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## Dye-sensitized solar cells using natural dye as light-harvesting materials extracted from *Acanthus sennii chiovenda* flower and *Euphorbia cotinifolia* leaf

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### Abstract

Natural dyes are environmentally and economically superior to ruthenium-based dyes because they are nontoxic and cheap. In this study, dye-sensitized solar cells (DSSCs) were fabricated using natural dyes light harvesting materials. The natural dyes were extracted from *Acanthus sennii chiov* flower and *Euphorbia cotinifolia* leaf. In the as prepared DSSC, a quasi-solid state electrolyte was sandwiched between the working electrode (photoanode) and counter electrode (PEDOT-coated FTO glass). The photoelectrochemical performance of the as prepared quasi-solid state DSSCs showed fill factors (FF) ranging from 47 to 60%, open circuit voltages ( $V_{OC}$ ) and short circuit current densities ( $J_{SC}$ ) ranging from 0.475 to 0.507 V and 0.352 to 0.642 mA  $cm^{-2}$  respectively at 100 mW  $cm^{-2}$  light intensity. The maximum power conversion efficiency ( $\eta$ ) of the as prepared DSSC prepared from *Acanthus sennii chiov*. Flower which was extracted by 1% HCl of ethanol reached 0.15% where  $V_{OC}$ ,  $J_{SC}$  & FF is 0.507 V, 0.491 mA  $cm^{-2}$  & 60% respectively. On the other hand, the maximum power conversion efficiency using *Euphorbia cotinifolia* leaf dye sensitizer with similar extraction solvent reached to 0.136%. This is the first study that reports fabrication of DSSC using natural dye sensitizers extracted from these plants in the presence of quasi-solid state electrolyte and PEDOT as a counter electrode.

**Keywords:** Dye-sensitized solar cell, *Acanthus sennii chiov*.flower, *Euphorbia cotinifolia* leaf, quasi-solid state electrolyte, PEDOT

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Natural dyes are environmentally and economically superior to ruthenium-based dyes because they are nontoxic and cheap. In this study, dye-sensitized solar cells (DSSCs) were fabricated using natural dyes light harvesting materials. The natural dyes were extracted from *Acanthus sennii chiovenda* flower and *Euphorbia cotinifolia* leaf. In the as prepared DSSC, a quasi-solid state electrolyte was sandwiched between the working electrode (photoanode) and counter electrode (PEDOT-coated FTO glass). The photoelectrochemical performance of the as prepared quasi-solid state DSSCs showed open circuit voltages ( $V_{OC}$ ) varied from 0.475 to 0.507 V, the short circuit current densities ( $J_{SC}$ ) ranged from 0.352 to 0.642 mA cm<sup>-2</sup> and the fill factors (FF) varied from 47 to 60% at 100 mWcm<sup>-2</sup> light intensity. The dye extracted from *Acanthus sennii chiovenda* flower, using acidified ethanol (in 1% HCl) as extracting solvent, exhibited best conversion efficiency with a maximum open circuit voltage ( $V_{OC}$ ) of 0.507 V, short circuit current density ( $J_{SC}$ ) of 0.491 mA cm<sup>-2</sup>, fill factor (FF) of 0.60 and an overall conversion efficiency ( $\eta$ ) of 0.15%. On the other hand, the maximum power conversion efficiency of the dye extracted from *Euphorbia cotinifolia* leaf was 0.136%. This is the first study that reports fabrication of DSSC using natural dye sensitizers extracted from these plants in the presence of quasi-solid state electrolyte and PEDOT as a counter electrode.

**Keywords:** Dye-sensitized solar cell, *Acanthus sennii chiovenda* flower, *Euphorbia cotinifolia* leaf, quasi-solid state electrolyte, PEDOT

### 1. Introduction

Dye sensitized solar cell (DSSC) is a promising alternative to conventional silicon solar cells, which effectively utilizes a property of nanocrystalline wide band gap semiconductor (metal

oxide) porous electrode [1]. It provides a prime attention as an alternative source of clean and green energy due to its several advantages, such as low price to performance ratio, low processing cost, and low intensities of incident light, mechanical robustness, light weight and aesthetically appealing transparent design [2, 3]. A DSSC consists of a fluorine-doped  $\text{SnO}_2$ (FTO) layer, a nanocrystalline wide band gap metal oxide semiconductor porous electrode, dyes, an electrolyte, and a counter electrode [4, 5] as shown in scheme 1. In the assembly of DSSC, the dye plays an important role in harvesting solar energy and converting it to electrical energy with the aid of a semiconducting photoanode [1, 6, 7]. Therefore, the cell performance is mainly dependent on the type of dyes used as a sensitizer [8]. Many metal complexes and organic dyes [1, 6, 9] have been synthesized and used as sensitizers. Ruthenium based complexes are considered as good sensitizers for DSSCs because their intense charge transfer absorption over the entire visible range and highly efficient metal to ligand charge transfer [10]. These complex dyes are capable of delivering DSSCs with high conversion efficiency [11] as compared to natural DSSCs [1, 12, 13]. On the other hand, natural dyes have several advantages over rare metal complexes (ruthenium based complexes) because ease of extraction with minimal chemical procedures, large absorption coefficients, low cost, non-toxicity, environmentally friendly, easily biodegradable and wide availability [8, 15-17]. Moreover, synthetic organic dyes have been fraught with problems, such as complicated synthetic routes and low yields [14]. Thus, several dyes extracted from natural pigments including anthocyanins, carotenoids and chlorophylls have been used as sensitizers in DSSC [12, 16-19]. Chlorophyll is the well-known and dominant natural pigment in terms of absorbing specific wavelengths of the visible light, converting sunlight to chemical energy [20]. The common types of chlorophyll are "chlorophyll a" present in all photosynthetic plants and "chlorophyll b" found widely in higher plants and algae [19]. It possesses a common basic structure that is a porphyrin structure consisting of four pyrrole rings [19]. The presence of magnesium ion in the center is the unique feature of the chlorophyll structure and it plays an important role in the absorption of light energy. Chlorophyll in its raw form is not an efficient sensitizer for DSSC applications because lack of binding sites to  $\text{TiO}_2$  [21]. Hence different approaches have been adopted to improve the photoelectrochemical performances [19]. Anthocyanin is one of such flavonoid compound present in many fruits, flowers, leaves and is responsible for the red, violet and blue colors [1, 19]. The advantage of anthocyanin is the binding of carbonyl and hydroxyl groups of the chlorophyll to the surface of a

porous TiO<sub>2</sub> film. This helps excess for anchoring the dye on the surface of TiO<sub>2</sub> film and also provides easy electron transfer from the anthocyanin molecule to the conduction band of TiO<sub>2</sub> [1].

In this study, DSSCs were assembled using locally available natural dyes extracted from *Acanthus sennii chiov.* flower and *Euphorbia cotinifolia* leaf using a very simple extraction technique. The optical properties of the extracted dyes were characterized by UV–Vis absorption spectroscopy. Those dyes that have the best optical properties were used as a light harvesting material for the construction of DSSC. To the best of our knowledge, no report has been shown for dyes extracted from these plants for DSSC application using quasi-solid state electrolyte and PEDOT as a counter electrode.

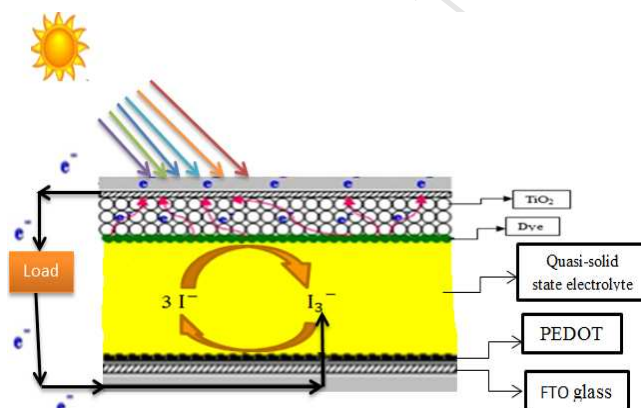
The blue-doped PEDOT film on FTO glass has a potential application for electrodes and has been used as an alternative to platinum due to its good conductivity, remarkable stability and a comparatively lower price than platinum [22]. A quasi-solid state electrolyte is a particular state of matter, neither liquid nor solid, or conversely both liquid and solid [23]. Because of the unique network structure of polymers, quasi-solid state electrolytes show better long-term stability, higher electrical conductivity, and better interfacial contact when compared to liquid electrolytes [24, 25]. The conductivity of the quasi-solid state electrolytes depends on the molecular weight and the morphology of the polymer because of the higher mobility of charges in the amorphous phase of polymers when compared to the crystalline phase. The photoelectrochemical performances of the as prepared DSSCs assembled from these dyes were measured.

A schematic representation of the as prepared DSSC is shown in scheme 1. The working principles or operating mechanisms of the as prepared DSSC begin with illumination of light energy. The following are the key operating steps of a typical DSSC.

- i. Photo-excitation of the dye via absorption of light. The dye is excited by the absorption of photon energy ( $h\nu$ ).
- ii. Injection of excited electrons in to the conduction band (CB) of TiO<sub>2</sub>, resulting in the oxidation of the dye.
- iii. Electron transport to the counter electrode. The electron in the conduction band of TiO<sub>2</sub> flows through the external circuit in to the counter electrode.

- iv. Reduction of tri-iodide ions ( $I_3^-$ ). The oxidized redox mediator, ( $I_3^-$ ), diffuses toward the counter electrode and is reduced to  $I^-$  ions.
- v. The oxidized dye accepts electrons from the  $I^-$  ion redox mediator, regenerating the ground state of the dye (regeneration of dye), and  $I^-$  oxidized to tri-iodide ion ( $I_3^-$ ).
- vi. The recombination of the injected electrons with the oxidized mediator (tri-iodide,  $I_3^-$ ) at the interface between  $TiO_2$  or FTO and electrolyte before the electron has been collected and passed through the load and reached to the counter electrode [26]. This process limits the efficiency of the DSSC.
- vii. The recombination of the injected electron with the oxidized dye [27] at the interface between the dyes and  $TiO_2$ . This is also another limiting reaction for the performance of DSSC.

The as prepared natural dye DSSC represented in scheme 1 uses the aforementioned processes/mechanism to convert solar energy in to electrical energy.



**Scheme 1.** A schematic representation of the as prepared DSSCs

## 2. Experimental Section

### 2.1. Chemicals and materials

Triton X-100 (sigma Aldrich), 3,4-ethylenedioxy-thiophene (EDOT, 97% sigma Aldrich), tetra ethyl ammonium tetra fluoroborate ( $(C_2H_5)_4NBF_4$ , 99%, sigma Aldrich), acetone ( $C_3H_6O$ , 99%, sigma Aldrich), acetonitrile ( $CH_3CN$ , 99.9%, sigma Aldrich), iodine (99%, G.P.R England), and 35% (w/w) of polyvinyl pyrrolidone (PVP),  $SnO_2$ : F transparent conductive glass (FTO, 2 cm  $\times$  1.5 cm, with sheet resistance 15  $\Omega$ /sq, sigma Aldrich), 3-ethyl-2-methylimidazolium iodide (EMIM-I), sodium iodide (BDH), glacial acetic acid (99-100%, SCR-china),  $TiO_2$  powder (P25, Degussa AG, a mixture of about 30% rutile and 70% anatase, sigma Aldrich), ethanol ( $CH_3CH_2OH$ , 97%, Fluka), 2-propanol (99.5%, Fluka) and natural dye extracted from *Acanthus sennii chiov.* flower and *Euphorbia cotinifolia* leaf. All the purchased chemicals and solvents were used without further purification.

**2.2. Preparation of natural dye sensitizers:** *Acanthus sennii chiov.* flower and *Euphorbia cotinifolia* leaf were collected from Bahir Dar city of Ethiopia and these samples were washed with pipe water to get ride off the dust particles. After washing, a sample was dried in the laboratory room in dark place for four weeks at room temperature. After that, the samples were crushed with a super blender to produce a fine powder. Scheme 2 shows the photographic picture of plants, respective powder and solution of natural dyes extracted from *Acanthus sennii chiov.* flower and *Euphorbia cotinifolia* leaf. These powders were used for extracting different dyes using different solvents (such as distilled water, ethanol, mixtures of distilled water and ethanol mixed with different concentration of hydrochloric acid (HCl) for each solvent at room temperature. For a typical extraction of dyes, 2 g of powdered *Acanthus sennii chiov.* flower was mixed with 50 ml distilled water containing 1% HCl by using a magnetic stirrer for 2 hrs to disperse the powder completely and then kept for 24 hrs. Then the solution was filtrated by decantation followed by a glass filter to obtain clear solutions. To prevent the dye from light exposure, the extract solution was covered with aluminum foil. The same amount of *Euphorbia cotinifolia* leaf powder was soaked in 50 ml distilled water containing 1% HCl in a separate bottle. Similar procedures were applied by taking the same amount of powder and solvent for all the rest extracting solutions except the concentration of the acid (different % of HCl was

employed for acidification of solvents). The representative images of plants, their respective powder and extracted solutions of the samples are shown below.



**Scheme 2.** (I) *Acanthus sennii chiov.* flower, (II) *Euphorbia cotinifolia* leaf along with its respective plant parts, powder and extracted solution, a and b represent extracted solutions using acidified (1% HCl) distilled water and acidified ethanol (1% HCl) solvents respectively.

**2.3. Preparation of photoanode:** The TiO<sub>2</sub> film on the FTO glass was prepared using a doctor blade technique [28]. The mesoporous titanium dioxide (TiO<sub>2</sub>) paste was prepared with similar methods described elsewhere [29]. First, FTO glasses (2 cm × 1.5 cm) were cleaned with ethanol, acetone and then 2-propanol for 20 minute in each step using ultrasonic bath. Then 3 g of commercial TiO<sub>2</sub> powder was mixed with a small amount of distilled water (1 ml) containing 0.1 ml of acetic acid to prevent aggregation of the particles. After the powder had been dispersed by the high shear forces in the viscous paste, it was diluted by slow stepwise addition of 4 ml distilled water and 0.05 ml Triton X-100 under continued grinding (mixing) with in a porcelain mortar and pestle. With the conductive side facing up, apply two parallel strips of scotch tape on the edges of the glass plate which was used to monitor the film thickness and to control the



active area for dye absorption. Titanium dioxide paste was deposited on the FTO glass between the two pieces of tape and was coated by “doctor blade” method (i.e. sliding a paste with a glass rod on the substrate) to spread the paste across the plate. This process was continued until the layer became homogenous. After the film dried at room temperature, the tape was removed carefully without scratching the TiO<sub>2</sub> coating. The as prepared TiO<sub>2</sub> film was sintered at 450°C for 30 minutes to enhance the film compactness and crystallinity. After sintering, the films were allowed to cool naturally and immersed into the extracted dyes for about 24 hrs until the TiO<sub>2</sub> film covered with the dyes. After the dye adsorbed, the film was taken out of the dye solution and was rinsed with ethanol to remove unabsorbed dye and any other residues available on the surface. Finally, it was dried with an air gun and ready to combine with the counter electrode for DSSCs device preparation.

**2.4. Preparation of counter electrode:** The counter electrode was prepared by electrochemical polymerization of 3, 4-ethylenedioxy-thiophene (EDOT) in a three electrode and one compartment electrochemical cell [30]. The electrochemical cell consisted of FTO glass (used as the working electrode), a platinum foil (used as the counter electrode), and a quasi-Ag/AgCl (used as the reference electrode). These three electrodes were immersed into a solution of 0.1 M EDOT and 0.1 M ((C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBF<sub>4</sub>) in 50 ml acetonitrile. The polymerization was carried out at +1.8 V for 2 seconds. At this deposition potential and time, the electrode surface has been covered with a blue-doped PEDOT film and the film was rinsed with acetonitrile and dried in air for use.

**2.5. Preparation of quasi-solid-state electrolyte:** The polymer gel electrolyte was prepared as reported elsewhere [31]. For a typical preparation, 0.9 M of 3-ethyl-2-methylimidazolium iodide (EMIM-I) was added to acetonitrile under stirring to form a homogeneous liquid electrolyte. 0.5 M of sodium iodide was added in the above homogeneous liquid electrolyte. Then, 0.12 M of iodine and 35% (w/w) of polyvinyl pyrrolidone (PVP) were also added. The resulting mixture was heated in the temperature range of 70 to 80°C under vigorous stirring to dissolve the PVP polymer, followed by cooling down to room temperature to form a gel electrolyte. Finally, the gel electrolyte was deposited in the form of thin film on top of the dye-coated TiO<sub>2</sub> electrode.

**2.6. Fabrication of Natural DSSCs:** The quasi-solid state electrolytes were deposited in the form of thin film on the surface of dye coated TiO<sub>2</sub> films [30]. These electrolytes were sandwich in between the photoanode and the PEDOT-coated FTO glass counter electrode. The assembly of DSSC was completed by attaching the non-titanium dioxide covered area of the photoelectrode and the non-overlapping edge of the counter electrode to the measuring equipment by means of cords and crocodile clips. The photoelectrochemical cell (PEC) was then mounted in a sample holder inside a metal box with an area of a 1 cm<sup>2</sup> opening to allow light to enter from the source.

**2.7. Optical properties of Natural dyes:** The optical absorption of the as-prepared dye solution was determined by UV-Vis absorption spectrophotometer (Perkin Elmer Lambda 35) in the wave length range of 300 to 800 nm. The effect of extracting solvents on the optical properties of dyes was also studied.

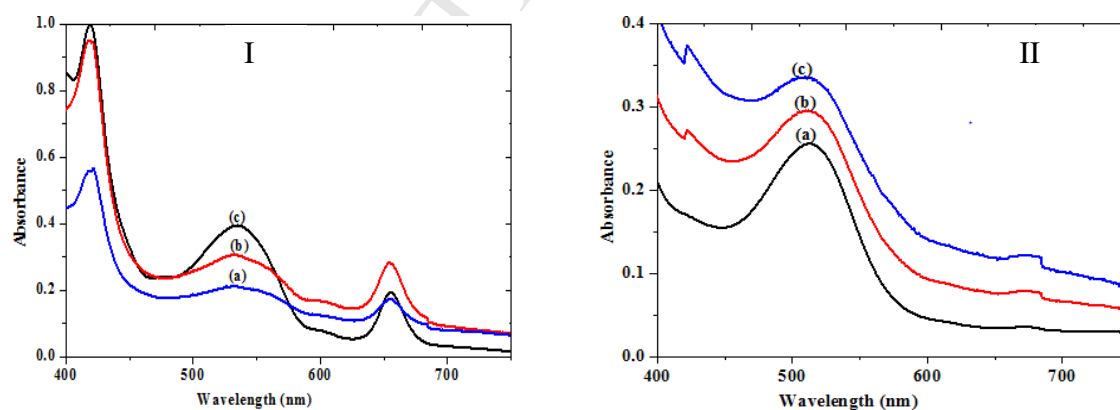
**2.8. Photoelectrochemical Measurements:** Photoelectrochemical measurements were performed by using a computer controlled CHI630A Electrochemical Analyzer. A 250-W tungsten–halogen lamp regulated by an Oriel power supply (Model 68830) was used to illuminate the as prepared DSSC. The measured photocurrent spectra were corrected for the spectral response of the lamp and the monochromatic by normalization to the response of a calibrated silicon photodiode (Hamamatsu, Model S1336-8BK) whose sensitivity spectrum was known [32]. The intensity of the incident light was 100 mW cm<sup>-2</sup>. All experiments were carried out at ambient temperature.

### 3. Result and Discussion

#### 3.1. Optical absorption measurements of the extracted natural dyes

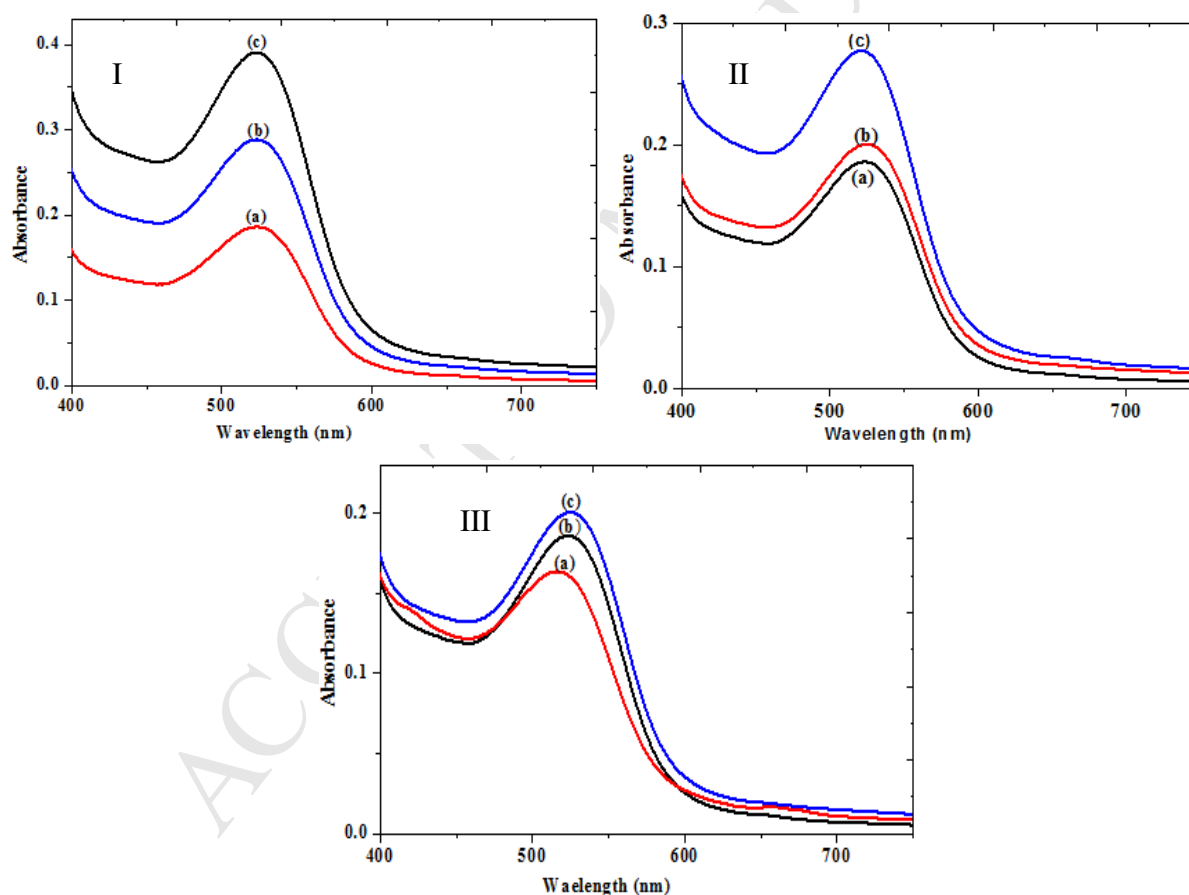
The UV-Vis absorption spectra for the dye solution extracted using different solvents are shown in Fig. 1 & 2 below. Fig. 1 (I) and (II) represent UV-Vis absorption spectra of dye solutions extracted from *Euphorbia cotinifolia* leaves using ethanol and distilled water acidified with various concentrations of HCl solvents. As shown in Fig. 1 (I), all the extracted solutions have shown an absorption peaks at 419, 536 & 655 nm. This absorption peak of extracted dyes shows almost closely related to chlorophyll and anthocyanin as reported earlier [1, 33]. Chlorophyll absorbs strongly in the blue and red regions of the absorption spectrum [9, 18] which

corresponds to the absorbs region from 400 to 500 nm and 600 to 750 nm respectively [33, 34]. It also absorbs very little in the green region of the spectrum from 500 to 600 nm and this also reflected in the absorbance region of anthocyanin since anthocyanin dyes absorb in the region between 500 and 600 nm [1, 33]. From Fig. 1 (II), the absorption peaks are 513, 510 and 510 nm for each (different acid concentration) 1, 2 and 3% HCl respectively. These absorption peaks are closely related to the absorption peaks of anthocyanin which indicates anthocyanin is the major components of the observed pigments as reported earlier. As shown from Fig.1 (I) and (II), solutions extracted by both 1% HCl acidified ethanol and distilled water have relatively higher absorbance than solutions extracted by 2% and 3% acidified ethanol and distilled water, due to an increase in the extraction of anthocyanin using an optimal acidification of extracting solvents which leads to a suitable protonation reaction. This indicates anthocyanin pigments are highly soluble in 1% HCl for these studies. A similar finding was reported so far [35]. In this study, extraction of dyes using different acid concentrations was also studied. The dye that was extracted at low acid concentration shows a good interaction with the working electrode results the best cell efficiency compared with the one extracted with higher acid concentration. This is due to the existence of the dye in a stable form with lower acid concentration, where the ions hydrated to form bases (a stable form). The optical properties also assures that the extracted solution have a higher absorbance at lowest acid concentration compared with the highest acid concentration.



**Figure 1.** UV-Vis absorption spectra of dye solutions extracted from *Euphorbia cotinifolia* leaves using (I) ethanol and (II) distilled water acidified with (a) 3% HCl (b) 2% HCl & (c) 1% HCl concentration as extracting solvents.

Fig. 2 (I-III) shows the UV-Vis absorption spectra of dye solutions of *Acanthus sennii chiov.* flower extracted using acidified ethanol, mixtures of acidified distilled water & ethanol, and acidified distilled water. Acidifications were carried out using different hydrochloric acid concentrations. All the extracted solutions show a broad absorption peak in the visible region between 500 - 600 nm with a maximum absorption wavelength at 523 nm, 524 nm and 524 nm for each acidified ethanol; 523, 525 & 522 nm for each mixtures of acidified distilled water and ethanol; and 517, 523 & 525 nm for each acidified distilled water with different hydrochloric acid concentration (1, 2 & 3% HCl) respectively. As shown in Fig.1(I) and (II) above, these absorption regions are also the main characteristics of anthocyanin pigments [1, 33]. Acidification leads to a protonation reaction and the equilibrium shifts from the quinonoidal to the flavylium form, which increases the extraction of anthocyanin.



**Figure 2.** UV-Vis absorption spectra of dye solutions extracted from *Acanthus sennii chiov.* flower using (I) acidified ethanol, (II) mixture of acidified distilled water and ethanol, and (III) acidified distilled water each with (a) 3% HCl (b) 2% HCl and (c) 1% HCl concentrations.

### 3.2. Photoelectrochemical measurements of natural DSSCs

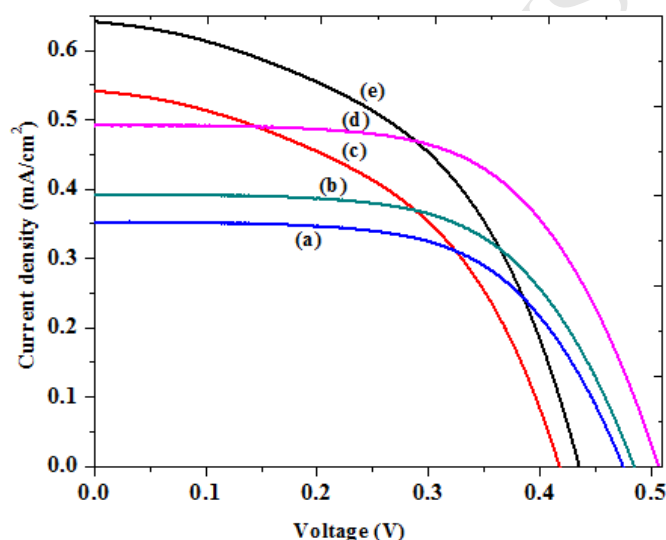
From the current density-voltage (J-V) curves of the as prepared DSSC, the performance of DSSCs was evaluated by short circuit current density ( $J_{SC}$ ), open circuit voltage ( $V_{OC}$ ), fill factor (FF), and power conversion efficiency ( $\eta$ ) [36]. The photovoltaic characteristic of DSSCs is defined as;

$$FF = \frac{P_{max}}{J_{sc} \times V_{oc}} \dots\dots\dots (1)$$

The overall energy conversion efficiency ( $\eta$ ) of DSSCs is calculated using

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \dots\dots\dots (2)$$

Where  $P_{max}$  is maximum output power and  $P_{in}$  is the power of incident light.



**Figure 3.** J-V curve of DSSCs sensitized by *Acanthus sennii chiov.* flower extracted with (a) acidified (in 1% HCl) distilled water, (b) mixtures of acidified distilled water (with 1% HCl) & ethanol, (d) acidified ethanol (with 1% HCl) while (c) acidified (in 1% HCl) distilled water, (e) acidified (in 1% HCl) ethanol extracts of *Euphorbia cotinifolia* leaf.

Fig.3. shows current density–voltage (J-V) curves using different natural dye sensitizers extracted by different solvents at different acid concentrations. The Fill Factors of DSSCs prepared by dyes extracted at different solvents are varied from 47 to 60%. The  $V_{OC}$  and  $J_{SC}$  ranges from 0.475 to 0.507 V and 0.352 to 0.642 mA cm<sup>-2</sup> respectively. The power conversion efficiency of the cell sensitized by the dye extracted from *Acanthus sennii chiov.* flower using ethanol (1% HCl) was relatively higher than DSSCs sensitized by dyes extracted from

*Euphorbia cotinifolia* leaves, where the cell parameters are  $V_{oc}$ ; 0.507 V,  $J_{sc}$ ; 0.491 mA cm<sup>-2</sup>, FF; 60% and  $\eta$ ; 0.150 %.

Table 1 summarizes the photoelectrochemical performances of DSSCs fabricated from various dye sensitizers. As shown in table 1 the efficiencies observed in this study are significantly higher than those of the DSSCs sensitized by other natural dyes. More importantly, it showed an optimal performance compared to other natural dyes employed so far by other groups. This is due to the interaction between TiO<sub>2</sub> and anthocyanin extracted from *Acanthus sennii chiov.* flower by the acidified ethanol resulted a good charge transfer and the higher solubility of anthocyanin in acidified (1% HCl) ethanol reduces the aggregation of dye molecules. While in *Euphorbia cotinifolia* leaves, the dominant components are chlorophyll pigments which have less interaction with TiO<sub>2</sub> film leading poor charge transfer. As a result, the DSSCs sensitized by natural dyes mainly composed of chlorophyll did not offer high conversion efficiencies. The FFs of DSSCs prepared by dyes extracted from *Euphorbia cotinifolia* leaves is lower than the FFs of that of *Acanthus sennii chiov.* flower due to the higher resistance and more recombination in a solar cell which can reduce the device's FF and power conversion efficiency [37]. As shown in table 1, the anthocyanin and chlorophyll dye extracted using different solvents showed lower power conversion efficiency. However, in this work, a quasi-solid-state electrolyte was employed as an electrolyte along with PEDOT as a counter electrode instead of platinum leading to a better performance of the as prepared DSSC.

Generally, as we mentioned in the abstract and introduction part ruthenium based complex dyes are capable of delivering DSSCs with high conversion efficiency as compared to natural DSSCs. However, processing of this complex contain heavy metal, which make this types of DSSCs be unpopular from the environmental aspects. Furthermore the high cost, long-term unavailability, rarity and the complicated synthesis of ruthenium complexes needs to search for alternative photosensitizers for the use in TiO<sub>2</sub> based photovoltaic devices. Hence natural dyes can be used as alternatives for the same purpose with an acceptable efficiency. The advantages of natural dyes include their availability, eco-friendly, low cost and biodegradable nature.

**Table 1.** The photoelectrochemical parameters of the as prepared DSSCs sensitized with dyes extracted from *Euphorbia cotinifolia* leaves and *Acanthus sennii chiov.* flower extracted at different solvents.

Natural dye	Solvent	$V_{oc}$ (V)	$J_{sc}$ ( $mA\ cm^{-2}$ )	FF (%)	H (%)	Reference
Ascf	Ethanol with 1% HCl	0.507	0.491	60.4	0.150	This work
EcL	Ethanol with 1% HCl	0.436	0.642	48.5	0.136	This work
Ascf	Mixtures with 1% HCl	0.485	0.392	60.4	0.115	This work
EcL	Distilled water with 1% HCl	0.418	0.542	47	0.106	This work
Ascf	Distilled water with 1% HCl	0.475	0.351	60.6	0.101	This work
Lyceum Shawii	Ethanol	0.580	0.420	42	0.100	[38]
Olive grain	Ethanol	0.550	0.580	38	0.120	[36]
Sal. S.F	Ethanol	0.214	0.071	56	0.015	[30]
J. M.F	Ethanol	0.221	0.034	52.6	0.004	[30]
Lemon leafs	Acetone	0.225	0.017	54.1	0.040	[9]

**Key:** *Ascf*: *Acanthus sennii chiov.* flower, *ECL*: *Euphorbia cotinifolia* leaves, *Sal. S. F*: *Salvia splendens* flower, *J.M.F*: *Jacaranda mimosifolia* flower, Mixtures: mixture of distilled water and ethanol.

#### 4. Conclusion

In this work, natural dyes extracted from two locally available plants such as *Acanthus sennii* flower and *Euphorbia cotinifolia* leaf were used as sensitizers for DSSC. These natural dyes used as a light harvesting material were extracted using different solvents at different acid concentrations. The comparisons of different acid concentrations as an extracting solvent and its effect on the absorption spectra were investigated. The dye solutions extracted from parts of the plant material contains anthocyanin and chlorophyll. The as prepared DSSC were assembled using PEDOT-coated FTO glass as a counter electrode, natural dye anchored TiO<sub>2</sub> film as a photoanode, and quasi-solid state electrolyte as an electrolyte sandwiched in between the two electrodes. The photoelectrochemical performances of the as prepared DSSC were evaluated. When chlorophyll pigments were used as a light harvesting, did not offer high conversion efficiencies, due to lack of available interaction between the dye and TiO<sub>2</sub> molecules resulting low loading on the surface TiO<sub>2</sub> films. The highest photoelectrochemical performance of the as prepared DSSCs was observed for a dye extracted using acidified (in 1% HCl) ethanol (where V<sub>OC</sub> of 0.507 V, J<sub>SC</sub> of 0.491 mA cm<sup>-2</sup>) and its power conversion efficiency reached 0.150%. Generally, natural dyes as sensitizers/light harvesting materials for DSSCs are promising because of their environmental friendliness, low-cost of production and simple manufacturing technique.

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## Reference

- [1] Y.-T.B. Hee-Je Kim , S.N. Karthick, K.V. Hemalatha, C. Justin Raj, S.Venkatesan, Songyi Park, G. Vijayakumar, Natural Dye Extracted from Rhododendron Species Flowers as a Photosensitizer in Dye Sensitized Solar Cell, *Int. J. Electrochem. Sci*, 8 ( 2013) 6734-6743.
- [2] M. O'Regan B. and Grätzel, A low-cost, high-efficiency solar cell based on dye sensitized colloidal TiO<sub>2</sub> films, *Nature*, 353 (1991) 737-740.
- [3] H.J. Won-Yeop Rho, Ho-Sub Kim, Woo-Jae Chung, Jung Sang Suh and Bong-Hyun Jun, Recent Progress in Dye-Sensitized Solar Cells for Improving Efficiency: TiO<sub>2</sub> Nanotube Arrays in Active layer, *J. Nanomater.*, 2015 (2015) 1-17.
- [4] T.M.E.-A. Sofyan A. Taya, Kamal S. El-Ghamri, Monzir S. Abdel-Latif, Dye-sensitized solar cells using fresh and dried natural dyes, *Turk. J. Phys*, 39 (2015) 24-30.
- [5] S.M.M.K. Mubarak A. Khan, Mahir Asif Mohammed, Sabia Sultana, Jahid M M Islam and Jasim Uddin, Sensitization of Nano-crystalline Titanium dioxide Solar Cells using Natural Dyes: Influence of Acids Medium on Coating Formulation, *American Academic & Scholarly Research Journal* 4(2012) 1-10.
- [6] G.R.A.K. G.G.G.M.N.Hemamali, Dye-Sensitized Solid State Solar Cells Sensitized with Natural Pigment Extracted from the Grapes *Int. J. Scienti. Res. Publi.*, 3 (2013) 1-3.
- [7] A.A.P. Aakash Umesh Bhanushali, Sachin Yadav, R. PratibhaNalini, spinach and beetroot extracts as sensitizers for ZnO based DSSC, *Int.J.Eng.Sci.Manag.Res*, 2(5) (2015) 37-42.
- [8] N.S.T.a.W.B. D. M. Mulati, The Absorption Spectra of Natural Dyes and their Suitability as a Sensitizer in Organic Solar cell, *Org. sol. cells*, 14(1) (2012) 45-60.
- [9] A.S.I. Mounir Alhamed, A. Wael Doubal, Studying of Natural Dyes Properties as Photosensitizer for DSSC, *J. Electron Devices*, 16 (2012) 1370-1383.
- [10] J.W. S. Hao, Y. Huang, J. Lin, Natural dyes as photosensitizers for dye-sensitized solar cell, *Sol. Energy*, 80(2) (2006) 209-214.
- [11] Y. Chiba, Islam, A, Watanab, Y, Komiya, R, Koide, N, Han, L, Dye-sensitized solar cells with conversion efficiency of 11.1%, *Jpn. J. Appl. Phys*, 45 (2006) 1638-1640.
- [12] R.H.a.A. Mohammadi, Improving optical absorptivity of natural dyes for fabrication of efficient dye-sensitized solar cells, *J. Theoret. Appl. Phys.*, 7:57 (2013) 1-7.

- [13] M. Gratzel, Photovoltaic and photo electrochemical conversion of solar energy, *Phil. Trans. R. Soc. A*, 365 (2007) 993-1005.
- [14] G.P.S. M.Grätzel, Demonstrating electron transfer and nanotechnology: a natural dye sensitized nanocrystalline energy converter, *J. Chemical Ed.*, 75 (1998) 752-756.
- [15] U.A. Kasim Uthman Isah, Adamu Idris, Mohammed Isah Kimpa, Uno Essang Uno, Muhammed Muhammed Ndamits, Betalain pigments as natural photosensitizers for dye-sensitized solar cells: the effect of dye pH on the photoelectric parameters, *Mater. Renew. Sustain. Energy.*, 4:39 (2015) 38-44.
- [16] M.E. Angel Ramon Hernández-Martínez, Susana Vargas and Rogelio Rodríguez, Stabilized Conversion Efficiency and Dye-Sensitized Solar Cells from Beta vulgaris Pigment, *Int. J. Mol. Sci*, 14 (2013) 4081-4093.
- [17] D.C.Z. Wu, Study on Extraction and Purification Process of Capsicum Red Pigment, *J. Agri. Sci.*, 1 (2009) 94-100.
- [18] N.H.M. Andery Lim, K.Tennakoon, R. L. N. Chandrakanthi, L. B. Leng Lim, J. M. R. Sarath Bandara and Piyasiri Ekanayake, Higher Performance of DSSC with Dyes from *Cladophora sp.* as Mixed Co-sensitizer through Synergistic Effect, *J. Bio. phys.*, 2015 (2015) 1-8.
- [19] M.R. NT\*, Pigments for Generating Electric Power - An Overview, *Res.J.Pharm.,Biol.Chem.Sci.*, 6(1) (2015) 691-698.
- [20] A.M.A.-A.M. N. A. Ludin, A. Bakar Mohamad, A. A. H. Kadhum, K.Sopian and N. S. Abdul Karim, Review on the development of natural dye photosensitizer for dye-sensitized solar cells, *Renew. Sustain. Energy. Rev.*, 31 (2014) 386-396.
- [21] L.D. I.Kartini, T. D. Wahyuningsih, Chotimahand L. Wang, The Sensitization of Xanthophylls-Chlorophyllin Mixtures on Titania Solar Cells, *Int. J. Sci. Eng*, 8(2) (2015) 109-114.
- [22] H.S.K. Chang Kook Hong, Eun Mi Han, Kyung Hee Park, Electrochemical Properties of Electrodeposited PEDOT Counter Electrode for DSSC, *Int. J. Electrochem.Sci.*, 10 (2015) 5521-5529.
- [23] J. Wu, Z. Lan, S. Hao, P. Li, J. Lin, M. Huang, L. Fang, Y. Huang, Progress on the electrolytes for dye-sensitized solar cells, *Pure. Appl. Chem.*, 80(11) (2008) 2241-2258.

- [24] P.W. N. Mohmeyer, H.-W. Schmidt, S. M. Zakeeruddin, M. Grätzel, Quasi-solid-state dye sensitized solar cells with 1,3:2,4-di-O-benzylidene-D-sorbitol derivatives as low molecular weight organic gelators, *J. Mater. Chem.*, 14(12) (2004) 1905-1909.
- [25] J. Y. Song, Y. Wang, C. C. Wan, Review of gel-type polymer electrolytes for lithium-ion batteries, *J. Power Sources*, 77(2) (1999) 183-197.
- [26] G.P. Smestad, Education and solar conversion: Demonstrating electron transfer, *Sol. Energy. Mater.Sol. Cells*, 55 (1998) 157-178.
- [27] E.B.M.G. Md. K. Nazeeruddin, Dye-sensitized solar cells: A brief overview, *Sol. Energy*, 85 (2011) 1172-1178.
- [28] A.G. Tamirat, J. Rick, A.A. Dubale, W.-N. Su, B.-J. Hwang, Using hematite for photoelectrochemical water splitting: a review of current progress and challenges, *Nanoscale Horizons*, (2016).
- [29] M. K. Nazeeruddin, K. Rodicio, I. Humphry-Baker, R. muller, E.liska, P. Volachopouloes , Conversion of light to electricity by cis-X<sub>2</sub>bis (2, 2'-bipyridyl-4,4'- dicarboxylate) ruthenium (II) charge-transfer sensitizers (X=Cl-, Br-, I-,CN- and SCN-) on nanocrystalline titanium dioxide electrodes, *J. Am. Chem. Soc.*, 115(14) (1993) 6382-6390.
- [30] A. L.Takele, G. G. Gonfa, T. Y. Anshebo, Dye-Sensitized Solar Cell using Extract of Jacaranda Mimosifolia and Salvia Spelendens as a Natural Sensitizer, *Chem.Mater. Res.*, 6(12) (2014) 126-133.
- [31] L. Fan, S. Kang , J. Wu, S. Hao, Z. Lan, J. Lin , Quasi-solid state dye-sensitized solar cells based on polyvinylpyrrolidone with Ionic liquid, *Energy Sources, Part A*, 32(16) (2010) 1559-1568.
- [32] A.G. Tamirat, W.-N. Su, A.A. Dubale, H.-M. Chen, B.-J. Hwang, Photoelectrochemical water splitting at low applied potential using a NiOOH coated codoped (Sn, Zr) [small alpha]-Fe<sub>2</sub>O<sub>3</sub> photoanode, *Journal of Materials Chemistry A*, 3 (2015) 5949-5961.
- [33] H. Chang, Y.-J. Lo, Pomegranate leaves and mulberry fruits as natural sensitizers for Dye sensitized solar cells, *Sol. Energy*, 84(10) (2010) 1833-1837.
- [34] A.R. Hernández-Martínez, M. Estevez, S.Vargas, F. Quintanilla, R. Rodríguez, Natural pigment based dye sensitized solar cells, *J. Appl. Res.Technol.*, 10 (2012) 38-47.

- [35] V.B.a.S.M. S. Sakthivel, Fabrication and Characterization of Dye Sensitized Solar Cell Using *Phyllanthus Emblica*, *Nano Vision*, 5(2) (2015) 17-24.
- [36] A.G. Tamirat, W.-N. Su, A.A. Dubale, C.-J. Pan, H.-M. Chen, D.W. Ayele, J.-F. Lee, B.-J. Hwang, Efficient photoelectrochemical water splitting using three dimensional urchin-like hematite nanostructure modified with reduced graphene oxide, *J. Power Sources*, 287 (2015) 119-128.
- [37] J.D.R.-M.a.I.A. Aksay, Graphene Materials and their use in DSSCs, *Chem. Rev.*, 114 (2014) 6323-6348.
- [38] M.B.A. Monzir, S. Abdel Latif, T. M. El – Agezand, S. A. Taya, Dye-Sensitized Solar Cells Using Dyes Extracted from Flowers, Leaves, Parks, and Roots of three trees, *Int. J. Renew. Energy. Res.*, 5 (2015) 294-298.

**Highlights**

- Natural dyes were extracted from different parts of plants using different extracting solvents
- Natural dyes were used as a light harvesting pigments for Dye-sensitized solar cell
- The effect of dye extracting solvents on the performance of solar energy conversion has been studied.
- Quasi-solid state electrolyte and PEDOT as a counter electrode has been used for DSSC assembly