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Optimization, fabrication, and characterization of anthocyanin and carotenoid derivatives based dye-sensitized solar cells



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ABSTRACT

The bracts of Poinsettia, Tamarillo fruit, Annatto seeds, and Pungent Chillies have been used to extract the dyes using ethanol and deionized water. A cocktail of the dyes has been made with equal concentration and will be used as a sensitizer in the proposed dye-sensitized solar cell. The individual and cocktail of the dyes are subjected to FTIR, UV-Visible spectroscopy for the identification of functional groups, and absorption wavelength to find the effectiveness of the dyes for absorption of energy of the photons. From the study, it is found that the sensitizers in the dyes have shown stronger electronic coupling and rapid electron transfer into the conduction band of the TiO₂ semiconductor on the FTO substrate. J-V analysis represents photovoltaic characterization of assembled thin film nano-crystalline solar cells. Anthocyanin derivative of *Poinsettia bracts* attained a photo-sensitized conversion efficiency of 1.74% achieving an overlong lifespan of electrons. Ethanol was chosen for attaining the best energy conversion efficiency owing to its polarity. The presence of phytoconstituents has an impact on the color of the sensitizers and the degradation in the power conversion efficiencies was also monitored. This research examines the parameters that influence the stability of anthocyanin and carotenoid pigments, as well as the solvents required for effective derivative extraction.

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1. Introduction

In today's globe, energy catastrophe is a major challenge. The burning of nonrenewable fuels source emits a ton of CO_2 that tainted the atmosphere. Renewable sources of energy such as solar energy are considered a practicable alternative because an enormous amount of sunlight that strikes on surface of the earth every hour is more than enough for all of the energy consumed by humans in an entire year (Susanti et al., 2014). This energy can be captured and converted into electricity using photovoltaic cells. A dye-sensitized solar cell is a third-generation photovoltaic (solar)

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cell that transforms any visible light into electrical energy (Najm et al., 2020). It is often alluded to as artificial photosynthesis. DSSC provides a novel alternative to standard multi-junction and silicon solar cells. Anodes, counter electrodes, electrolytes, and photosensitizers have been subjected to extensive research to improve overall efficiency and durability while lowering the cost of DSSCs (Bai et al., 2008). The power conversion efficiency of 14% was reported for efficient DSSCs fabricated using TiO2 as a photo-anode. Photoelectrochemical devices can effectively harvest and transfer visible light into useful electricity through sensitization of broadband gap nano-crystalline TiO₂ substrate (Singh and Koiry, 2018). Titanium dioxide is an electron acceptor that occurs naturally as titanium oxide. Anatase, ilmenite, and rutile are the most common sources. The anatase phase of TiO₂ has been favored due to its strong chemical stability and inflated conduction band edge energy (3.2 eV). It is used as a photo electrode to intensify light-harvesting efficiency and enlarge the sensitized photo electrode's surface area. It exhibits better-prefilled water solvents performance and significantly decreased device costs, is non-toxic, biocompatible, and has good chemical stability and abundance. They don't need to be refined or purified, and they're non-polluting (Iqbal et al., 2019).

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Dye-sensitized solar cells proffer the aim of fabricating solar cells showing effective efficiency with the facile fabrication process (O'Regan and Grtazel, 1991; Adedokum et al., 2016). Formerly, DSSC employs Polypyridyl compounds of Ru (II) dyes as potential sensitizers (Syafinar et al., 2015) which when exposed to sunlight for a long duration start to degrade, causing stability problems. Nevertheless of the impoverished performance in dye-sensitized solar cells, extraction of dyes from natural sources will ensure non-toxicity, low-priced, availability, complete biodegradation and reduce complex chemical synthesis (Richhariya et al., 2017). The typical DSSC configuration comprises nanostructured TiO₂, potent sensitizer, iodide/triiodide (I^-/I_{3-}) as electrolyte for dye regeneration, and counter cathode for electrolyte regeneration (Li et al., 2013). The dye's lowest unoccupied molecular orbital (LUMO) should be higher in energy than the semiconductor's conduction band so that, upon excitation, the dye can introduce electrons into the TiO₂ conduction band. (Hemmatzadeh and Mohammadi, 2013). Anthocyanin and Carotenoid are subjected to the coloring of natural sensitizers which enhance the absorption coefficient. The absorption spectrum of the sensitizer and its functional group upgrades the injection of exciting electrons into the nanoporous semiconductor layer which enhances the efficiency of DSSC (Ludin et al., 2014). DSSC fabricated using bracts of Poinsettia, Tamarillo, Annato seeds, Pungent Chilli, and a cocktail of these dyes were investigated in this article. The dye molecules absorb visible photons, which produce charge carriers (electric current) and transport electrons to the TiO₂ material (Tribawono et al., 2016).

In India, *Poinsettia* is a popular garden plant known for its bright red bracts that resemble leaves and can be used to make a pH indicator due to its chemical composition. *Tamarillo* is rich in soluble fiber, energy, carbohydrates, anthocyanins, and carotenoids. Only *tamarillo* includes both polar (anthocyanins) and non-polar (carotenoids) colors among the fruits. The pigment bixin is found in Annatto, a small tree of the Bixaceae family. Annatto seeds (Joseph et al., 2021) produce a dark-red liquid that is commonly used as food coloring and flavoring. Carotenoids are abundant in the pericarp of the seeds, with *cis*-bixin accounting for up to 80% of the total and trans -and *cis*-norbixin accounting for the remaining 20% (Joseph et al., 2021). The carotenoids capsanthin and capsorubin are responsible for the chilli's bright red colour.

Thus in this research article, DSSC was fabricated by anatase structure of TiO_2 as a nanocrystalline semiconductor material for counter cathode, natural cocktail sensitizers as photo-catalyst, and graphene as the catalyst for its lower price than Platinum (Susanti et al., 2014). The TiO_2 paste was coated onto the FTO glass substrate using Doctor-Blade Technique (Furukawa, 2011). The ratio of power output (voltage × current density) of the built dye-sensitized solar cells to average solar power input was used to calculate the power efficiency of the produced dye-sensitized solar cells. Colored bracts of *Poinsettia* reveal higher photoelectric performance owing to the good electron transfer between the dyes of *Poinsettia bracts* and TiO_2 photo-anode surface. The consequence which hinder the PV performance and sources that affect DSSC is illustrated in Fig. 1.

2. Experiment

2.1. Materials

Components employ FTO glass substrate, anatase TiO₂, Nitric acid (HNO₃), Acetic acid (CH₃COOH), Ethanol (C₂H₅OH), Deionized water (DI), natural potential sensitizer, Lithium iodide (LiI), Iodine (I) and acetonitrile and graphite coated FTO.

2.2. TiO₂ preparation and cleaning of FTO

0.2 g of colloidal nano-powdered TiO_2 is blended with 1.5 ml of HNO_3 and stirred for 10 min. Every 1 ml of dilute CH_3COOH solution is slowly introduced till a thick homogenous lump-free TiO_2 paste is prepared. Meanwhile, Fluorine-doped tin oxide (FTO) substrates were cleaned in a beaker of distilled water followed by ethanol and acetone solutions inside an ultrasonic bath each for 30 min.

2.3. Dye extraction

10 g of Poinsettia bracts and Tamarillo were washed in deionized water and ground with ethanol and deionized water using mortar to extract anthocyanin pigment. To obtain a free dye solution, solid residues are filtered away using Whatman filter paper.

The carotenoid derivative of Annatto Seeds was cut into small sizes of about 0.4 cm \times 0.4 cm and 5 g was weighed separately using an electronic weighing machine. The samples were crushed separately using a porcelain mortar and pestle to extract the respective pigments and then mixed with ethanol and deionized water in a beaker overnight at room temperature. The solid dregs in the solution were filtered out and the extract was used as a sensitizer.

The red hue of Chilli powder is due to the red pigmented carotenoids which are dissolved in ethanol and deionized water for 24 h. The remnants of the solution were sifted out and the filtrate is used as a photo catalyst.

Poinsettia and *Tamarillo* extract each of 10 g is prepared by blending the extracts using a mortar and pestle and filtered to remove the solid sediments. The cocktail extract was kept in ethanol and deionized water solvent for a week. In parallel, a 5 g mixture of Annatto and Chilli was weighed individually on a weighing balance and then crushed the sample using a mortar and pestle. The lees were filtered out to obtain a pure dye solution.

2.4. Electrolyte

0.67 g of Lil is dissolved in 10 ml of acetonitrile solution and stirred for 10 min by a magnet. 0.13 g of iodine is added to the solution and stirred for 15 min until the iodine balls are completely dissolved.

2.5. Fabrication of DSSC using Doctor Blade technique

The thickness of transparent conducting FTO film is limited by applying scotch tape on two sides of the glass substrate. The lump-free TiO₂ paste is introduced to FTO coated substrate and evened out with a razor blade until a homogenous layer of aggregate-free TiO₂ paste was achieved. The TiO₂ paste was allowed to dry before annealing the film and the scotch tape was removed after the drying of the paste. The glass substrate is annealed at 450 °C for 30 min using a muffle furnace to obtain a nano-crystalline semiconductor TiO₂ layer. Before immersing the film in dye extract for a week, it has been cooled at room temperature for 15 min after the annealing process.

For counter cathode preparation, the conducting surface of the FTO glass substrate is sketched using graphite in pencil. The film is taken from the dye extract solution and the sealant is introduced on TiO_2 coated FTO substrate to evade electric contact. Both photo-anode and counter electrode is sandwiched together using binder clips and electrical performance is measured by dripping electrolyte solution into the photo-anode. Hence the fabricated solar cell using derivatives viz. anthocyanin and carotenoid is taken for I-V characteristics.



Fig. 1. Illustration of the consequence which hinder the PV performance and sources that affect DSSC.

2.6. Result and discussion

2.6.1. UV-Vis absorption spectra

Photo-sensitizers play an imperative role in the working of DSSCs. The absorption spectra of the dyes and the injection of electrons from the activated sensitizers to the TiO₂ thin nanocrystalline layer surface play a critical role in cell efficiency (Najm et al., 2020). The UV-Vis absorption band of Poinsettia bracts, Tamarillo fruit, Annatto Seeds, Chilli along with their cocktail extract were carried out in the range of 200-800 nm by using UV-Visible spectrometer 2450 is depicted in Figs. 2a-2f. A spectral shift from UV to visible was seen in all the extracted dyes. The absorption peaks of colored Poinsettia bracts in ethanol symbolize the sharp peak of natural extract in the visible region at 419 nm and a broad peak at 506 nm respectively shown in Fig. 2a. Anthocyanin derivatives appear in Poinsettia bracts contain polyphenols which impart a red color to the dye and intensify artificial photosynthesis (Swarnkar et al., 2015). Tamarillo fruit in deionized water displays a broad peak at 583 nm and ethanol with maximum absorption at 428 nm. Tamarillo pulp had the maximum potential to absorb photons from light, the combination of fruit peel and

pulp increased light absorption (Susanti et al., 2014) in the 400-650 nm region, and hence it was chosen as the dye for the entire DSSC assembly. Chilli has the highest photon absorption in ethanol at 507 nm due to the presence of a red-pigmented carotenoid derivative, as shown in Fig. 2e. From the observed results, it is suggested that the Poinsettia bracts dye is a good candidate for the sensitization of the semiconductor due to their excellent photon absorbing capacity and hence it is gauged to issue surpass photovoltaic performance(Gomez-Ortiz et al., 2010). The variations in the characteristics of absorption of the natural extracts can be ascribed to their affinity towards adsorption onto the nanocrystalline TiO₂ thin film layer. After a week, the efficiency dropped by around 50%. The main causes of PV performance degradation are liquid electrolyte leakage or solvent evaporation. The separation of the dye from the TiO_2 surface has also been linked to the loss of solar cell efficiency (Isah et al., 2017). When the dyes were loaded into TiO₂, UV analysis predicted a shift in their absorption spectra (Batty et al., 2022). The differing chemical structures of these dyes are primarily responsible for the shifts in absorption peaks. The absorption spectrum was lengthened to the whole visible region (Batty et al., 2022) due to all these moderately better



Fig. 2a. UV-Visible Spectrum of Poinsettia bracts in Ethanol and DI.



Fig. 2b. UV-Visible Spectrum of Tamarillo fruit in Ethanol and DI.



Fig. 2c. UV-Visible Spectrum of Poinsettia and Tamarillo in Ethanol and DI.



Fig. 2d. UV-Visible Spectrum of Annatto Seeds in Ethanol and DI.



Fig. 2e. UV-Visible Spectrum of Chilli in Ethanol and DI.



Fig. 2f. UV-Visible Spectrum of Annatto Seeds and Chilli in ethanol and DI.

properties (Varsha et al., 2020). Accordingly, a superior DSSC performance is anticipated from anthocyanin, carotenoid (Batty et al., 2022), and the functional groups, which are considered the core components of natural dyes (Batty et al., 2022). Cocktail dyes in ethanol have a wide optical absorbance spectrum compared to deionized water (Eli et al., 2016). Although the conversion efficiency for ethanol extract was greater, the sensitized cell demonstrated low stability due to TiO₂ photocatalytic degradation of anthocyanin in the presence of ethanol. Higher amounts of dye were adsorbed to the TiO₂ surface when ethanol was used as solvent extraction. This could be because anthocyanin is more soluble in ethanol than in deionized water, resulting in higher amounts of dye being adsorbed to the TiO₂ surface.

The optical bandgap or Tauc gap in potent sensitizers is determined using a Tauc plot (Ramay et al., 2022). Typically, it displays the square root of the product of the absorption coefficient (α) and photon energy (eV) on the ordinate and photon energy (eV) on the abscissa. The curve should include a part of a straight line and the curve should incorporate a portion of a straight line. The optical band gap is the x-intercept of this line when it is extended to the x-axis. The potent sensitizers' band gap was calculated using Eq. (1)

$$E_g = \frac{hc}{\lambda e} \tag{1}$$

Planck's constant (h) is 6.63×10^{-34} J sec, C is 3×10^8 m/sec light velocity, is the absorption wavelength, and e is the electron charge. Absorption spectra of natural sensitizers with their bandgap energy is depicted in Table 1 respectively.

2.6.2. FTIR Spectroscopy

FTIR analysis confirmed the chemical structure of the extracted colors. To efficiently adsorb on the TiO₂ films, natural dyes must contain specific functional groups (Alhamad et al., 2012). Major active bio compounds of the Poinsettia bracts were evaluated and investigated using FTIR spectroscopy (Shimadzu FTIR-8400S) with KBr pellets in the range of 4000–400 cm⁻¹. FTIR spectrum is used for the analysis of functional groups present in the sensitizers which confirms the compatibility of the dye with the TiO₂ layer. The study reports exhibit the significance of natural sensitizers with any of these functional groups (-OH), (COOH), (C=O), and (=O) shows maximum cell efficiency [Asmaa]. The recorded spectra range from 4000 to 400 cm⁻¹ for colored *Poinsettia bracts*,

P. Prakash, B. Janarthanan, M. Ubaidullah et al.

Table 1

Absorption spectra of natural sensitizers with their bandgap energy.

Serial No.	Sensitizers	Ethanol		Deionized water		
		λ_{max} (nm)	Bandgap energy (eV)	λ_{max} (nm)	Bandgap energy (eV)	
1.	Poinsettia bracts	419 nm, 506 nm	2.61	443 nm	3.16	
2.	Tamarillo fruit	401 nm, 428 nm, 615 nm	2.73	583 nm	2.56	
3.	Cocktail dyes	403 nm, 469 nm, 546 nm	2.08	400 nm, 463 nm	2.31	
5.	Annatto Seeds	452 nm, 589 nm	2.44	416 nm	3.11	
6.	Chilli	507 nm	4.37	537 nm	5.77	
7.	Cocktail dyes	604 nm	3.29	441 nm	3.73	



Fig. 2g. FTIR Spectrum of sensitizers in (a) ethanol and (b) DI.

Tamarillo fruit, Annatto Seeds, Chilli, and a cocktail of dyes in ethanol and deionized water is shown in Fig. 2g. The peaks of *Poinsettia* and *Tamarillo* were observed at 3610. 74 cm⁻¹, 3387 cm⁻¹, 3603 cm⁻¹, 3286 cm⁻¹ correlating with the hydroxyl group (surface adsorbed water). Annatto Seeds and Pungent Chilli in ethanol have peaked at 3603 cm⁻¹, 3680 cm⁻¹, and 3379 cm⁻¹ relating to the hydroxyl group. Poinsettia anthocyanin extracts also include significant amounts of the following main groups: C—H (2960 cm⁻¹), C—H aliphatic (1419 cm⁻¹), C—H aromatic rings (886 cm⁻¹), C=C (1657 cm⁻¹), and C—O (1047 cm⁻¹). The O—H stretching vibration in annatto is 3410 cm⁻¹. The C–H stretches are brought on by the methyl and methylene groups at 22915 cm⁻¹and 2850 cm⁻¹, respectively. The alkene C=C stretch is visible at 1608 cm⁻¹, whereas the carboxylic C=O group may be detected at 1722 cm⁻¹. The peaks at 1438 cm⁻¹ and 1378 cm⁻¹ correspond to the C–H bending of the methyl groups, whereas the peak at 1287 cm⁻¹ corresponds to the C–O vibrations. The symmetric and asymmetric vibrations of the C–O–C ester group are shown by peaks at 1254 cm⁻¹ and 1159 cm⁻¹, respectively. The influence of solvent, namely ethanol, also plays an indispensable role in

0,6



Fig. 2h. J-V characteristics of the cell using Poinsettia bracts in Ethanol and DI.



Fig. 2i. J-V characteristics of the cell using Tamarillo in Ethanol and DI.

Fig. 2j. J-V characteristics of the cell using Cocktail dyes in ethanol and DI.

Fig. 2k. J-V characteristics of the cell using Annatto Seeds Ethanol and DI.

Fig. 21. J-V characteristics of the cell using Chilli in Ethanol and DI.

dye-based solar cell performance as compared to deionized water. The anchoring groups confirm the presence of anthocyanin and carotenoid pigments. Several anthocyanins have been identified in Poinsettia bracts and are responsible for their coloration range. Furthermore, Poinsettia dye has high efficiency because of its longer charge carrier lifetime, and natural dyes bonded to TiO_2 show a larger impedance. Phytoconstituents such as terpenoids, flavonoids, alkaloids, saponin, steroids, polyphenols, thiazole, nor-bixin, apocarotenoid bixin, and other less important lutein, methylbixin, cryptoxanthin, and zeaxanthin may be responsible for the observed functional groups. The presence of phytochemicals affects the color of plant materials and can bind with the TiO₂ semiconductor. In the FTIR spectrum, the diluting salts with polar solvents dilute the molecular configurations by weakening the bonds, resulting in the disappearance and shifting of peaks. The long lifetime implies enhanced electron collection efficiency and reduced recombination.

2.6.3. J-V characteristics

The plot of the current versus voltage curve determines the performance of the dye-sensitized solar cell fabricated. Under illumination, the maximum power of DSSC fabricated was analyzed from the J – V curve and the DSSC parameters namely fill factor (FF) and efficiency (η) are acquired using the upcoming equation with irradiance around 100 mW/cm².

$$FF = (J_m \cdot V_m) / (J_m \cdot V_m) \tag{2}$$

$$\eta \% = \frac{FF \cdot J_{sc} \cdot V_{oc}}{Input \ power} \cdot 100$$
(3)

To measure the performance of the fabricated solar cell, the Peccell Solar Simulator of 100 W was chosen to simulate sunlight and using the J-V curve (Batty et al., 2022) analyzer, the Power Conversion Efficiency of the constructed DSSC was studied (Taya et al., 2014). The operational characteristics determined by the J-V curve

Fig. 2m. J-V characteristics of the cell using Cocktail dyes in Ethanol and DI.

Fig. 3a. Photo-sensitization performance of DSSC in Ethanol.

Fig. 3b. Photo-sensitization performance of DSSC in DI.

intercepts include short-circuiting current density (Jsc), opencircuit voltage (Voc), fill factor (FF), and conversion efficiency (η). The output power for the fabricated DSSC was calculated using J-V characteristic data (Adedokun et al., 2018). The performance of DSSC using colored *bracts of Poinsettia* in ethanol has Jsc, Voc, FF, and η around 0.4 mA/cm², 0.6, 0.4, and 0.1%. The maximum conversion efficiency of *Annatto Seeds* in ethanol and deionized water ranged from 0.1 % and 0.1% respectively. Therefore *Poinsettia bracts* in ethanol and *Annatto Seeds* in ethanol and deionized water as potential sensitizers are stable candidates for effective DSSC. The power conversion efficiency of natural dye-based solar cells was depicted in Figs. 2h–2m respectively.

Comparison of photo-sensitization performance of DSSC in ethanol and DI is displayed in Figs. 3a and 3b along with Table 3. When light strikes the working electrode, photons penetrate the DSSC, are absorbed by dyes in the inner pores of the TiO_2 layer, and urge electrons to neighbor particles' conduction bands, leaving oxidized molecules on the thin film's surface (Batty et al., 2022). The electrolyte aids in the diffusion of ions and the expansion of the DSSC's connection. The cell efficiency of *Poinsettia* dye was improved because of its functional groups. It improves absorption by raising dye molecule excitement and making electron transport from the ground to the excited state easier (Batty et al., 2022). The concentration of anthocyanin in each extract may also contribute to the current density values in the DSSC employing different types of dyes (Sadasivuni et al., 2019). Pigment solutions containing substantial levels of byproducts such as sugar alcohols, proteins, sugars, amino acids, and organic acids are obtained by nonselective extraction of anthocyanin from plants. Anthocyanin breakdown is accelerated by these pollutants during storage. The power conversion efficiency of dyes in ethanol and DI is depicted in Tables 2a and 2b respectively. Other metal oxides and sensitizer have also been used for energy applications (Palanisamy et al., 2022; Naushad et al., 2021; Vignesh et al., 2022; Prakash et al., 2022) but Anthocyanin-based DSSC should have higher efficiency and a longer lifetime due to dye aggregation on the TiO₂ surface. The results of this research suggest an additional investigation into the usage of novel natural dye sensitizers that are anthocyaninenriched in order to improve the efficacy and durability of DSSCs for the market.

P. Prakash, B. Janarthanan, M. Ubaidullah et al.

Table 2a

Power conversion efficiency of dyes in ethanol.

Dye (Ethanol)	V _{oc}	J _{sc} (mA/cm ²)	V _m	J _m (mA/cm ²)	FF	η %
Poinsettia bracts	0.6	0.4	0.31	0.3	0.4	1.74
Tamarillo fruit	0.4264	0.969	0.3005	0.2337	0.1699	0.05
Cocktail dyes	0.5	0.3	0.3	0.14	0.3	0.74
Annatto Seeds	0.4	1.0	0.3	0.2	0.2	1.5
Chilli	0.4	0.1	0.3	0.05	0.4	0.31
Cocktail dyes	0.6	0.3	0.5	0.1	0.3	1.5

Table 2b

Power conversion efficiency of dyes in DI.

V _{oc}	J _{sc} (mA/cm ²)	Vm	$J_m (mA/cm^2)$	FF	η %
0.4	0.3	0.3	0.13	0.3	0.75
0.4	0.1	0.3	0.1	0.7	0.4
0.4	0.2	0.3	0.1	0.4	0.4
0.4	0.5	0.3	0.3	0.5	0.1
0.2	0.1	0.1	0.1	0.5	0.2
0.1	0.04	0.04	0.01	0.1	0.02
	V _{oc} 0.4 0.4 0.4 0.4 0.2 0.1	V_{oc} J_{sc} (mA/cm ²) 0.4 0.3 0.4 0.1 0.4 0.2 0.4 0.5 0.2 0.1 0.1 0.04	V_{oc} J_{sc} (mA/cm ²) V_m 0.4 0.3 0.3 0.4 0.1 0.3 0.4 0.2 0.3 0.4 0.5 0.3 0.2 0.1 0.1 0.1 0.5 0.3 0.2 0.1 0.1 0.1 0.04 0.04	V_{oc} J_{sc} (mA/cm ²) V_m J_m (mA/cm ²) 0.4 0.3 0.3 0.13 0.4 0.1 0.3 0.1 0.4 0.2 0.3 0.1 0.4 0.5 0.3 0.3 0.2 0.1 0.1 0.1 0.1 0.04 0.01 0.1	V_{oc} J_{sc} (mA/cm2) V_m J_m (mA/cm2)FF0.40.30.30.130.30.40.10.30.10.70.40.20.30.10.40.40.50.30.30.50.20.10.10.10.50.10.040.040.010.1

Table 3

Conversion Efficiency of Photo-Sensitizers.

Serial No.	Authors	Material	Sensitizer	η %	Reference
1.	A.K. Swarnkar et al.	TiO ₂	Poinsettia bracts	0.56	Swarnkar et al. (2015)
2.	Haryanto et al.	TiO ₂	Annatto seeds	0.19	Haryanto et al. (2014)
3.	Present Work	TiO ₂	Poinsettia bracts	1.74	-
4.	Present Work	TiO ₂	Cocktail dye (Annatto seeds + Chilli)	1.5	-

3. Conclusion

Absorption spectra for stimulating sunlight were identified using natural sensitizers from bracts of Poinsettia, Tamarillo, Annato seeds, Pungent Chilli, and a cocktail of natural extracts with ethanol and deionized water as solvent. The solar cell is fabricated using anthocyanin and carotenoid pigments as potent sensitizers due to its capacity in absorbing particles of energy under the illumination of sunlight and having a photon stimulating spectrum which was observed using a UV-Vis spectrophotometer. Increased solar cell efficiency is possible due to a wider absorption spectrum and increased absorbance in the visible range. The potency of fabricated DSSC using Poinsettia bracts showed a wider spectrum in the range of about 1.74 % when compared to other candidate dyes owing to the wider absorption range and effective passage of charge carriers to the guide band of nanostructured semiconductors. Effective light-sensitization performance procured by annatto seeds and its cocktail with chilli has an efficiency of around 1.5 %. The study report conclude that the level of light absorption in the ethanol-based extracted pigments was greater than that of deionized water. Solar cell efficiency was ameliorated owing to the immersion of TiO₂-coated FTO substrate for more than 24 h in dye solutions. When liquid electrolytes are utilized in DSSCs, corrosion at the counter electrode, photo-degradation of the attached dyes, desorption, leakage, and volatilization can all occur. Anthocyanin-based DSSC should have higher efficiency and a longer lifetime due to dye aggregation on the TiO₂ surface. The results of this research suggest an additional investigation into the usage of novel natural dye sensitizers that are anthocyaninenriched in order to improve the efficacy and durability of DSSCs for the market.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Adedokum, O., Titilayo, K., Awodugba, A.O., 2016. Review on natural dye-sensitized solar cells (DSSCs). Int. Jo. Eng. Technol. 2, 6–13.
- Adedokun, O., Awodele, M.K., Sanusi, Y.K., Awodugba, A.O., 2018. Natural dye extracts from fruit peels as sensitizer in ZnO-based dye-sensitized solar cells. Earth Environ. Sci. 173, 012040.
- Alhamad, M., Issa, A.S., Wael Doubal, A., 2012. Studying of natural dyes properties as photo-sensitizer for dye sensitized solar cells (DSSC). J. Electron. Devices 16, 1370–1383.
- Bai, Y., Cao, Y., Zhang, J., Wang, M., Li, R., Wang, P., Zakeeruddin, S.M., Gratzel, M., 2008. High Performance dye-sensitized solar cells based on solvent-free electrolytes produced from eutectic melts. Nat. Mater. 7, 626–630.
- Batty, S.A., Al-Jubouri, S.M., Hakami, M.W., Sarief, A., Manirul, S.K., Haque, 2022. Innovative economic anthocyanin dye source for enhancing the performance of dye-sensitized solar cell. J. Taibah Univ. Sci. 16, 415–422.
- Eli, D., Musa, G.P., Ezr, D., 2016. Chlorophyll and Betalain as Light- Harvesting Pigments for Nanostructured TiO₂ Based Dye-Sensitized Solar Cells, Journal of Energy and Natural. Resources 5, 53–58.
- Furukawa, S., 2011. Dye-Sensitized Solar Cells Using Natural Dyes and Nanostructural Improvement of TiO2 Film, Energy Efficiency and Renewable Energy through. Nanotechnology 31, 299–316.
- Gomez-Ortiz, N.M., Vazquez-Maldonado, I.A., Perez-Espadas, A.R., Mena-Rejon, G.J., Azamar-Barrios, J.A., Oskam, G., 2010. Dye-sensitized solar cells with natural dyes extracted from achiote seeds. Sol. Energy Mater. Sol. Cells 94, 40–44.
- Haryanto, D.A., Landuma, S., Purwanto, A., 2014. Fabrication of Dye-sensitized Solar Cell (DSSC) Using Annato Seeds (Bixa orellana Linn).
- Hemmatzadeh, R., Mohammadi, A., 2013. Improving optical absorptivity of natural dyes for fabrication of efficient dye-sensitized solar cells. J. Theoret. Appl. Phys. 7, 57.
- Iqbal, M.Z., Ali, S.R., Khan, S., 2019. Progress in dye-sensitized solar cells by incorporating natural photosensitizers. Sol. Energy 181, 490–509.
- Isah, K.U., Sadik, A.Y., Jolayemi, B.J., 2017. Effect of Natural Dye Co-Sensitization on the Performance of Dye- Sensitized Solar Cells (DSSCS) Based on Anthocyanin and Betalain Pigments Sensitisation. Eur. J. Appl. Sci. 9, 140–146.
- Joseph, S., Paul Winston, A.J.P., Muthupandi, S., Shobha, P., Margaret, S.M., Sagayaraj, P., 2021. Performance of Natural Dye Extracted from Annatto, Black Plum,

P. Prakash, B. Janarthanan, M. Ubaidullah et al.

Turmeric, Red Spinach, and Cactus as Photosensitizers in TiO2NP, TiNT Composites for Solar Cell Applications. J. Nanomater.

- Li, Y., Ku, S.-H., Chen, S.-M., Ajmal Ali, M., AlHemaid, F.H.M.A., 2013. Photoelectrochemistry for Red Cabbage Extract as Natural Dye to Develop a Dye-Sensitized Solar Cells. Int. J. Electrochem. Sci. 8, 1237–1245.
- Ludin, N.A., Al-Alwani Mahmoud, A.M., Mohamad, A.B., Kadhum, Abd. A.H., Sopian, K., Karim, N.S.A., 2014. Review on the development of natural dye photosensitizer for dye-sensitized solar cells. Renew. Sustain. Energy Rev. 31, 386–396.
- Najm, A.S., Ludin, N.A., Abdullah, M.F., Almessiere, M.A., Ahmed, N.M., Al-Alwani, M.A.M., 2020. Areca catechu extracted natural new sensitizer for dyesensitized solar cell: performance evaluation. J. Mater. Sci. Mater. Electron. 31, 3564–3575.
- Naushad, M., Ahamad, T., Ubaidullah, M., Ahmed, J., Ghafar, A.A., Al-Sheetan, K.M., Arunachalam, P., 2021. Nitrogen-doped carbon quantum dots (N-CQDs)/Co₃O₄ nanocomposite for high performance supercapacitor. J. King Saud Univ. – Sci. 33, 101252.
- O'Regan, B., Grtazel, M., 1991. A low cost, high efficiency solar cell based on dyesensitized colloidal TiO₂ films. Nature 353, 737–740.
- Palanisamy, G., Vignesh, S., Srinivasan, M., Venkatesh, G., Elavarasan, N., Pazhanivel, T., Ramasamy, P., Shaikh, S.F., Ubaidullah, M., Reddy, V.R.M., 2022. Construction of magnetically recoverable novel Z-scheme La (OH) 3/α-MnO₂/MnFe₂O₄ photocatalyst for organic dye degradation under UV-visible light illumination. J. Alloys Compd. 901, 163539.
- Prakash, P., Balasundaram, J., Al-Enizi, A.M., Ubaidullah, M., Pandit, B., 2022. Effect of photovoltaic performance of plant-based cocktail DSSCs and adsorption of nano TiO₂ onto the solvent-influenced dye sensitizers. Opt. Mater. 133, 113031.
- Ramay, S.M., Mansoor Ali, S., Kassim, H., Amer, M.S., 2022. Ab-initio and experimental studies for the electronic and optical response of Zn–MoS₂ thin films. Phys. B: Condens. Matter 628, 413558.

Journal of King Saud University - Science 35 (2023) 102625

- Richhariya, G., Kumar, A., Tekasakul, P., Gupta, B., 2017. Natural dyes for dye sensitized solar cell: A review. Renew. Sustain. Energy Rev. 69, 705–718.
- Sadasivuni, K.K., Kalim Deshmukh, T.N., Ahipa, A.M., Basheer Ahamed, M., Khadheer Pasha, S.K., Al-Maadeed, M.-A., 2019. Flexible, biodegradable and recyclable solar cells: a review. J. Mater. Sci. Mater. Electron. 30, 951–974.
- Singh, L.K., Koiry, B.P., 2018. Natural Dyes and their Effect on Efficiency of TiO₂ based DSSCs: a Comparative Study. Mater. Today:. Proc. 5, 2112–2122.
- Susanti, D., Nafi, M., Purwaningsih, H., Fajarin, R., Kusuma, G.E., 2014. The Preparation of Dye Sensitized Solar Cell (DSSC) from TiO_2 and Tamarillo Extract. Procedia Chem. 9, 3–10.
- Swarnkar, A.K., Sahare, S., Chander, N., Gangwar, R.K., Bhoraskar, S.V., Bhave, T.M., 2015. Nanocrystalline titanium dioxide sensitised with natural dyes for ecofriendly solar cell application. J. Exp. Nanosci. 10, 1001–1011.
- Syafinar, R., Gomesh, N., Irwanto, M., Fareq, M., Irwan, Y.M., 2015. Chlorophyll Pigments as Nature Based Dye for Dye-Sensitized Solar Cell. DSSC. Energy Procedia 79, 896–902.
- Taya, S.A., El-Agezl, T.M., Abdel-Latif, M.S., El-Ghamri, H.S., Batniji, A.Y., El-Sheikh, I. R., 2014. Fabrication of Dye-Sensitized Solar Cells Using Dried Plant Leaves. Int. J. Renewable Energy Res. 4, 384–388.
- Tribawono, D.S., Wibowo, D., Nurdin, M., 2016. Electrochemical profile degradation of amino acid by flow system using TiO₂/Ti nanotubes electrode. Anal. Bioanal. Electrochem. 8, 761–776.
- Varsha, Y., Swati, C., Chandra, M.S.N., 2020. Textile dyes as photo-sensitizer in the dye-sensitized solar cells. Opt. Mater. 109, 110306.
- Vignesh, S., Suganthi, S., Srinivasan, M., Tamilmani, A., Sundar, J.K., Sreedevi, G., Palanivel, B., Shaikh, S.F., Ubaidullah, M., Raza, M.K., 2022. Investigation of heterojunction between α-Fe₂O₃/V₂O₅ and g-C₃N₄ ternary nanocomposites for upgraded photo-degradation performance of mixed pollutants: Efficient dual Zscheme mechanism. J. Alloys Compd. 902.