponds to the energy of 2.39 eV. Again, dyes extracted by ethanol, methanol, and acetone have absorption peak at around 665 nm (Fig. 5.23 C, D, E) corresponds to the energy of 1.87 eV and another higher absorption peak at around 430 nm correspond to the energy of 2.89 eV. The energy associated with the longer wavelengths corresponds to lower energies are not sufficient to overcome the band-gap of P25 (3.1 eV) which has been used on photo anode as semiconductor oxide. So, it can be assumed that extracted dyes having absorption peak of longer wavelengths will not be a good sensitizer

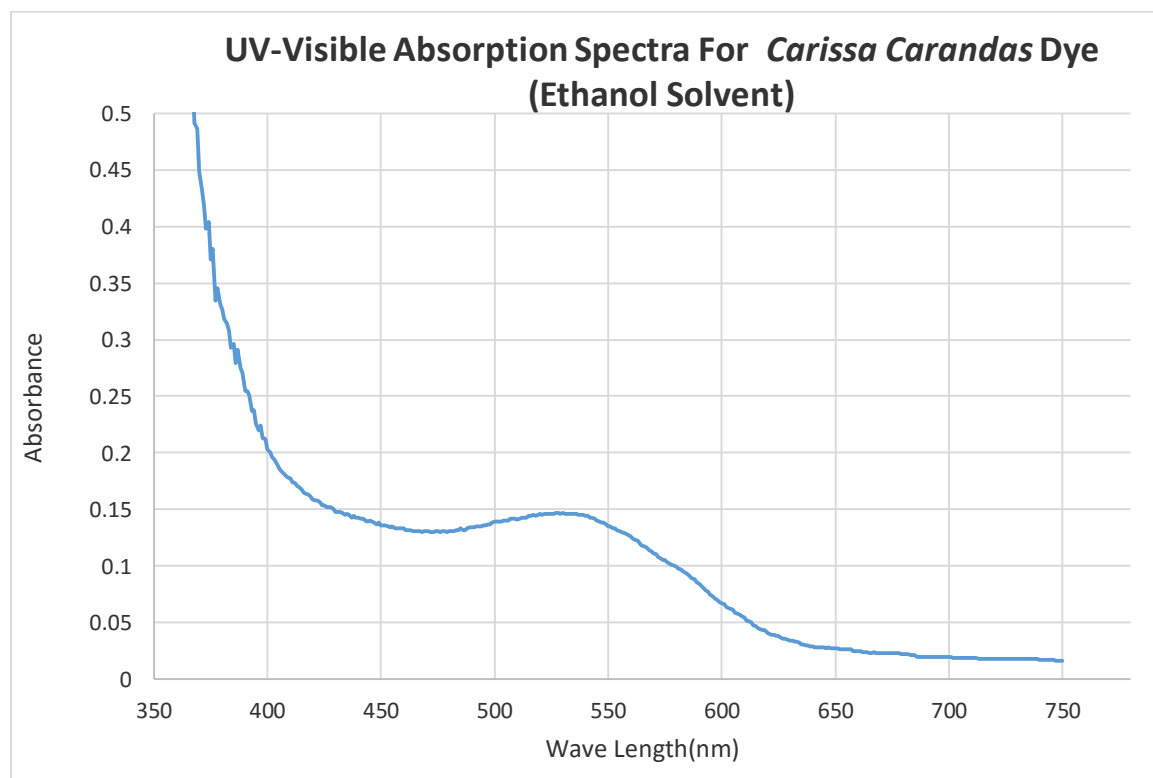


Figure 44 UV-Visible Absorption Spectra For *Carissa Carandas* Dye (Ethanol Solvent)

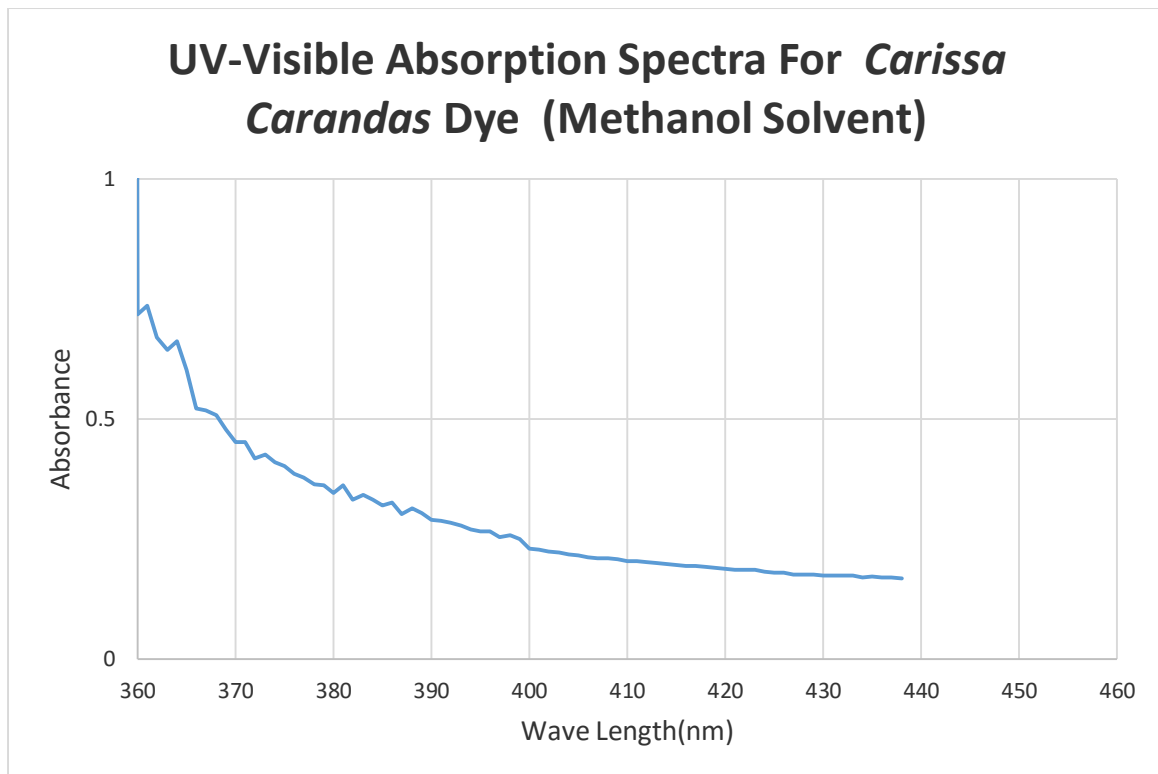


Figure 45 UV-Visible Absorption Spectra For *Carissa Carandas* Dye (Methanol Solvent)

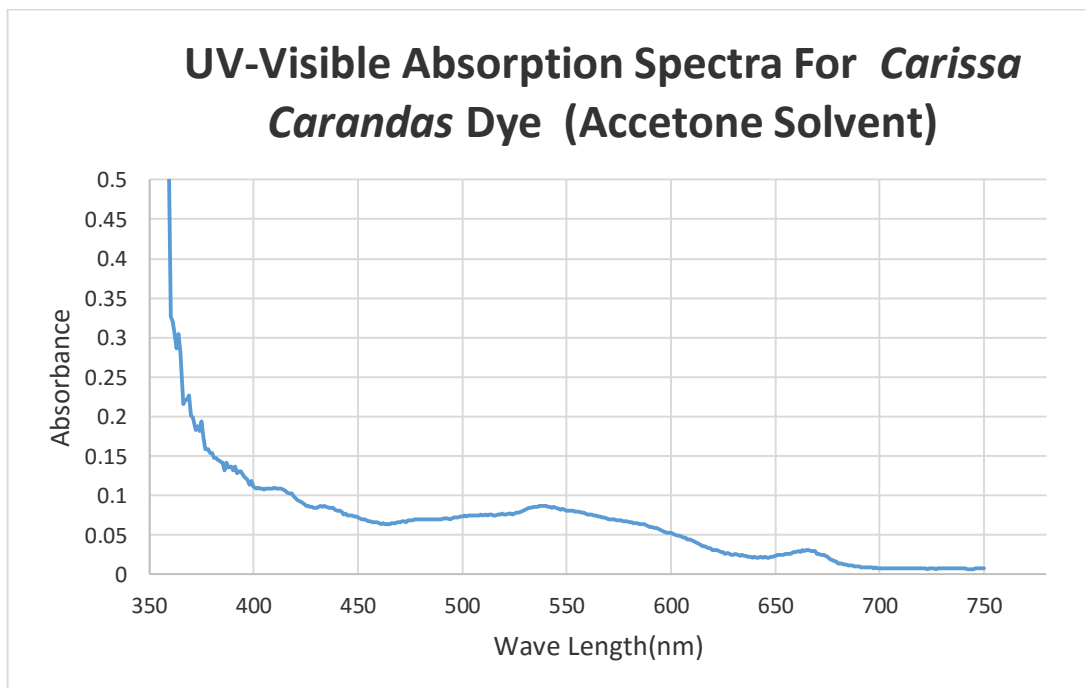


Figure 46 UV-Visible Absorption Spectra for *Carissa Carandas* Dye (Acetone Solvent)

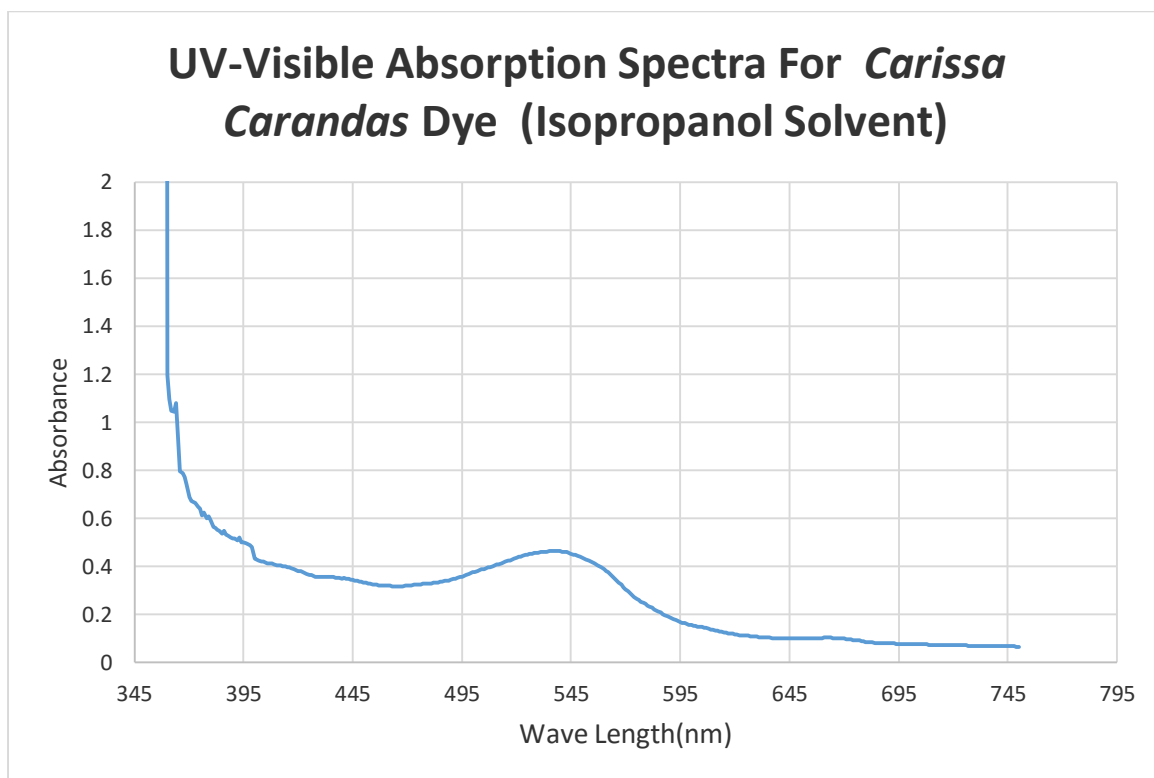


Figure 47 UV-Visible Absorption Spectra For Carissa Carandas Dye (Isopropanol Solvent)

On the other hand, the energy associated with the absorption peak (430 nm) of ethanol, methanol, and acetone extracted dyes were near similar to the band gap energy of Degussa P25. So, mostly the energy associated with second absorption peaks are responsible for the transition of electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Though ethanol, methanol, and acetone extracts showed almost same absorption peaks but from table 5.16 it was found that acetone extract showed maximum cell efficiency which suggested that the pigment which responsible for the peak around 430 nm in acetone extract have higher electron splitting ability compared to the pigments of ethanol and methanol extract.

4.4 FTIR of Best Dye

The fruit has been credited for various phytoconstituents. To analyze the phytochemicals found in AEE, we used complementary measurement by FTIR spectroscopy (fingerprints of functional groups). The IR spectra (fig.2) lies in the range of 4000-500 cm^{-1} and can be approximately divided into four regions and the nature of the group frequency may generally be determined by the region in which it is located

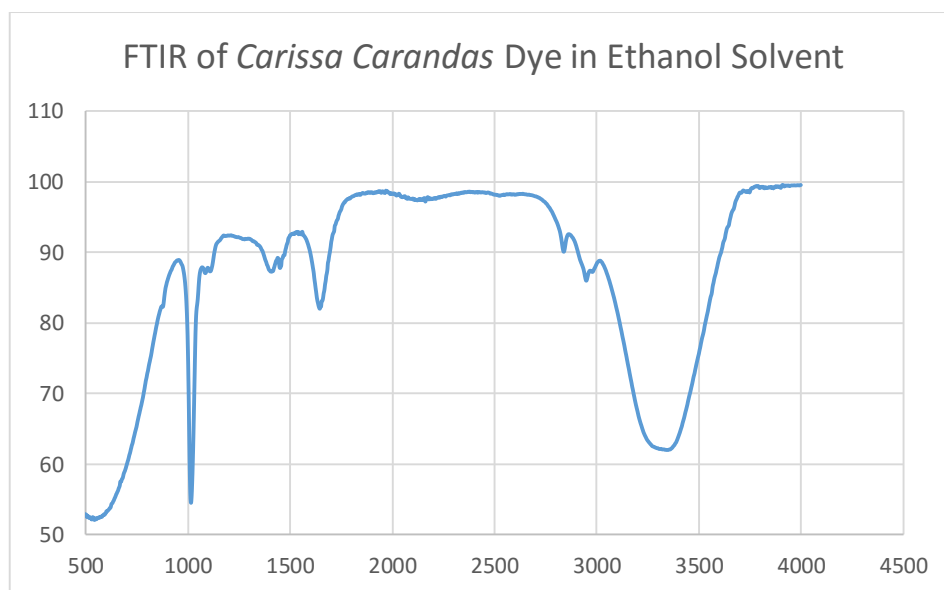


Figure 48 FTIR of Carissa Carandas Dye in Ethanol Solvent

The regions are generalised as X-H stretching (4000- 2500 cm^{-1}), triple bond stretching (2500-2000 cm^{-1}), double bond stretching (2000-1500 cm^{-1}) and fingerprint region (1500-600 cm^{-1}). The broad peak at 3357.70 cm^{-1} corresponding to O-H stretching, that may due to the presence of phenols and alcohols. The band at 2934.25 cm^{-1} attributed as an alkanes that may bearing methylene asymmetric C-H stretching. The double bond region has a short band at 2109.44 cm^{-1} assigned an alkynes that may due to C=C stretching. The bands at 1725.62 cm^{-1} and 1634.36 cm^{-1} , corresponds the stretching vibration of (C=O) aldehydes and ketones. The movement of a group of atoms, or the bending or stretching bands of a particular bond shows many bands in the fingerprint region. The band at 1414.51 cm^{-1} attributed to =C-H in-plane bending may indicate the existence of alkenes. The two small bands at 1341.26 cm^{-1} and 1254.18 cm^{-1} represented as aromatic C-N stretching and may attribute as amines. The peak at 1060.46 cm^{-1} stands for carboxylic acids within the bending vibration of C-O-H. The bands between 916.89 cm^{-1} and 629.75 cm^{-1} assigned as out-of-plane C-H bending and may correspond to aromatic and halogen compounds. The spectra clearly evident for the presence of alcohols, phenols, aldehydes, ketones, carboxylic acids and halogen compounds. The chemical constituents were in compliance with other published reports .The spectrographic study may facilitate in analysing and classification of chemical constituents with their functional groups

5.0 Conclusion

5.1 Findings

- *Carissa Carandas* Soaked in ethanol for 24 hours give the best result. . The light conversion efficiency of the Dye-sensitized solar cell reached 0.09582% with short circuit density .8566 mA/cm² ,open circuit voltage 405mV and a fill factor of .2761.
- Anode should be soaked for 1 hour in dye.
- Among the four testing solvents Isopropanol can be used after ethanol. In case of this solvent the fruit should be soaked for 24 hours.
- For Methanol solvent best result is found when *Carissa Carandas* is soaked for 48 hours in solvent.
- For Acetone solvent best result is found when *Carissa Carandas* is soaked for 48 hours in solvent

5.2 Problem Faced

- The Titanium Dioxide Coating was given manually. So it was not spread evenly. Which has a bad impact on the efficiency and fill factor.
- In the experimental setup where the voltage and current is measured a loss occurred due to clips.
- The furnace had fluctuating temperature that affected the titanium coating
- While testing the photo conversion efficiency in the solar simulator the probes connected for measurement make some electrical losses. Due to which the actual data is not being able to pull down from the simulator.
- While measuring the output there was some losses due to lose connection that may have decreased the efficiency.

5.3 Future scope

- In this study paste was applied by Doctor Blade method so the coating was not uniformed resulting less efficiency. A screen printing technique may be introduced to get higher efficiency.
- A technique of sealing liquid electrolyte should be introduced for the long term stability and practical use of DSSC.
- In this study ITO was used as a conductive and transparent mechanical support, since it is expensive so in order to make a cost effective dye sensitized solar cell alternate of ITO should be searched.

- Glass substrate of DSSCs should be replaced by flexible substrates, which would ease the installation of DSSCs for various applications
- Anode variation can be done using the optimum condition found from the study.

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