

## Influence of Dye Adsorption Period And Electrode Temperature At Dye Adsorption Stage on The Performances of Dye Sensitized Solar Cell Using *Solanum melongena* Linn extract As Photosensitizer .

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**Abstract:** The dependence of the photoelectrochemical performances of Dye sensitized solar cell (DSSC) on the temperature and bath time of  $\text{TiO}_2$ -photoanode in natural dye sensitizer using *solanum melongena* linn extract as a case study has been investigated under simulated AM 1.5 light intensity. The efficiency of DSSC was found to be optimized with a photoanode temperature of  $65^\circ\text{C}$  at immersion point while those photoanodes immersed at ambient temperature were highly favoured with a minimum of 15 hours of immersion period. However, above 15 hours of immersion period of the electrode at room temperature in dye extract the efficiency became saturated whereas the efficiency nose-dives at electrode temperature above  $65^\circ\text{C}$  before immersion. The use of a natural product as the  $\text{TiO}_2$  wide bandgap semiconductor sensitizer is observed to enable a faster and simpler production of cheaper, efficient and environmentally friendly solar cells.

**Keywords:** Solar cells, photoanode, photoelectrochemical, electrode, *solanum melongena* linn, efficiency.

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### Introduction

The world energy requirement is ever growing, particularly since the last centuries. It is expected to grow further in the future. This ever growing demand is a consequence of growth in world population and the techno-economic growth of the countries, particularly the developing countries. This increase in energy demand has greatly put a lot of pressure on the conventional energy sources (oil, coal, gas). Consequently, the search for new energy sources gained momentum in the 1970s following the oil crisis when the price of energy in form of fossil fuel rose dramatically and energy insecurity felt. The oil crisis led to a general public awareness of the limitation of fossil fuels. Many governments, including those of the USA, Japan, and several European countries started ambitious programmes in search of new renewable energy sources. Apart from the fundamental limitations of fossil fuel, ecological considerations linked with the production of the greenhouse gases and global warming are other driving forces promoting renewable energy sources while excessive dependence on oil import, unstable energy prices, high level of financial risk and other factors, deterred the use of conventional energy sources.

Therefore, there is need for alternative energy source which would provide us energy in a sustainable manner. This challenge has to be answered with a low-cost solution using abundantly available raw materials. Solar electricity is a steadily growing energy technology today and solar cells have found markets in variety of applications ranging from consumer electronics and small scale power distributing systems to centralized megawatt scale power plants. The conversion of solar radiation to electrical energy has become more and more important because sunlight is a clean and limitless energy source compared to the traditional fossil energy sources [1].

In the Laboratory of Photonics and Interfaces in Ecole Polytechnique Federale de Lausanne, Switzerland, Grätzel and his co-workers developed a solar cell by the successful combination of nanostructured electrodes and efficient charge injection dyes. This cell was then termed the dye sensitized nanostructured solar cell (DSSC).

The use of sintered mesoporous Titanium dioxide ( $\text{TiO}_2$ ) was the breakthrough that established DSSC technology and raised the DSSC efficiency from 1% (for cells having a non-porous  $\text{TiO}_2$  surface) to 7%. [2,3]. DSSC was also called Grätzel cells named after their publication in 1991 [4].

It is worth mentioning that the conventional Silicon solar cell is expensive and its efficiency is highly affected when the illumination is low. DSSCs have many advantages over silicon solar cells. They are cheaper, there is no need for clean room technology, and the efficiency in low light conditions is not highly affected.

Dye-sensitized solar cells usually employ ruthenium(II) polypyridinic complexes as sensitizers of wide band gap semiconductors [5–7], although the energy conversion can also be achieved by natural dyes. Tennakonee *et al.* investigated the use of tannins and related phenolic substances extracted from black tea, nuts or pomegranate bark, as well as the photosensitization promoted by anthocyanin extracted from flowers [8,9] or leaves [10]. Dai and Rabani examined the use of anthocyanin extracted from pomegranate seeds and the employment of aqueous mediator for such cells [11]. Aduloju and Shitta have also studied the effect of the mediator solvents in the performance of solar cells sensitized by dye from *Lawsonia inermis* [12]. Kay and Gratzel [13] investigated the use of chlorophyll derivatives, as well as anthocyanin compounds obtained by extracts of California blackberries as dye sensitizers [14]. Smestad and Gratzel pointed out advantages of the use of natural dyes in experiments for educational purposes [15]. We have been investigating some natural dyes, such as those obtained in extracts of *Khaya senegalensis* and *Solanum melongena* Linn [16], *Kola nitida* [17], red leaf onion peels [18], *Morinda lucida* [19], *Cocos nucifera* [20], *Mucuna flangellipse* and Zea mays [21] and comparing their performance with the inorganic/synthetic dye sensitized ones.

In this work, we extend our investigations to the effects of dye adsorption period at ambient temperature and photoanode temperature at point of immersion/adsorption of dye extract on the performances of DSSC using natural dye extracts gotten from *Solanum melongena* Linn (purple eggplant skin) as photosensitizer with the hope of optimizing the efficiency of naturally sensitized DSSCs. The absorption spectra of these dyes were carried out and the photoelectrochemical data of all fabricated cells were measured and analyzed. The efficiencies at different conditions of preparation of DSSCs were equally determined.

Note; the colour of eggplant within reach ranges from white egg-shaped fruits to purple ones that run from violet and striped to magenta. However regardless of variety or color, eggplant is smooth, firm and taut. As shown in Fig. 1 the glossy skin and a bright-green stem indicate freshness.



**Fig. 1 fresh eggplant**

### 1.1 Chemical and Materials

Eggplants from a fruit – garden. Unless otherwise indicated, all chemical reagents were the guaranteed reagent grade.

## II. Experiments

Experimental steps were done in three parts, which are the preparation of the TiO<sub>2</sub> photoelectrode (cathode electrode), preparation of the carbon counter electrode (anode electrode) and the preparation of the dye-sensitized solution followed by the assembling of the DSSCs.

### 2.1 Preparation of the Dye-Sensitized Solution

The eggplant fruits were harvested at noon time from an orchard in Ado-Ekiti, Nigeria. Firstly, the fruits were washed with pipe-bone water to get rid of dust particles. The eggplant's dye was extracted from the peels of the fresh fruit using Ethanol solution with 1% in acetic acid and 2% in HCl at room temperature, the solution was filtrated by decantation followed by a glass filter to obtain clear solutions. In order to achieve a desired homogeneity the filtrate was centrifuged to obtain a homogeneous dye extract. The filtrate obtained was covered up with aluminum foil and kept in a dark place to prevent the dye from light exposure.

### 2.2 preparation of the photoelectrode

The Fluorine doped Tin-oxide (FTO) conductive glass sheets each of 1.5 x 1.5 cm<sup>2</sup> were immersed in isopropanol for 48 h to remove any impurities that may be present on the surface, then rinsed with deionized

water and ethanol to prevent traces of minerals on it and later dried using hot-air blower and kept in desiccator for a later use.

Strips of scotch tape (#810, thickness 50 $\mu$ m ) was fixed on the four sides of the hazing side of the conductive glass to restrict the thickness and area of TiO<sub>2</sub> paste to be deposited such that area of about 1 x 1 cm<sup>2</sup> is available for the spreading of TiO<sub>2</sub> paste .

TiO<sub>2</sub> paste was prepared by blending commercial TiO<sub>2</sub> powder (0.2 g) ,nitric solution (0.1M) of 0.4 ml, polyethylene glycol ( 0.08 g) and one drop of a non-ionic surfactant, Triton X-100. The mixture was well mixed in an ultrasonic bath for 50 minutes to ensure complete dispersion of TiO<sub>2</sub> nanoparticles.

Droplets of the paste were placed onto the prepared FTO glass arranged on the turn-table of a spin coater. The spin coater was operated for about 10 seconds to facilitate uniform spreading of the colloid on the FTO glass. Thickness of the TiO<sub>2</sub> film was controlled by multiple coating processes in which the coated substrates were subjected repeatedly to spin-coating and drying steps.

The prepared TiO<sub>2</sub> film was sintered at 450<sup>o</sup>C for 30 minutes in open cylindrical furnace to enhance the film/ TiO<sub>2</sub> particles compactness and crystallinity as the vehicle of the paste burns away. After sintering, the films were allowed to cool in-step naturally to avoid glass cracking. The fore-mentioned procedures were repeated to obtain twelve photoelectrodes.

However at different temperatures 27, 35, 45, 55, 65, and 70  $^{\circ}$ C respectively, Six of the samples were taken out of the furnace one after the other, immersed (face-down) into the extracted dye solution for equal adsorption duration of 1 hours .

Also, the other six photoelectrodes were allowed to cool down to ambient temperature, they were immersed face-down into the extracted dye solution and allowed for different dye adsorption time ; 5, 10, 15, 20, 25, 40 hours respectively . All the treated photoanodes were taken out of the dye solution , rinsed with ethanol to remove unabsorbed dye and any other residues available on the surface then, dried with hot-air dryer and stored in desiccator for later use (to avoid moisture absorption from ambient air). Furthermore , the left over dye solution was kept away from light and moisture in a sealed bottle to avoid degradation / for a later use. For simplicity, the prepared photoanode could be labelled as indicated in ‘‘Table 1’’.

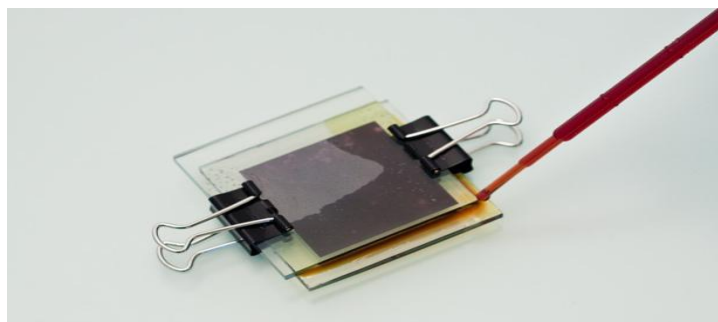
### 2.3 Preparation of the Counter Electrode

The counter electrode used in this study is the Carbon anode electrode, starting with the (1.2x1.2)cm FTO conductive glass . the glass haze- surface was first wiped with ethanol, dried and colored by using graphite carbon pencil. After which, the surface was checked to ensure that there was no space left uncovered with carbon .

### 2.4 The Open Cell Configuration

Starting with the freshly made electrodes. The electrodes were put against each others such that the stained titania/photoanode is facing the carbon / counter-electrode i.e; The conductive sides of each electrode (face to face) forms the inside of the cell. Care was taken to slightly shift the two glass plates in order to leave room for electrical contacts, then two similar clips were used to hold the electrodes together. Immediately the DSSC cell assembled was filled with electrolyte before getting damaged by ambient air.

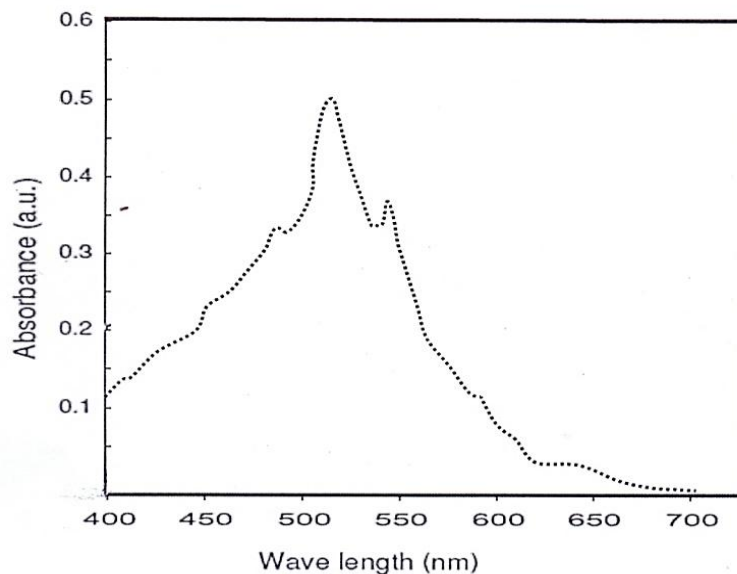
The redox electrolyte solution composed of 2 ml acetonitrile (ACN), 8 ml propylene carbonate (p-carbonate), 0.668 mg potassium-iodide (KI), and 0.0634 mg iodine (I<sub>2</sub>). The redox electrolyte solution was sandwiched between the two electrodes as shown in ‘‘Fig 2’’. Few drops of the electrolyte was put at the interface of the two glass plates with a small pipette then tarry a little to allow the liquid to be drawn into the cell by capillary effect until the entire internal surface of the solar cell was wetted with the electrolyte. Later, wipe off any excess liquid with a paper towel. The DSSC is now operational and will last until the electrolyte solvent evaporates.



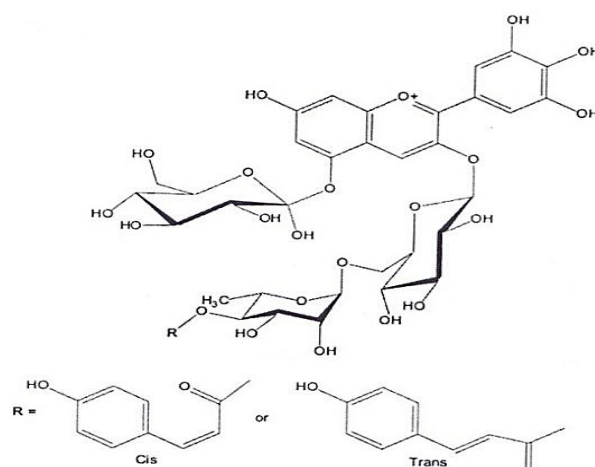
**Fig.2** open cell configuration

### III. Measurements

The absorption spectra of the dye solution was recorded using a double beam UV-Vis spectrophotometer, the absorption analysis was conducted in the wavelength range from 400 to 750 nm covering the UV-Vis range as shown in “Fig.3a”;



(a)



**Fig.3 (a)**Optical absorption spectrum of Eggfruit dye **(b)** Chemical Structures of Nasunin [25]

The I-V characteristic curves under simulated (AM1.5, 100 mW/cm<sup>-2</sup>) / direct solar spectrum were conducted using Newport/Oriel solar simulator, model 91160, with appropriated filters[26] . The simulated AM 1.5 light intensity was also measured by thermopile detector model 70261 connected to a power meter model 70260 .Based on I-V curve, the fill factor (FF) can be calculated as ;

$$FF = \frac{I_m V_m}{I_{sc} V_{oc}} \quad (1)$$

Where  $I_m$  and  $V_m$  are the photocurrent and photovoltage for maximum power output (P<sub>m</sub>),  $I_{sc}$  and  $V_{oc}$  are the short-circuit photocurrent and open-circuit photovoltage, respectively.

The overall energy conversion efficiency ( $\eta$ ) is defined as ;

$$\eta = \frac{FFI_{sc} V_{oc}}{P_{in}} \quad (2)$$

Where  $P_{in}$  is the power of incident light.

On the cost estimate of photosensitizers, The price of the dye utilized in this study can be calculated using the following equation as adapted from Calogero *et al* , 2012[22];

$$P_{total} = \Gamma \times M_{dye} \times P_{mass} / I_{AM1.5} \times \eta \quad (3)$$

$P_{total}$  is the price per Watt peak ( $\text{€ W}^{-1}$ ),  $\Gamma$  is surface coverage of the dye ( $\text{mol. cm}^{-2}$ ),  $M_{dye}$  is the molecular mass of the dye ( $\text{g mol}^{-1}$ ),  $P_{mass}$  is the price per mass ( $\text{€ g}^{-1}$ ),  $I_{AM1.5}$  is the sun light intensity of AM 1.5 ( $\text{W m}^{-2}$ ) and  $\eta$  is the efficiency described in equation (2). It has been estimated that the dyes contribute to 10–15% to the total costs of a DSSC.

$P_{total}$  for organic dyes has been claimed to be in a range lower than those for ruthenium based dyes of  $0.8 \text{ € W}^{-1}$  [23]. This is mainly due to costly synthesis. However, stability has not been included in the formula.

Therefore, the costs for natural dyes are currently very difficult to estimate. They mainly depend on the availability of the source and the extraction method [24].

## IV. Results And Discussion

### 4.1 Optical Spectrum of Eggplant (peels) Dye

The extract from eggplant skin is rich in anthocyanins, it contains nasunin, a mixture of cis– trans isomers of delphinidin 3-[4-(p-coumaroyl)- L-rhamnosyl(1–6)-glucopyranoside]-5-glucopyranoside [25] shown in “Fig 2b” . “Fig 2a” depicts the result obtained from the spectrophotometric analyses in the range of 400 - 700nm wavelength (UV-Vis range) at room temperature .The most striking feature that has been observed from these figures is that eggplants skin extract has absorption peak in the visible region at 530nm , a wide absorption band in the region from 450-550 nm but poor absorption in the red part of the spectrum.

Typically, organic dye molecules like the eggplant extract generally have poorer absorption in the red part of the spectrum compared to silicon , which means that fewer of the photons in sunlight are usable for current generation. These factors limit the current generated by a DSSC.

Apart from the absorption spectrum of the dye , the anchorage of the dye to the surface of  $\text{TiO}_2$  is another important parameters determining the efficiency of the cell [22]. Carbonyl and hydroxyl groups present in the anthocyanin molecule (fig.3b) can be bound to the surface of a porous  $\text{TiO}_2$  film. This makes electron transfer from the anthocyanin molecule to the conduction band of  $\text{TiO}_2$  possible [13]. As reported [22], anthocyanins from various plants gave different sensitizing performances.

### 4.2 Photoelectrochemical Performance of Eggplant Dye Sensitizer in DSSCs

Natural pigments can be used as photosensitizers in DSSCs. However, the efficiency ( $\eta$ ) is still by a factor of 3–4 lower than synthetic dyes. But natural pigments are normally non-poisonous, can be disposed easily, cheaper and more environmentally friendly than synthetic metal complexes. Therefore, natural dyes as light harvesting elements in DSSCs can contribute to a sustainable solution for the future energy production.

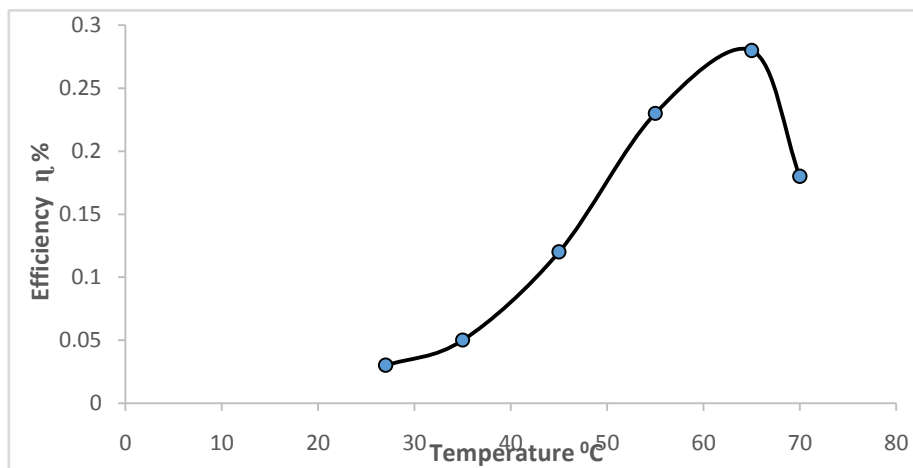
Generally, several important measures are used to characterize solar cells. The most obvious is the total amount of electrical power produced for a given amount of solar power shining on the cell. This is usually expressed in percentage, it is known as the solar conversion efficiency given by equation 2 , in order to understand the underlying physics, the "quantum efficiency" is used to compare the chance that one photon (of a particular energy) will create one electron, in quantum efficiency terms, DSSCs are extremely efficient. Due to their "depth" in the nanostructure there is a very high chance that a photon will be absorbed, and the dyes are very effective at converting them to electrons. Most of the small losses that do exist in DSSC's are due to conduction losses in the  $\text{TiO}_2$  and the clear electrode, or optical losses in the front electrode.

**Table 1.** Efficiency of DSSC for Photoanode immersed in Dye extract at different Temperatures

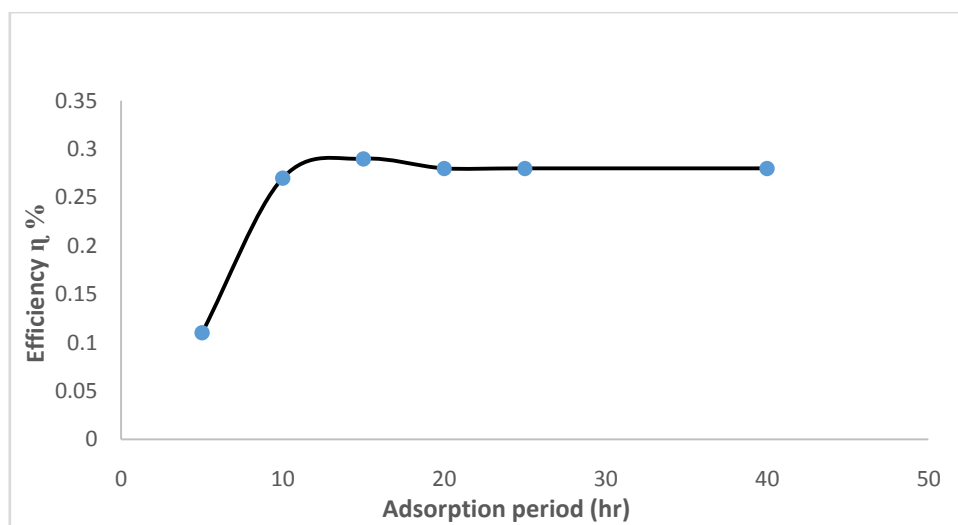
Temperature at immersion ( $^{\circ}\text{C}$ )	27	35	45	55	65	70
Efficiency ( $\eta$ ) %	0.03	0.05	0.12	0.23	0.28	0.18
Photoanode Samples	A	B	C	D	E	F

**Table 2.**Efficiency of DSSC forPhotoanode soaked in Dye extract at ambient Temperature for different adsorption durations

Bath time in dye extract (hr)	5	10	15	20	25	40
Efficiency( $\eta$ ) %	0.11	0.27	0.27	0.28	0.28	0.28
Photoanode Samples	G	H	I	J	K	L



**Fig.4** Graph Of DSSCs Efficiency Dependence On Photoanode Temperature At Dye Adsorption Stage



**Fig.5** Graph Of DSSCs Efficiency Dependence On Photoanodes' Dye- Adsorption Periods

Developing and optimizing materials for organic solar cells is generally not yet rational, but rather empirical. The reason for this is that multiple parameters have to be taken into account when new types of dyes/materials are designed for organic solar cells. Although, the efficiency of DSSC could be affected by some parameters like; those originating from different experimental conditions, irradiated light source spectrum and intensity, the nature of electrolyte salt, solvent, additives, co-absorbers and catalyst, the size of cell active area and the thickness of TiO<sub>2</sub> films. In this study, we focus on the efficacy of adsorption temperature and immersion time of photoanode in the dye. The Efficiency is calculated at each temperature using Eq.(2) corresponding to the respective values of Voc, Jsc and FF at each temperature. The efficiency as a function of the photoanode dye adsorption temperature is as depicted in ‘‘table 1’’ and ‘‘Fig.4’’, this shows that the efficiency is enhanced with increase in the dyeing adsorption temperature from ambient temperature 27°C to 65 °C then, it declines towards lower values with further increase in the temperature. In conclusion, a photoanode dye adsorption temperature of 65 °C could be used as an optimal value.

In the same vein, the time of immersion of the photoanode in dye solution at room temperature was equally optimized (Table 3). “ Fig 4” illustrates the efficiency of the fabricated DSSCs as a function of the immersion time of TiO<sub>2</sub> electrode in the dye solution at ambient temperature.

The efficiency of the cell increases as bath-time increases and become saturated after 10 hours of immersion. However, as depicted in “Fig4” further increase in bath-time ( i.e 15,20,25 hr and so on) does not have any significant impact on the efficiency.

In conclusion, above findings revealed that the photoelectrochemical performances of DSSC could be optimized either through a prolong hour of dye-adsorption of photoanode at ambient temperature or by raising the photoanode temperature at the point of dye-adsorption.

## V. Conclusion

Inspired by the principle of natural photosynthesis in green parts of plant, DSSC is fast becoming a credible alternative to solid-state p-n junction devices. Their excellent performance in diffuse light gives them a competitive edge over silicon in providing electric power for stand-alone electronic equipment both indoor and outdoor.

However, the major disadvantage to the DSSC design is the use of the liquid electrolyte, which has temperature stability problems. At low temperatures the electrolyte can freeze, ending power production and potentially leading to physical damage. Also, higher temperatures cause the liquid within the cell to expand, making sealing of the panels a serious problem. Another disadvantage is that costly ruthenium complex-dye (in inorganic DSSC), platinum (catalyst) and conducting glass or plastic (contact) are needed to produce a DSSC. Furthermore, another major drawback is that the electrolyte solution contains volatile organic compounds / solvents which must be carefully sealed as they are hazardous to human health and the environment. This, along with the fact that the solvents permeate plastics, has precluded large-scale outdoor application and integration into flexible structure.

Using eggplant skin natural extract as a case study in our investigation into the efficacy of photoanode immersion time and photoanode temperature at immersion time on the performances of DSSCs under AM 1.5 illumination, we recorded an optimal efficiencies of 0.29% with 15 hours immersion time and 0.28% at a photoanode immersion temperature of 65<sup>o</sup>C beyond which the efficiency became saturated / diminished. These observations betoken that to optimize the efficiency of DSSC using natural dye sensitizer the temperature of photoanode at the point of adsorption of dye should be well above ambient temperature and among other things, a long hour immersion time should be considered to allow for proper chemo-adsorption.

Effective conversion of visible light into electricity had been achieved with the use of extract of *solanum melongena* Linn as the semiconductor sensitizer in photoelectrochemical solar cells. The use of a natural product enables a faster, simpler, efficient and environmentally friendly solar cell production without the requirement of all steps involved in the preparation and purification of synthetic dyes. Nevertheless, stability and long-term operation are fundamental issues for the development of DSSC-devices and further studies are in progress.

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