

# SYNTHESIS AND CHARACTERIZATION OF DYE SENSITIZED SOLAR CELL USING FRUIT EXTRACTS

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## Abstract

In this report we present a general approach for the preparation of Dye Sensitized Solar Cell (DSSC) using fruit extract. DSSC's show the most promising future due to their independence, environmental friendly, low maintenance, and low cost. The TiO<sub>2</sub> nanopowder were successfully synthesized by sol-gel method. By using simple method, dyes were prepared from Basella Alba (Malabar Spinach), Scutia Myrtina (Cat Thorn) and Opuntia (Prickly Pear). Then the electrodes were prepared by using FTO and TiO<sub>2</sub> nanoparticles and it is coated to form anode electrode. The cathode electrode was prepared by coating graphite in FTO glass plate. Structural and optical properties of the TiO<sub>2</sub> were characterized by X-ray diffractometer and UV-VIS spectrophotometer respectively. The XRD result exhibit the structure of anatase phase of TiO<sub>2</sub> and UV exhibit TiO<sub>2</sub> which was in conformity with its wide band gap nature. TiO<sub>2</sub> was subjected or treated to Scanning Electron Microscopy (SEM). From JV characterization, the DSSC properties such as conversion efficiency, short current density, open circuit voltage, and fill factor were measured. In this work three natural dyes were selected and based on that, DSSC were fabricated and the efficiencies were calculated.

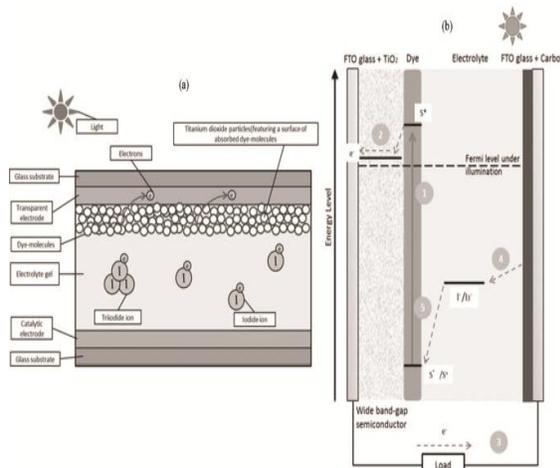
**Keywords:** Dye sensitized solar cell, TiO<sub>2</sub> nanomaterial, Basella Alba, Scutia Myrtina and Opuntia.

## 1. INTRODUCTION

A solar cell, which also known as photovoltaic cell is one of the promising options of renewable energy. A solar cell is a photonic device that converts photons with specific wavelengths to electricity. Solar cell is divided into two groups which are the crystalline silicon and thin film. The first and second generation of photovoltaic cells are mainly constructed from semiconductors including crystalline silicon, III-V compounds, cadmium telluride and copper indium selenide/sulfide [1]. The dye-sensitized solar cells

(DSSC) which belong to the thin film group, emerged as a new class of low cost energy conversion devices with simple manufacturing procedures. Incorporation of dye molecules in some wide bandgap semiconductor electrodes was a key factor in developing electrochemical solar cells. Since the low cost solar cells have been the subject of intensive research work for the last three decades [2], Michael Gratzel and coworkers at the Ecole Polytechnique Federale de Lausanne [3] succeeded to produce "Gratzel Cell" or which known as dye-sensitized solar cells that imitate the photosynthesis process by sensitizing a nanocrystalline TiO<sub>2</sub> film using novel Rubipyridil complex [4]. Therefore, the dye sensitized solar cells (DSSC) (Fig. 1(a)) have been intensively studied as a new type of solar cells which composed of nanocrystalline porous semiconductor electrode which absorbed dye, a counter electrode and an electrolyte of iodide-triiodide ions. It is a device for the conversion of visible light into electricity, based on photosensitization produced by the dyes on the wide band-gap mesoporous metal oxide semiconductors. This sensitization is due to the dye absorption of a part of the visible light spectrum. The sensitized dye works by absorbing the sunlight which then convert it into electrical energy. The operation principle of DSSC is displayed in Fig.1(b). It can be divided into following flows [5]:

- 1) An electron passed through a cycle of excitation;
- 2) Injection in the TiO<sub>2</sub>, and the iodine reduction occur at the counter electrode and the electron passing through TiO<sub>2</sub> to the electrode;
- 3) External work of electron;
- 4) Diffusion in the electrolyte;
- 5) Regeneration of the oxidized dye.



**Fig-1:(a) The structure of DSSC and (b) The mechanism of DSSC.**

Recently, titanium dioxide ( $\text{TiO}_2$ ) has attracted attention from researchers worldwide due to its potential applications in environmental protection and energy generation and has been applied largely in DSSC due to its nanocrystalline mesoporous nature that translates to high surface area for dye adsorption. The absorbed dye molecules can then be excited by the solar energy to generate electron-hole pairs that are subsequently separated and transported within the lattice of  $\text{TiO}_2$  [6]. The absorption spectrum of the dye and the anchorage of the dye to the surface of  $\text{TiO}_2$  are important parameters in determining the efficiency of the cell [7]. Since the dye plays an important role in absorbing visible light and transferring photon energy into electricity, much attention has been paid to survey the effective sensitizer dyes [8]. Several metal complexes and organic dyes have been synthesized and used as sensitizers including porphyrins [9], platinum complex [10] and others. Ru-based complexes sensitizers have been widely used because they have better efficiency and high durability. However, these advantages are offset by their high cost and tend to undergo degradation in the presence of water [11]. Besides, it is also regarded as highly toxic and carcinogenic.

Therefore, in order to overcome these problems, we chose to use natural pigments as sensitizing dye. Unlike the artificial dyes, the natural dye is easily available, easy to prepare, low cost, non-toxic, environmental friendly and fully biodegradable [12]. In most cases, their photo activity is due to the presence of anthocyanin family [13]-[15]. Anthocyanins from strongly colored fruits, leaves and flowers are capable of attaching to  $\text{TiO}_2$  surface and inject

electrons into the conduction band of  $\text{TiO}_2$  [16], [17]. In DSSC, natural pigments extracted from fruits and vegetables, had been proven to be applicable of producing high power efficiency.

## 2. EXPERIMENTAL PROCEDURE

### Materials used

Isopropyl alcohol, titanium isopropoxide, distilled water, ethanol, polyethylene glycol, iodine electrolyte, potassium iodide, graphite carbon pencil, and FTO (Fluorine doped tin oxide coated glasses) were used. For the dye, Basella Alba, Scutia Myrtina and Opuntia fruits were used.

Experimental steps were done in three parts, which are the preparation of the cathode electrode ( $\text{TiO}_2$  photoelectrode), preparation of the anode electrode (carbon counter electrode) and the preparation of the dye-sensitized solution.

### 2.1 PREPARATION OF $\text{TiO}_2$ NANOPARTICLES AND DYE EXTRACT

#### (a) Sol-gel method

All the reagents used were of analytical grade and no further purification was done before use. The sol-gel synthesized  $\text{TiO}_2$  was obtained from 100 ml isopropyl alcohol was added in absolute 15 ml of titanium isopropoxide and it was stirred for 30 minutes. Then 10 ml of distilled water was added to the solution drop wise. Immediately the resultant gel was formed and it was stirred for few minutes. After aging for 24 hours, the solution was filtered and it was washed by three times distilled water. Finally it was transferred into oven under  $100^\circ\text{C}$  for 6 hours to evaporate water and organic material to the maximum extent. Then the material was grinded to fine powder, and then dried resultant powder was calcinated at  $500^\circ\text{C}$  for 2hrs to obtain  $\text{TiO}_2$  nanoparticles [18].

#### (b) Dye preparation

2g of Basella alba (Malabar spinach), Scutia myrtina (Cat thorn) and Opuntia (Prickly pear), fruits are mixed into few drops of ethanol at room temperature separately. The fruits were mashed using a mortar and pestle. The fruit extracts were placed into an ultrasonic cleaner for 15 minutes with the frequency of 37 Hz using 'degas' mode at the temperature of  $30^\circ\text{C}$  [19].



Fig-2:(a)Basella alba (b)Scutia myrtina (c)Opuntia

## 2.2 Photo anode

The photoanode is prepared by adsorbing a dye (s) on a porous titanium dioxide,  $TiO_2$  layer deposited on Fluorine-Doped tin oxide, FTO conducting glass. By this approach, the dye extends the spectral sensitivity of the photoanode, enabling the collection of lower energy photons. The  $TiO_2$  paste was prepared by blending 2g of synthesized  $TiO_2$  nanopowder, 2ml of 0.1M acetic acid, and few drops of ethanol. The resulting suspension was stirred for 1h. Two edges of the FTO glass plates were covered with a layer of adhesive tape to control the thickness of the film and to mask electric contact strips. Successively the  $TiO_2$  paste was spread uniformly on the substrate by sliding a glass rod along the tape spacer. After spreading the  $TiO_2$  paste, the tape was removed from the FTO glass plate and allowed to heat for about one hour  $100^\circ C$ . The sintering process was completed and the  $TiO_2$  deposited- electrode was cooled down from  $100^\circ C$  to room temperature to avoid cracking of the glass.

## 2.3 Graphite coated counter electrode

To prepare the Carbon counter electrode, the FTO glass was wiped with ethanol. Then, the FTO glass surface was colored by using graphite carbon pencil. After that, the surface was checked to ensure that there was no space that the carbon did not cover.

## 2.4 Electrolyte preparation

In the preparation of liquid electrolyte, 10ml of ethylene glycol was taken in a beaker. Then, 0.127g of iodine (I) was added ethylene glycol. After that, 0.83g of potassium iodide was added. By using the glass rod, the mixture was mixed until there was no grain of iodine and potassium iodide can be seen[20].

## 2.5 DSSC Assembling

The cathode electrode and the anode electrode were put together, overlapping each other, and at the end of each

electrode a space was made. Next, both electrodes were fixed using the double clip. Three drops of iodide solution were added at the end of the electrode and the solutions were spread over the entire electrode. Then, the remaining iodide solution were wiped off using cotton swab soaked with alcohol. After that, a tester with crocodile clip were attached at both ends of the electrode.

## 3.RESULT AND DISCUSSION

### 3.1 XRD analysis

The powdered sample was used by a Cu  $K\alpha$  - X Ray Diffractometer ( $\lambda = 0.15406$  nm) for confirming the presence of  $TiO_2$  and analyze the structure and shown in Fig-3. XRD is used to determine crystal structure and crystallite size can be calculated using Debye Scherrer equation. The calculated crystallite size was  $D=14$ nm. XRD patterns of  $TiO_2$  powders calcinated at  $500^\circ C$  is shown in Fig-3 and it shows the peaks corresponds to the planes (101), (004), (200), (105), (211), (204), indicate anatase form[21-22]. All the peaks in the XRD patterns can be indexed as anatase phases of  $TiO_2$  and the diffraction data were in good agreement with JCPDS files # 21-1272 having tetragonal structure with lattice parameter  $a=b=3.785$  Å,  $c=9.514$  Å,  $Z=4$ .

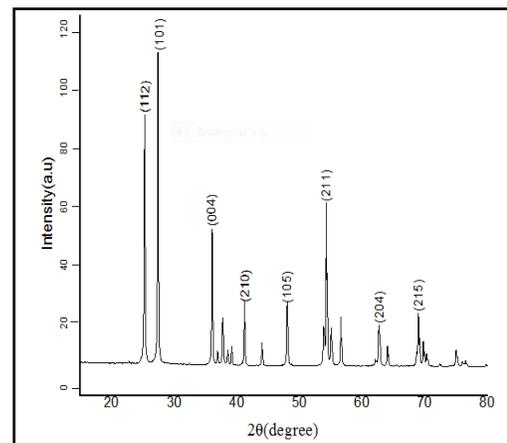


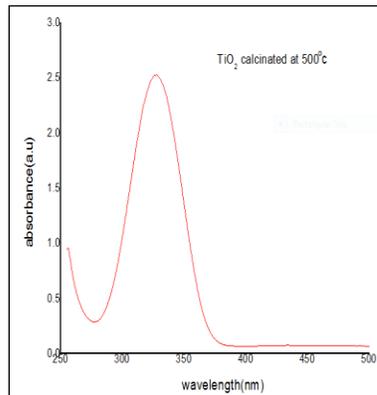
Fig-3: XRD pattern of  $TiO_2$  nanoparticles calcinated at  $500^\circ C$ .

### 3.2 UV-VIS spectroscopy

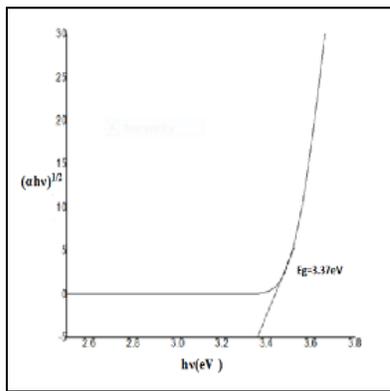
The optical absorption behavior and band gap energy of  $TiO_2$  was studied by means of UV-visible Spectroscopy.

The optical absorption spectrum of TiO<sub>2</sub> is found to be 350 nm shown in Fig-4(a):[23].

The band gap analysis is done using Tauc plot which are shown in the fig-4:(b)[24]. The value where the tangent is intersecting the x-axis is considered as the bandgap which is observed as 3.37eV.

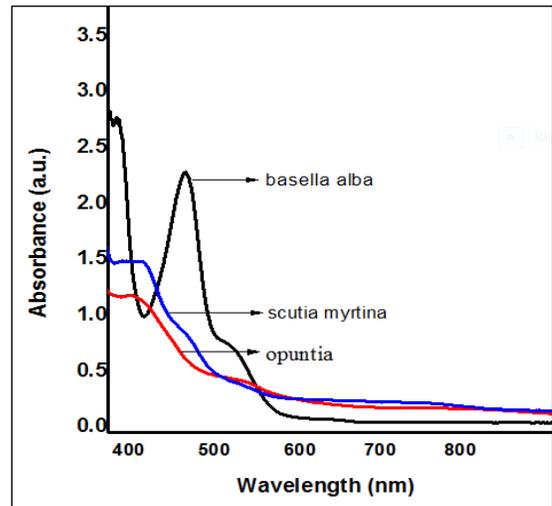


(a)



(b)

**Fig-4: (a).UV-Vis absorption spectra of TiO<sub>2</sub> nanoparticle  
(b)  $(\alpha h\nu)^{1/2}$  as a function of  $h\nu$ (eV) for TiO<sub>2</sub> nanoparticles.**

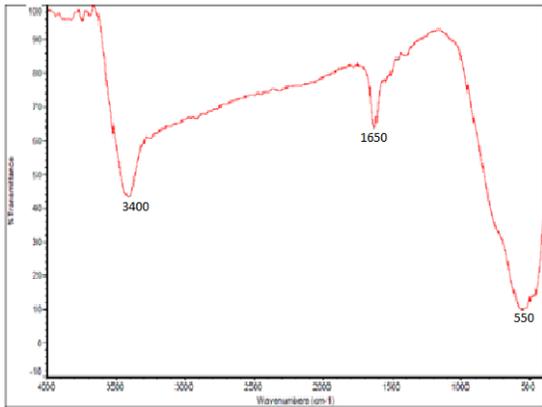


**Fig-4(c):UV-Vis absorption spectra of natural dyes.**

The absorbance of Malabar Spinach (Basella Alba), Prickly Pear (Opuntia) and Cat Thorn (Scutia Myrtina) correlating with wavelength using UV-Vis spectrophotometer from 300 nm to 700 nm which present in the visible region as shown in fig.4(c). [25] The peak which is found in 490 nm which can be associated to the presence of betacyanin pigments which is present in basella alba fruit [26]. For Opuntia, the peak is present in the range of 430 nm shows the presence of betalins (which is a type of betacyanins found in fruit) [27]. For Scutia Myrtina fruit the peak is present in the range of 440 nm, shows the presence of anthocyanin's. The spectra show an absorption peak in the region of 400 - 550 nm which is the peak of anthocyanin containing dyes. This is because of the diverse pigmentation from orange to red, purple, and blue pigment which are found in anthocyanin containing pigment and shows an absorption in the visible region [28].

### 3.3 FTIR spectroscopy

FTIR analysis was used to determine the functional groups of TiO<sub>2</sub> nanoparticles [29]. Fig.5 represents the FTIR spectra of TiO<sub>2</sub> nanoparticles with different peaks formed at different wave number. It is observed in the graph that TiO<sub>2</sub> Nanoparticles have various frequency vibrations which are shown by different peaks formed.

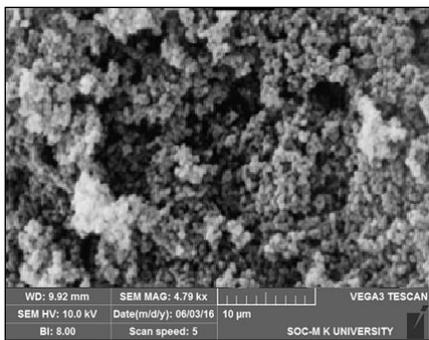


**Fig-5: FTIR spectra for TiO<sub>2</sub> nanoparticles calcinated at 500°C.**

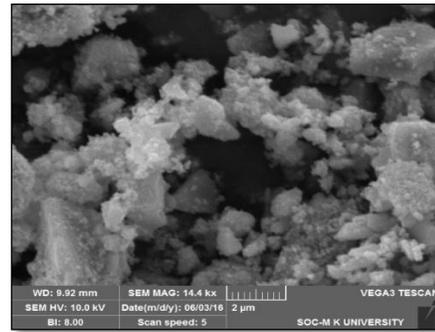
The peaks at 3400 and 1650cm<sup>-1</sup> in the spectra are due to the stretching and bending vibration of the -OH group[30].In the spectrum of TiO<sub>2</sub> the peaks at 550cm<sup>-1</sup> show stretching vibration of Ti-O and peaks at 1450cm<sup>-1</sup> shows stretching vibrations of Ti-O-Ti.

### 3.4 Morphological Analysis (SEM)

Scanning electron microscopy (SEM) studies were used to examine morphology and shape of nanomaterials. The morphology was changed to non hard-grained aggregates that are constituted of nearly spherical nanoscaled particles. SEM image has roughly spherical spongy shape and agglomeration nanoparticles.[31].



(a)

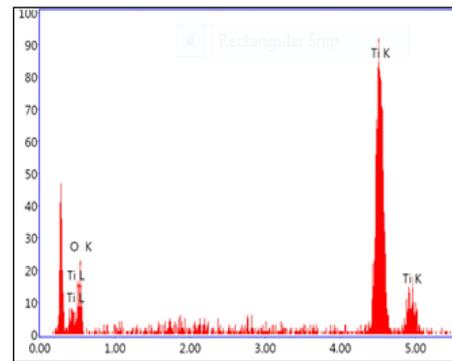


(b)

**Fig-6:SEM images of TiO<sub>2</sub> nanoparticle calcinated at 500°C at (a)10µm (b) 2 µm.**

### 3.5 EDX spectrum

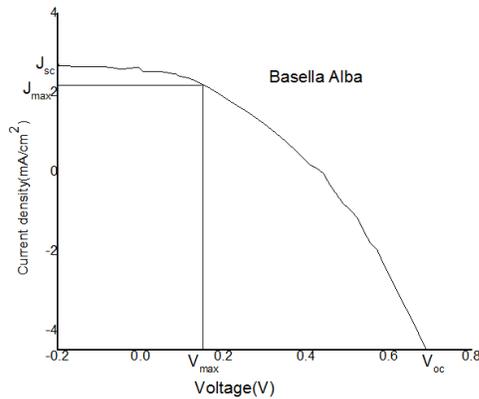
Energy dispersive X-ray spectroscopy indicates the presence of Ti and O with 66.86, 33.14 weight percent respectively. There is no impurity peak is observed in the EDX spectra. This confirms that the prepared samples are in pure form.



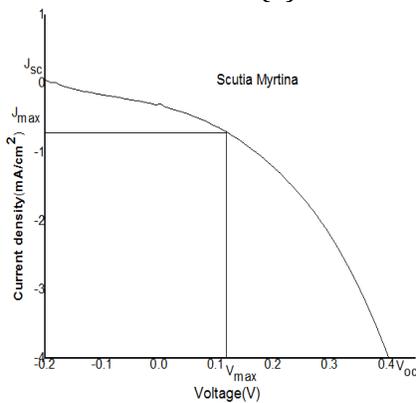
**Fig-7: EDX images of TiO<sub>2</sub> nanoparticle calcinated at 500°C.**

### 3.6 J-V characterization curve

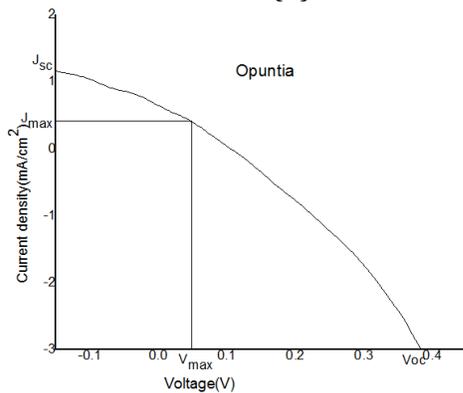
The photovoltaic characterizations of the DSSCs were carried out using a solar simulator. Fig.8 depicts the comparison of the J-V curves of DSSCs based on TiO<sub>2</sub> based photo anodes.



(a)



(b)



(c)

**Fig-8: J-V characterization curve for (a) Basella Alba (b) Scutia Myrtina (c) Opuntia.**

The efficiency of a solar cell represents the ratio where the output electrical power at the maximum power

point on the J-V curve is divided by the incident light power – typically using a standard AM1.5G(100m A/cm<sup>2</sup>) simulated solar spectrum. TiO<sub>2</sub> paste was applied on the conductive electrode using doctor blade method the effective area of the irradiated part of the cell is 1 cm × 1.5 cm.

Most of the natural dye which have a good and a broader absorption in the visible spectrum show a good rectification of the J-V curve that is responsible for good current density and power conversion efficiency. In these studies ethanol extract of Basella Alba, Scutia myrtina and Opuntia shows a better rectification which results relatively good photoelectrochemical performance for ethanol extract.

The efficiency of natural dye based DSSC is correlated to the maximum absorption coefficient of the dye and the interaction of the dye molecules to the TiO<sub>2</sub> surface. It is also dependent on intensity and range of the light absorption of the extract on TiO<sub>2</sub>. Higher interaction between TiO<sub>2</sub> and dye molecules leads to better charge transfer[32].

**Solar conversion efficiency measurement**

The fill factor (FF) of a DSSC can be estimated using the formula

$$FF = \frac{V_{max} \times J_{max}}{V_{oc} \times J_{sc}}$$

V<sub>oc</sub> is the open-circuit voltage and J<sub>sc</sub> is the short-circuit current.

The solar conversion efficiency (η) of a DSSC can be estimated using the conversion efficiency formula:

$$\eta = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}}$$

Dye	Voc (V)	Jsc (mA/cm <sup>2</sup> )	Vmax (V)	Jmax (mA/cm <sup>2</sup> )	FF	η (%)
Basella Alba	0.69	2.632	0.149	2.184	0.17	2.16%
Scutia Myrtina	0.40	0.064	0.705	0.118	3.32	0.56%
Opuntia	0.38	1.14	0.049	0.414	0.04	0.14%

**CONCLUSION**

TiO<sub>2</sub> nanomaterials were synthesized using the most convenient ways of synthesizing method known as sol gel

synthesis. TiO<sub>2</sub>Nano powders were successfully synthesized by using Titanium tetra isopropoxide and Isopropanol. They were calcinated to 500°C to get high degree of crystallization. The calcinated TiO<sub>2</sub>nanopowders were characterized by Powder XRD,UV, SEM, EDX and J-V characterization. From UV-Vis plot the band gap of TiO<sub>2</sub> is 3.37 eV. The Powder XRD spectra reveal that, the main phase of TiO<sub>2</sub>nanopowders are anatase phase. SEM image displayed the uniform morphology in the form of roughly spherical spongy shape. EDX spectra confirm the samples were in pure form.

Natural dyes prepared from the fruits *Basella Alba*, *Scutia myrtina* and *Opuntia* were successfully extracted by using ethanol. The broad absorption peak for the dyes shows different absorption rate with different wavelength in the visible light spectrum (400- 700 nm). The photo anode was prepared by coating the TiO<sub>2</sub>nano paste on FTO glass plate and it was allowed to dip on the prepared dyes. The cathode electrode was prepared by coating graphite carbon pencil. Both electrodes are clipped by using a binder clip, between that two electrodes few drops of electrolyte solution was added. Thus DSSCs device were fabricated using TiO<sub>2</sub> nanoparticles for the three sensitizers and their photovoltaic performance were determined. The J-V characteristic curves were measured and the photoelectrochemical properties were investigated. The highest conversion efficiency was obtained for the DSSC fabricated using *Basella Alba* records - open-circuit voltage ( $V_{oc}$ ) = 0.69V, short-circuit current density ( $J_{sc}$ ) = 2.63 mA/cm<sup>2</sup>, fill factor (FF) = 0.178 and conversion efficiency ( $\eta$ ) is 2.16%.

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