Fabrication of *DSSC* with Nanostructured TiO₂ Photoanode and Natural Dye Sensitizer extracted from fruits of *Phyllanthus reticulatus*

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ABSTRACT

DSSCs have wide attention because they are made from cheap materials and are environmentally friendly. The natural dye anthocyanin was extracted from *Phyllanthus reticulatus* using a simple extraction technique without any further purification. The solvents such as water and ethanol were used for dye extraction. They were then used as sensitizers in dye-sensitized solar cells (DSSCs), and their characteristics were studied. The dyes were characterized using Uv-Vis spectrophotometer. Titanium dioxide (TiO₂) nanoparticles were synthesized using sol–gel technique. The morphological, structural, and optical properties of prepared samples were characterized by High-resolution scanning electron microscopy HRSEM, EDAX, X-ray diffraction [XRD], and Uv-Vis absorption spectroscopic studies. The short-circuit photocurrent; the open-circuit photovoltage, and the power conversion efficiency of DSSC were measured using J–V measurement system.

Keywords: XRD, DSSC, HRSEM, *Phyllanthus reticulatus*, Uv-Vis spectroscopy.

I. INTRODUCTION

Solar cell is a promising renewable energy technology that converts sunlight to electricity with specific wavelength, with broad potential to contribute significantly to solving the future energy problem that humanity faces [1, 2]. Professor Grätzel reported a new low cost chemical solar cell by the successful combination of nanostructured electrodes and efficient charge injection dyes, known as Grätzel cell or dye-sensitized solar cell which falls under the third generation photovoltaic cell [3]. DSSC was achieved in an attempt to imitate photosynthesis, the natural processes plants convert sunlight into energy by sensitizing a nanocrystalline TiO₂ film using novel ruthenium (Ru) bipyridl complex. In dye sensitized solar cell, charge separation is accomplished by kinetics competition like in photosynthesis leading to photovoltaic action. While the organic dye monolayer in the photoelectron chemical or dye sensitized solar cell replaces light absorbing pigments, the wide band gap nanostructured semiconductor layer replaces oxidized dihydro-nicotinamide adenine-dinucleotide phosphate (NADPH), and while carbon dioxide acts as the electron acceptor, the electrolyte replaces the water while oxygen as the electron donor and oxidation product, respectively [4-5].

However, the low efficiency of conversion and stability are the major problems confronting it. In optimizing the device performance and stability of DSSC, various light harvesting systems are employed to enhance a photovoltaic performance and investigate their properties. It was once reported that the presence of sensitizer in the vicinity of TiO₂ can absorb more photons [6].The dye is an important part of the DSSCs, playing a significant role in absorbing light, generating photo stimulated carriers and injecting these carriers into the conduction band of TiO₂ network. Thus, the light absorption capability of

the dye and how many carriers it stimulates directly affect carrier injection and DSSCs performance [7].Therefore, enhancing dye light absorption should be an effective way to increase the conversion efficiency. The use of natural dyes have been considered as potential alternatives to the expensive synthetic dyes in enhancing the light response of semiconductor in active layers of solar cells, and have been demonstrated on several solar-cell materials[8-15].

In this work, we have chosen the low cost natural dye extracted from *Phyllanthus reticulatus* fruit that belongs to the family of Euphorbiaceae the natural dye used as a sensitizer for the preparation of DSSCs. The fruits were extracted with solvents such as water and ethanol which acts as sensitizer to fabricate DSSC and the solar cell performances were analyzed. The morphological, structural, and optical properties of prepared samples were characterized by HRSEM, XRD and Uv-Vis spectroscopy. The natural dye extracts were subjected to Uv-Vis analysis.

II. EXPERIMENTAL METHODS

2.1 Synthesis of TiO_2 nanoparticles

Titanium isopropoxide (TTIP), deionized water and isopropyl alcohol were preferred as the starting materials for synthesizing nanoparticles using sol gel method. All the reagents used were of analytical grade and used without any further purification. The isopropyl alcohol was mixed thoroughly with distilled water and this solution was stirred vigorously. About 5 mL of titanium isopropoxide solution was added drop wise to result in white precipitation. The pH of sol was adjusted to 2-3 by adding 1 or 2 drops of ammonia with stirring at room temperature for 12h. This yields a high viscous white suspension which is washed in distilled water and then in ethanol to remove the impurities. The resultant gel was kept for the drying at 100°C for 1h in order to evaporate the water and other organic contents. As a result, the final

product of amorphous powder was obtained. The powder was calcined at 400°C for 4h to obtain TiO_2 nanoparticles. The neodymium (0.5%) doped TiO_2 was synthesized using the same procedure.

2.2 Preparation of natural dye

The natural dyes were extracted with deionized water and ethanol employing the following procedure. *Phllanthus reticulatus* fruits were collected from Thiruvannamalai region and washed with running tap water. 10 g of the *P. reticulatus* fruits were grinded to small particles using mortar and pestle. The residue was soaked in 100 ml of deionised water and 100 ml of ethanol respectively. The solutions were filtered to separate the solid residue from the solvents and the filtrate was used as the light harvesting pigment without further purification (Figure 1).

Figure1. *Phyllanthus reticulatus* plant with fruits; Dye extracted with a) Water b) Ethanol

2.3 Preparation of electrolyte

The I^-/I_3^- is a common electrolyte in organic solvents, such as acetonitrile, which was used in this study. Lithium ion was added to facilitate electron transport. This electrolyte is suitable for ion diffusion and infiltrates well into the TiO_2 film, exhibiting the highest efficiency among all DSSCs. The electrolyte solution was prepared by dissolving 0.3 M of Lithium Iodide (LiI) and 0.03 M of Iodine (I_2) in tert-butyl alcohol and acetonitrile in 1:1 volume ratio, which can be used as charge transport mediator between photoanode and counter electrode in DSSC.

2.4 Fabrication of DSSC

The FTO glass (Fluorine doped tin oxide) (sheet resistance 7.5kΩ/cm²) was used as the current

collector. The FTO plate was first cleaned using an ultrasonic bath with acetone, ethanol, and water for about 15 min respectively. FTO glasses were rinsed well with distilled water and air dried which are used as anode and cathode in DSSC. Scotch tape was used as a spacer to control the film thickness and to provide non-coated areas for electrical contact. The prepared TiO_2 nanoparticles were made as paste by mixing with polyethylene glycol binder and coated on FTO by doctor blade technique to prepare DSSC photoanode. The prepared TiO_2 film was air dried at 70°C for 30 min and the films were annealed at 450°C for 1h to eliminate the polymer binder. The coated glasses were soaked in *P. reticulatus* dye extracts for 12h. After the dye-sensitization process, the photoanode was washed with ethanol to remove the unanchored dye molecules and air dried. A platinum coated FTO glass plate was used as the counter electrode. The dye-covered TiO_2 electrode and Pt counter electrode were assembled as a sandwich-type cell. The electrolyte solution was injected in between the cells which act as charge transport mediator between photoanode and counter electrode in DSSC. In the Nd^{3+} doped TiO_2 based DSSC fabrication, the photoanode was prepared by repeating the same procedure as that of undoped TiO_2.

2.5 DSSC assembly

The TiO_2 nanoparticles coated on FTO glass was placed facing upward, and the conductive side of the platinum coated counter electrode faced the TiO_2 film. A DSSC was assembled by introducing liquid electrolyte (0.3 M of Lithium Iodide (LiI) and 0.03 M of Iodine (I_2) in tert-butyl alcohol and acetonitrile in 1:1 volume ratio) into the space between the TiO_2 electrode (photo anode) and the counter electrode (cathode) by capillary action. The two electrodes were clipped together using two binder clips to prevent the electrolyte from leaking.

2.6 Characterization and measurements

The absorption spectrum of *P. reticulatus* dye solution was determined using UV-Vis spectrophotometer in the wavelength range of 200–800 nm. The J-V response of the fabricated solar cells was studied using standard solar simulator (Oriel Sol3A Class AAA) of 1 Sun intensity (1000 W/m²) with AM 1.5-G filter. The current–voltage (J-V) curve was used to determine short-circuit current (Jsc) and open-circuit voltage (Voc). The solar cell parameters fill factor (FF) and efficiency (η) have been calculated using the following Equations

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

$$\eta = \frac{J_{sc}.V_{oc}.FF}{P_{in}} \times 100\%$$

Where J_{sc} is the short-circuit photocurrent density (mA cm^{-2}), V_{oc} the open-circuit voltage (volts), P_{in} is the intensity of the incident light (W cm^{-2}) and J_m (mA cm^{-2}) and V_m (volts) are the maximum current density and voltage in the J–V curve, respectively, at point of maximum power output.

III. RESULTS AND DISCUSSION

3.1 Absorption of natural dyes

Figure 2 shows the UV-Vis absorption spectra of dyes extracted from *P. retculatus* fruits with water and ethanol. *P. reticulatus* fruits extracted with water and ethanol shows the broadest absorption level detected between 490- 560nm which confirms the presence of anthocyanin. The structure of anthocyanin is shown in Figure 3.Anthocyanin is a suitable material used as photosensitizer in the visible-light region.
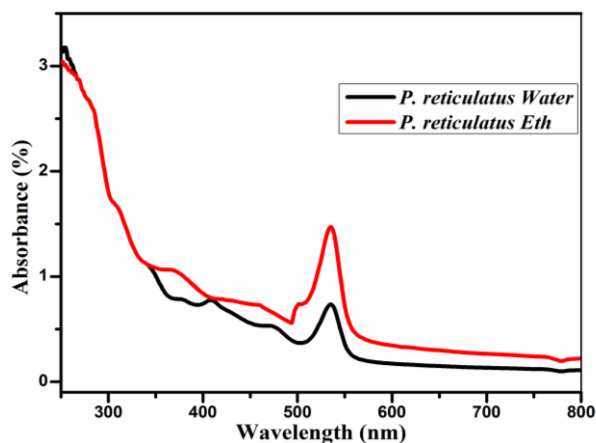
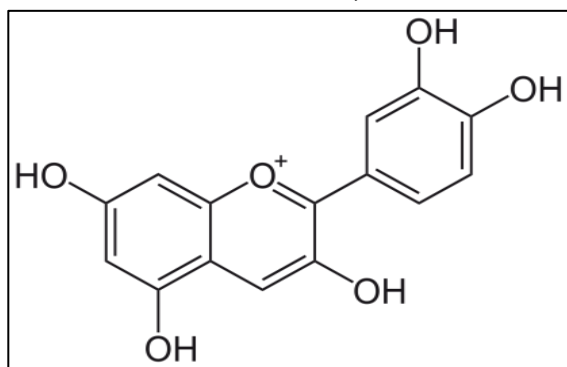**Figure 2.**UV – Visible spectrum of *Phyllanthus reticulatus* dye

Figure 3. Structure of anthocyanin

3.2 Powder XRD analysis

The crystalline phase of TiO_2 nanoparticles were analyzed by X-ray diffraction [XRD] measurements which were carried out at room temperature by using Siemens X-ray diffraction D500 with CuKα. Fig. 4 shows the powder XRD pattern of as- prepared TiO_2 nano particles and the presence of sharp diffraction peaks in the XRD confirm that products are highly crystalline. The diffraction peaks corresponding to 2θ value are identified ass (101), (004),(200),(211),(204),(220) and (215) and it matches well with the titania peaks (JCPDS 73-1764). The crystalline size was calculated by the debye scherrer formula D =0.89λ/β cos θ, where D is the crystalline size, λ is the wavelength of X-ray radiation (0.154 nm), 'β' is the full width half maximum and θ is the diffraction angle. It was found that the average crystalline size of TiO_2 surface were 20 nm.
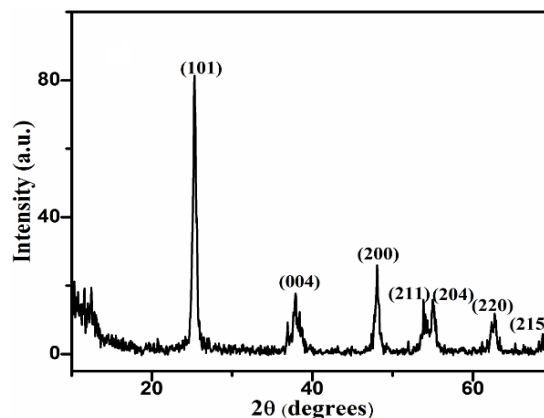

Figure 4. Powder X-ray diffraction analysis of TiO_2 nanoparticles

3.3 Uv-Vis Absorption spectroscopy

Optical properties of the synthesized samples were investigated through Uv–Vis absorption spectrum. As observed from Fig.5a, absorption value increases with enhancement of Nd doping level especially in 300-400nm wavelengths and there is shift in doped samples spectra compared to undoped TiO_2. It is related to charge transferring between valence band of TiO_2 and 4f levels of Nd ion. It has been reported that lanthanide ions form multi-energy level below theTiO_2 conduction band and reduce band gap in doped samples. The band gap energy of the synthesized powder was calculated with the help of the optical absorption coefficient of the photon energy. The relation between the optical band gap (E_g) absorption coefficient and energy ($h\nu$) of the incident photon is given by

$$\alpha h\nu = A(h\nu - E_g)^r$$

where$E_g$is optical energy gap, A is constant, h is the Planck's constant (6.625×10^{-34} J/s)

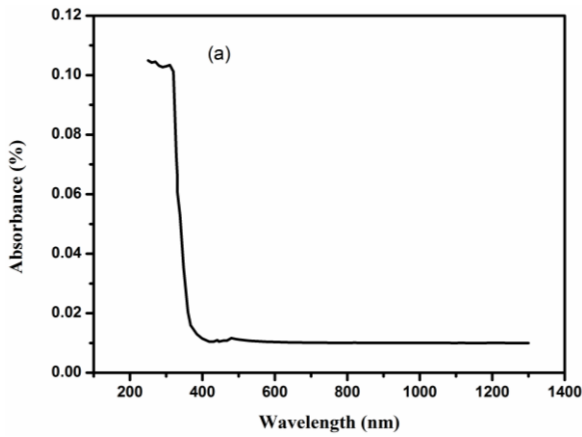$$\alpha = \frac{(h\nu - E_g)^{1/2}}{h\nu}$$

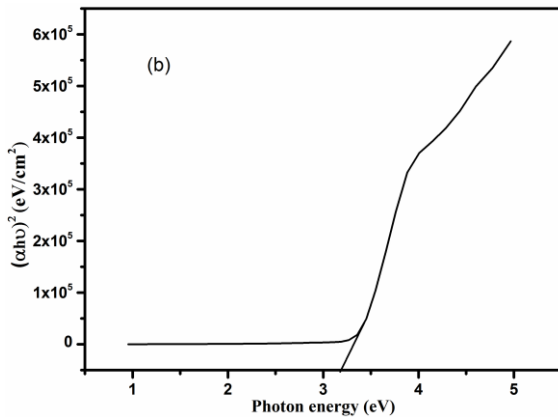**Figure 5a.**Uv-Vis absorption spectra of TiO₂ nanoparticles

Figure 5b. Band gap value of TiO₂ nanoparticles

The optical band gap (E_g) of undoped and Nd^{3+} doped TiO₂ nanoparticles were obtained by extrapolating the linear part of the plots of $(\alpha h\nu)^2$ versus$h\nu$. The band gap value is obtained as 3.31 and 3.09 eV respectively as shown in Fig. 5b. As the band gap value of the doped TiO₂ is decreased it increases the conducting property of the material which is more suitable for DSSC fabrication.

3.4 High Resolution Scanning Electron Microscopy (HRSEM)

High resolution scanning electron microscope (HRSEM) was used to examine the surface morphology of prepared samples. The HRSEM image of undoped and doped TiO₂ nanoparticles are shown in Fig. 6 revealed that TiO₂ particles aggregated to form nanoclusters. The HRSEM investigation of the synthesized samples reveals that the crystallites are

of nanometer size and all samples show uniform morphology in the form of TiO₂nano clusters. The aggregation of the TiO₂ particles was enhanced, and the spherical shape of the particles slightly changed because of the adsorption of dopant on the surface of TiO₂.
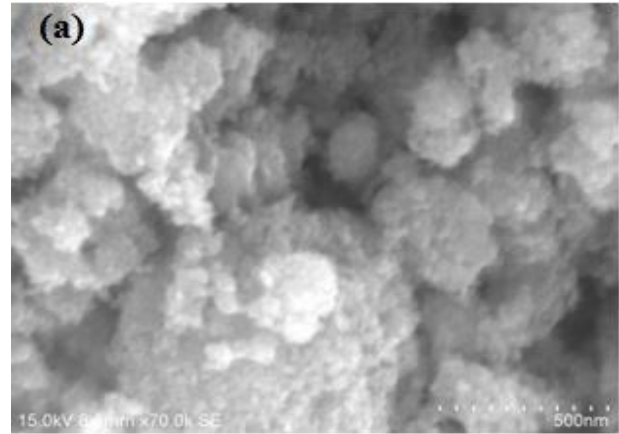

Figure 6.HRSEM image of TiO₂ nanoparticles

3.5. Energy Dispersive X-Ray (EDAX) analysis

To identify the type of elements present in the samples, Energy dispersive X-ray spectroscopy (EDAX) was carried out. The EDAX spectra of the TiO₂ nano particles were recorded and they are depicted in figure 7. From the results, it is confirmed that Ti and O ions are present in the sample.
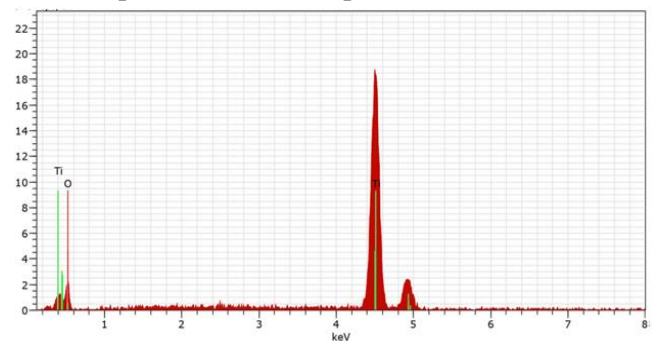

Figure 7.EDAX spectra of TiO₂ nanoparticles

3.6 I-V characteristics of Dye sensitized solar cell (DSSCs)

Figure 8 shows the J - V characteristics of TiO₂ based solar cells using plant dyes. The photo electrochemical activity is dependent on the morphology of the TiO₂ photo anode. The photocurrent density-voltage (J-V curve) measurement of the DSSCs is based on

TiO$_2$nanoparticles. The sensitization was performed using standard solar simulator at 1Sun intensity (AM 1.5 G). The overall efficiency (η) was calculated from the current density–voltage (J–V) curves using the following equation,

Power conversion efficiency (η) = $\frac{P_{max}}{P_{input}}$

$$\eta = \frac{J_{sc}.V_{oc}.FF}{P_{in}} \times 100\%$$

where the P$_{max}$ is the maximum power output point in the J–V curve yielding maximum product of current and voltage, P$_{input}$ is the radiation power incident on the cell, J$_{sc}$ is short circuit current density generated under illumination, and V$_{oc}$ is the open-circuit voltage. FF is the fill factor calculated from the following equation and summarized in Table 1.
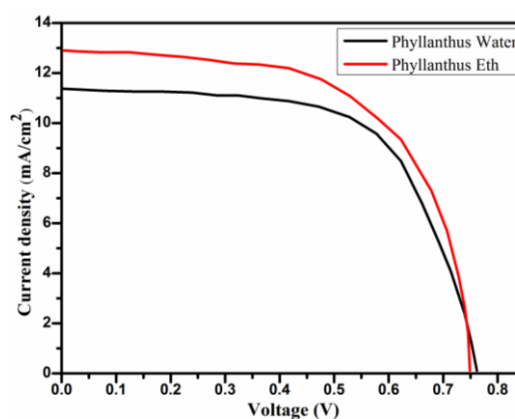
$$FF = \frac{I_{max}.V_{max}}{J_{sc}.V_{oc}}$$

Figure 8. J-V characteristics of TiO$_2$ based solar cells sensitized by using natural dye

Table 1. Performance parameter of *Phyllanthus reticulatus* dyes

Dyes	Photoanode	Solvent(s)	J$_{sc}$ (mAcm^{-2})	V$_{oc}$ (V)	FF (%)	η (%)
Phyllanthusr	TiO$_2$	Water	11.37	0.761	63.54	5.49
eticulatus	TiO$_2$	Ethanol	12.91	0.749	61.27	5.91

The TiO$_2$ solar cell fabricated using *P. Reticulates* ethanolic dye extract exhibited a power conversion efficiency of 5.91% with a short circuit current density (Jsc) of 12.91 mA/ cm^2, open circuit voltage (Voc) of 0.749 V and fill factor (FF) of 61.27%. The power conversion efficiency exhibited by the solar cell fabricated using TiO2 sensitized by fruits *of P. reticulatus* water extract exhibited a power conversion efficiency of 5.49% with a short circuit current density (Jsc) of 11.37 mA/ cm^2, open circuit voltage (Voc) of 0.761 V and fill factor (FF) of 63.54%.

IV. CONCLUSION

Natural dyes can be safely and economically extracted from its source and do not need any complicated technique for synthesis. As it is synthesized from natural source therefore no need to test its toxicity. This makes natural dye an important entity for development of economically and commercially available DSSC. In this study, TiO$_2$ photoanode have been investigated for their performance in DSSCs. TiO$_2$ nanoparticles were synthesized by Sol-gel method and were further characterized by XRD, Uv-Vis, HRSEM and EDAX. The natural dyes were extracted from fruits of *P. reticulatus* using water and ethanol as solvents and were subjected to Uv- Vis spectroscopy. The broad spectrum obtained coincides with that of anthocyanin pigment. The current density obtained by *P. reticulatus* was 11.37mAcm^{-2} and 12.91 mAcm^{-2} for ethanolic and water extract respectively. However, this investigation showed a great potential for natural sensitizers in improving the DSSCs performance. The results demand additional studies to optimize the DSSCs with natural dyes, and we are planning new experiments to address more scientific photochemical aspects.

V. REFERENCES

[1]. O'regan B, Gratzel M, A low-cost, high-efficiency solar cell based on dyes ensitized colloidal TiO2 films, Nature 353 (6346) (1991) 737-740.

[2]. Zhang H, Han Y, Liu X, Liu P, Yu H, Zhang S, Zhao H, Anatase TiO2 microspheres with exposed mirror-like plane {001} facets for high performance dye-sensitized solar cells (DSSCs), Chem. Commun. 46 (44) (2010) 8395-8397.

[3]. Sanjay P, Deepa K, Madhavan J, Senthil S, Performance of TiO2 based dye-sensitized solar cells fabricated with dye extracted from leaves of Peltophorum pterocarpum and Acalypha amentacea as sensitizer, Materials Letters 219 (2018) 158-162.

[4]. Ghaedi M, Nasab A, Khodadoust S, Sahraei R, Daneshfar A, Characterization of zinc oxide nanorods loaded on activated carbon as Cheap and efficient adsorbent for removal of methylene blue, Journal of Industrial and Engineering Chemistry. 21 (2015) 986-993.

[5]. Sanjay P, Deepa K, Victor Antony Raj M, Madhavan J, Senthil S, Structural, Optical, Morphological, and Dielectric Properties of CdSe Nanoparticles by Hydrothermal Method, International Journal of Scientific & Engineering Research, 7, (8), (2016) 1144-1148.

[6]. Yazie N, Worku D, Reda A, Natural dye as light-harvesting pigments for quasi-solid- state dye-sensitized solar cells. Mater. Renew. Sustain. Energy 5, 13 (2016).

[7]. Prima E.C, Yuliarto B, Suendo V, Suyatman, Improving photochemical properties of Ipomea pescaprae, Imperata cylindrical (L.) Beauv and Paspalum conjugatum Berg as photosensitizers for dye sensitized solar cells. J. Mater. Sci. 25, 4603-4611 (2014).

[8]. Vijayalakshmy S, Subramanian B, Effect of ZnO block layers fabricated by pulsed laser deposition and mesoporous layers by chemical method on the performance of dye sensitized solar cells. Electrochim. Acta 137, 131-137 (2014).

[9]. Teoli F, Lucioli S, Nota P, Frattarelli A, Matteocci F, Di Carlo A, Caboni E, Forni C, Role of pH and pigment concentration for natural dye-sensitized solar cell treated with anthocyanin extracts of common fruits. J. Photochem. Photobiol. A 316, 24-30 (2016).

[10]. Chein C.Y, Hsu B.D, Optimization of the dye-sensitized solar cell with anthocyanin as photosensitizer. Sol. Energy 98, 203-211 (2013).

[11]. Ye M, Wen X, Wang M, Iocozzia J, Zhang N, Lin C, Lin Z, Recent advances in dye- sensitized solar cells: from photoanodes, sensitizers and electrolytes to counter electrodes. Mater. Today 18, 155-162 (2015).

[12]. Mathew S, Yella A, Gao P, Humphry-Baker R, Curchod B.F.E, Ashari-Astani N, Tavernelli I, Rothlisberger U, Nazeeruddin K, Grätzel M, Nat. Chem. 6, 242-247 (2014).

[13]. Ying L, Ku S, Chen S, Ali M.A, Alhemaid F.M, Photo electrochemistry for cabbage extract as natural dye to develop a dyesensitized solar cells. Int. J. Electrochem. Sci. 8(1), 1237-1245 (2013).

[14]. El-Ghamri S.H, El-Agez T.M, Taya S.A, Abdel-Latif M.S, Batniji A.Y, Dye-sensitized solar cells with natural dyes extracted from plant seeds. Mater. Sci. Pol. 32(4), 547-554 (2014).

[15]. Ananth S, Vivek P, Arumanayagam T, Murugakoothan P, Natural dye extract of Lawsonia Inermis seed as photo sensitizer for titanium dioxide based dye sensitized solar cells. Spectrochim. Acta Part. A 128(7) 420-426 (2014).