Chapter 45
Opuntia spp. in Dye-Sensitized Solar Cells

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Abstract Solar energy is one of the most important renewable and sustainable forms of energy. Different technologies have been developed to harness this free energy and contribute to the world economy, especially in countries with no seasonal variations in solar radiation. Dye-sensitized solar cells (DSSCs) are simply used to collect solar energy and convert that visible light into electricity. This depends on the photosensitization of wide band-gap metal oxide semiconductors. The photoelectrode spectral sensitivity needs specific chemical dyes for the lower energy photons collection. Significant research efforts for identifying new organic dyes from natural sources have been carried out. Higher plants contain many natural pigments well-known to interact with solar radiation. The fruit of the *Opuntia* spe-

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cies contains a particular type and unique pigment called betalain. This type of compound has an interesting conjugation system with nitrogen atoms forming an unusual natural dye. Betalain has a potential interest in the photosensitization process when added to the DSSCs system. This chapter provides a review on the structural features and potential applications of the betalain pigments in the photo-sensitization solar cells.

Keywords Solar energy · Photovoltaic cell · Counter electrode · Green nanotechnology · Dye-sensitized solar cells · DSSC · Betalain pigments

Abbreviations

CE	Counter electrode
DSSCs	Dye-sensitized solar cells
FTO	Fluorine-doped tin oxide
HOMO	Highest occupied molecular orbital
HTMs	Hole transport materials
ITO	Indium-doped tin oxide
LUMO	lowest unoccupied molecular orbital
OPV	Organic solar cells
PCE	Power conversion efficiency
Ru	Ruthenium

1 Solar Cells

Solar energy is the most basic energy source that is free, clean, renewable, and an abundant alternative to reducing real-time dependency on traditional fossil fuels (Buscaino et al., 2008; Ammar et al., 2019). Over the past decade, the development of different types of solar cells has been deliberated. These cells were shaped to convert the visible light into electricity through the photovoltaic effect. Recently, different solar cells have been used extensively for various industrial applications and national domestic use (Dang et al., 2018; Schindler et al., 2018).

The solar cells are generally characterized based on their material composition into different types such as organic solar cells (OPV) (Steim et al., 2010); dye-sensitized solar cells (DSSCs) (Jamalullail et al., 2018); gallium arsenide based solar cell (Abdin et al., 2013), amorphous, multiple crystals or polycrystalline, and single-crystal silicon solar cells; where they reveal different efficiency values. The traditional solar cell is usually made of a silicon crystal material despite its high cost compared to OPV and DSSCs solar cell types (Adedokun et al., 2016). DSSCs are attracting great interest in terms of fabrication cost, design simplicity, environmental friendliness, and performance (Abdel-Latif et al., 2013). However, their large-scale applications' operation is still limited due to long-term stability issues, which will also be covered with future improvement efforts.

1.1 Organic Solar Cell (OPV)

Organic solar cells (photovoltaic cells) are promising cells that received much attention due to cheap cost architecture, characteristics, wide applications, and significant improvement in power conversion efficiency. Organic bilayer solar cells were reported for the first time in 1986 by Tang using complementary electron donor and acceptor organic molecules, exhibiting a power conversion efficiency close to 1% in sunlight (Abdulrazzaq et al., 2013). OPV revealed a substantial increase in stability, with reports providing evidence of the stabilities of 7 years. Compared to inorganic solar cells, OPV has the additional advantage that they can be processed at a modest temperature from solution, without the need of a vacuum, and by fast roll-to-roll processes. The organic photoactive materials used in organic solar cells show high absorption coefficients, which implies that only a very thin photoactive layer (100 to 200 nm) is required to absorb sufficient light. The recent developments give increasing credence that OPV can be a viable alternative technology to the present inorganic solar cells (Cao & Xue, 2014).

1.2 Construction and Working Principle of Organic Solar Cells

Organic photovoltaic solar cells reveal a heterostructure of two different semiconductor types. The heterostructure is sandwiched between two functional electrodes for collecting the electrons and holes separately and is seated on a thin substrate of glass or PET. All devices need to be encapsulated to eliminate water and oxygen exposure (Cao & Xue, 2014; Kippelen & Brédas, 2009; Mazzio & Luscombe, 2015). The interaction of the photovoltaic cells with the light creates an excitonic cell. The electron is stimulated in either the donor or the acceptor from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (Osman, 2017). Orbitals bandgap energy defines the possible light wavelength(s) that can be absorbed.

OPV cells have a limitation in the large scale production attributed to the devices' stability and lifetime in addition to the power conversion efficiency (PCE) (Scharber & Sariciftci, 2013). The PCE could be enhanced by increasing the absorption of light. However, there is a limitation on the absorption due to the active layer's thickness control up to 100 nm maximum. That thickness restriction comes from the short lifetime of the excitons and the conducting layer's low mobility. Metallic nanoparticles have been used to enhance the absorption without increasing the active layer thickness (Kour & Mehra, 2017; Scharber & Sariciftci, 2013).

2 Dye-Sensitized Solar Cell (DSSC)

DSSCs are unique photovoltaic third-generation devices known as Grätzel cells. O'Regan and Grätzel (1991) reported the DSSC for the first time through sensitizing titanium dioxide NPs films with ruthenium bipyridyl complex (Jamalullail et al., 2018). It is commonly well known as low-cost cells due to their materials composition and low fabrication cost. These new solar cell types mainly convert solar energy (photons) into electrical energy through the sensitization of a wide-band-gap semiconductor (Sharma et al., 2018). Different parameters, such as voltage, current density, and conversion efficiency, are highly considered for the solar cell electrical performance. That performance relies totally on the solar cell dye type, which is generally categorized into inorganic and organic dyes (Jamalullail et al., 2018). One of the most common inorganic dyes with a high energy conversion efficiency (11–12%) in DSSCs is ruthenium complexes (Qin & Peng, 2012). Ruthenium (Ru) is one of the rare transition noble metals belongs to the platinum group metals. In addition to Ruthenium's high price (Gunn, 2013), its toxicity limits its use in many fields. Even though the Ru complex dyes and others like osmium complexes reveal high stability and efficiency, their toxicity, rarity, and fabrication cost eliminate their use in the DSSCs. A new research study on green extracted organic (natural) dyes has received much attention recently (Mansour, 2018). Many reports confirmed the efficiency of different natural dyes such as betalain (Isah et al., 2015; Ramamoorthy et al., 2016; Zhang et al., 2008), anthocyanin (Ramamoorthy et al., 2016), and chlorophyll (Arof & Ping, 2017; Syafinar et al., 2015), in supporting the DSSC electrical performance. Using such natural pigments is attracting much interest from an economical and environmental aspect.

2.1 Structure of DSSCs

DSSCs have a different basic structure compared to other PV solar cells, which rely on solid-state semiconductor materials, while DSSC rely on a combination of solid and liquid phases. The DSSC consist of transparent and conductive substrates (to allow sunlight to reach the cells), working electrodes (a semiconducting oxide, e.g., TiO_2), dye (photosensitizer; to absorb the light), an electrolyte, and a counter electrode (CE). To understand the DSSC structure, a general working concept of the DSSC could be summarized as soaking a specific working electrode with a dye and sealing it to the counter electrode soaked with a thin layer of electrolyte (Sharma et al., 2018).

2.1.1 Transparent and Conductive Substrate

Based on the DSSC components, the DSSC mainly has two electrodes. One electrode should use a transparent substrate for the visible light and be considered an anode (Bauer et al., 2002). That transparent electrode should also have a high conductivity characteristic to eliminate the loss of the transferred energy. The most commonly used conductive substrates are fluorine-doped tin oxide (FTO, SnO_2: F) and indium-doped tin oxide (ITO, In_2O_3: Sn). These transparent conductive oxides are usually used to cover the glass. While, FTO reveals ~75% transmission efficiency, the ITO shows >80% transmittance in the visible solar light (Hug et al., 2014; Ludin et al., 2014).

2.1.2 Working Electrode Construction

FTO or ITO transparent conductive substrates are used as a base for further deposition of thin layer oxide semiconducting material with a wide band-gap. That layer has a typical thickness of 10μm with a 50% porosity. Different oxides could be used, however TiO_2, ZnO, and Nb_2O_5 are the preferred photo-electrodes (Jose et al., 2008).

2.1.3 Dye (Photosensitizer)

The dye is the third component in the DSSC structure, which plays a vital role in absorbing solar light and its conversion to electrical energy. The DSSC's performance depends on the dye type that acts as a sensitizer (Suganya & Jaisankar, 2019). According to Qin and Peng (2012), any selected dyes for DSSC should have the following specific physical and chemical properties:

1. High absorption performance of the light under both the ultraviolet-visible (UV-vis) and near-infrared region (NIR)
2. High adsorption ability to the semiconductor surface (TiO_2) of the working electrode
3. High ability for efficient injection of the electrons into the conduction band of the semiconductors
4. Have characteristic luminescent properties
5. Have a hydrophobic property to enhance the DSSC stability by reducing the contact between the anode and electrolyte
6. Electro and photo-chemically stable.

Moreover, to the previous features, for more efficient stability, additional co-absorbents such as chenodeoxycholic acid and alkoxysilyl- (Fung et al., 2003), carboxylic- (Hagberg et al., 2008), and phosphoric acids groups (Zaban et al., 1998) should be placed between the dye and the semiconductor layer (e.g., TiO_2) to avoid dye aggregation above that layer and decrease the recombination response between the electrons and electrolyte (Neale et al., 2005). Accordingly, dyes were categorized into two types: inorganic and natural organic dyes.

3 Electrolyte

The electrolyte has an essential role in charge transfer between the anode and the counter electrode and should also enhance the connectivity between them. It contains a redox couple, solvent, additives, ionic liquids, and cations. High dielectric properties, low viscosity, high boiling temperature, non-corrosive, non-volatility, chemical, thermal, and electrochemical stability are properties for the optimum electrolyte (Gorlov & Kloo, 2008). The electrolyte spectra should not overlay the dye spectra, while the redox couple, such as I−/I−, should restore the oxidized dye efficiently (Sharma et al., 2018).

4 Counter Electrode (CE)

The counter electrode is an essential part of the DSSC structure since it is responsible for transferring the electrons from the external circuit back to the redox couple electrolyte. It collects the holes from the hole transport materials (HTMs). It should therefore have a conducting capability to transport the current through the DSSC solar cell. Counter electrodes are mainly made of platinum (Pt) or carbon (C). However, Pt is the most effective material due to its high performance in I−/I − 3 liquid electrolyte reduction process (Adedokun et al., 2016).

5 Dye Types

5.1 Inorganic Dyes

The most important feature for determining DSSC efficiency is the rate of absorption efficiency of the solar light and dye anchorage to the semiconductor working electrode cell (Lee & Yang, 2011). The best example is ruthenium complexes, which showed good light-harvesting efficiency (around 12%), outstanding stability, good electrochemical properties, and a wide range of light absorption (Hernández-Martínez et al., 2012).

5.2 Natural Organic Dyes

Natural dyes are eco-friendly, cheap, non-toxic, widely available, and biodegradable with a high ability to reduce noble metals instead of using chemical reducing agents (Calogero et al., 2013). Therefore, they have received attention for use as photosensitizers in the DSSC fabrication as an alternative to the synthetic ones. Different natural dyes can simply be extracted from the plant's different parts (Adedokun et al., 2016). The nature of these pigments can impact their conversion efficiency performance (Narayan, 2012). Several studies reported the ideal conditions of DSSC operation and the possible useful dyes from different plants (Godibo et al., 2015).

Different natural dyes such as anthocyanin, betalain, betaxanthin, bixin, carotenoid, chlorophyll, crocetin, crocin, cyanine, flavonoid, lutein, mangostin, neoxanthin, rutin, violaxanthin, and tannin were tested (Hug et al., 2014; Ludin et al., 2014; Calogero et al., 2015; Ghann et al., 2017; Atli et al., 2019; García-Salinas & Ariza, 2019; Kabir et al., 2019; Sreeja & Pesala, 2019; Duan et al., 2020; Ishak et al., 2020; Onah et al., 2020; Sabagh et al., 2020; Zhang et al., 2020). Among those different tested natural dyes, betalains, anthocyanins, and chlorophylls were the most promising natural dyes for DSSCs.

6 Betalains

Betalains are nitrogen-containing plant pigments classified under alkaloids and different from the commonly known plant pigments anthocyanins. These pigments are divided into two main structural groups, betacyanins (red-violet pigments) and betaxanthins (yellow pigments) (Fig. 45.1). Betalains are found in the plant leaves, flowers, stems, and bracts (Gandía-Herrero et al., 2016) of certain families of flowering plants such as Cactaceae. Both betacyanins and betaxanthins possess a

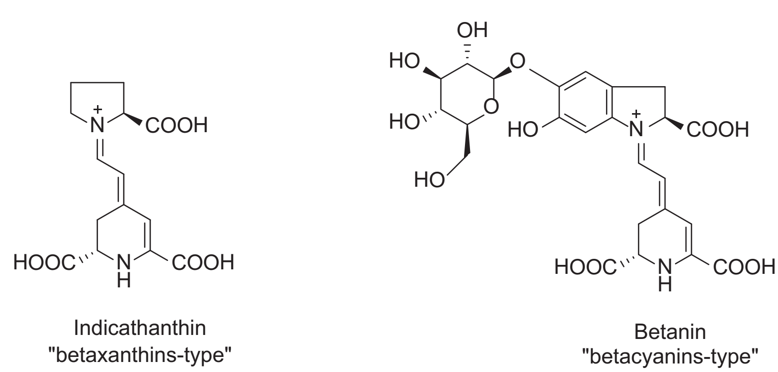

Fig. 45.1 Structure of betanin and indicathanthin

dihydropyridine moiety attached *via* a vinyl group to another nitrogenous group. The basic chromophore of the betalain pigments is the 1,7-diazaheptamethinium system (Clement et al., 1994). *Opuntia* genus belongs to the Cactaceae family and is considered to be the most promising source of betalains (Castellar et al., 2008; Calogero et al., 2010).

Betalains are water-soluble pigments that absorb the light in the visible region (Ludin et al., 2014). It has a strong solar absorption efficiency in the range of 400–600 nm. Betacyanins absorb the light at $\lambda_{max} = 536$ nm, and betaxanthins absorb at wavelength $\lambda_{max} = 480$ nm (Miguel, 2018). These two structures are easily found in *Opuntia* (mainly *Opuntia ficus indica*), the dragon fruits from *Hylocereus* cacti (mainly *Hylocereus polyrhizus)*, the Swiss chard, and red beetroots (*Beta vulgaris*) (Azeredo, 2009; Rodriguez-Amaya, 2018). Due to the hydrophilic characteristic of betacyanins and betaxanthins, betalains are accumulated in the epidermal and sub-epidermal plant tissues (Wink, 1997).

Betalain binds easily to the semiconductor layer (TiO_2) of the working electrode through its carboxylic group. As much as the dye molecules are attached to the TiO_2 layer, the DSSC will equally gain higher energy conversion efficiency. Betalain can also effectively interact with the redox couple in the electrolyte (iodine/iodide) (Sandquist & McHale, 2011).

6.1 Betalain for DSSC

Zhang et al. (2008) reported the efficiency of using the betacyanin in DSSC, where it reveals the energy conversion efficiency of around 0.67%. Calogero et al. (2010) did a comparative study between the betalain and the synthetic Ru-complex common dye, N719. The study revealed a 1.7% energy conversion efficiency for betalain, which was less than the Ru dye. The thermal stability of the natural pigment was confirmed under solar irradiation. However, no confirmation was reported on the long term stability and the lifetime of the betalain sensitized solar cell (Calogero et al., 2010). A better energy conversion efficiency of betalain based DSSC of 2.06% was obtained using betalains from wild Sicilian prickly pear (Calogero et al., 2012). An electrochemical and optical study of betalain as a sensitizer in the DSSC revealed the interaction effect of the carboxylic acid functional group of betalain with the semiconductor layer, which enhanced the conductivity of the cell. That effect of the functional group of the dye was demonstrated later in 2016 by Ramamoorthy et al., where betalain and anthocyanin were extracted from *Opuntia dillenii* and *Tamarindus indica* for DSSC fabrication. Both dyes revealed a sensitized effect to the semiconductor layer (TiO_2) (Ramamoorthy et al., 2016). For betalain pigments, its carboxylic acid group connected to the hydroxyl group in the TiO_2 layer, facilitating electron transfer by a coupling effect (Hernandez-Martinez et al., 2011), while for anthocyanin pigment, its carbonyl and hydroxyl groups attached to the TiO_2 layer. Both dyes showed a UV absorption band at 525 nm. The betalain based DSSC revealed a higher energy conversion efficiency (0.47%) than anthocyanin based DSSC (0.14%), attributed to their functional group's sensitizer effect. In comparison, the dye mixture in a 1:1 ratio showed a 0.20% energy conversion efficiency, which is higher than that of anthocyanin based DSSC and lower than betalain based DSSC.

Isah et al. (2015) extracted betalain dye from *Bougainvillea glabra* flower for DSSC fabrication. The effect of pH on the betalain dye as a sensitizer in the DSSC was tested under different pH values (1.2, 3.0, and 5.7). The results indicated that the best conversion efficiency of 0.9% was achieved at pH 3. When the pH was 1.2, the efficiency was very low (~0.2%), which could be due to betalain's degradation process at high acidity. Meanwhile, at a pH of 5.7, the efficiency was 0.57%, which was also less than the efficiency obtained at pH 3 due to lack of absorption of betalain on the TiO_2 layer (Isah et al., 2015). Gokilamani et al. (2015) reported betalain pigments'effect in sensitizing the TiO_2 annealed thin film in the DSSC. The betacyanin from *Basella alba* var. *rubra* spinach leaves was extracted and used to prepare a DSSC, which exhibited 0.70% energy conversion efficiency. This was attributed to the effective sensitive nature of the day and the thin film crystalline structure (Gokilamani et al., 2015).

The co-sensitization effect of a mixture of two natural dyes on the DSSC semiconductor layer was tested by Kumar et al. (2016). It has been described as an effective strategy for harvesting more solar light effectively. Among different tested extracts, cactus (*Opuntia ficus indica*) and Bermuda grass (*Cynodon dactylon*) co-sensitized DSSC showed a 1.1% power conversion efficiency, which was higher compared to their mono sensitized DSSC (Bermuda ~0.1%, and cactus ~0.6%). Almost the same result as for the cactus dye was achieved by Ganta D. 2017, where cladodes of *Opuntia ficus indica* was tested as a sensitizer of DSSC. A comparison between *Aloe vera* dyes extract, and cladodes extract reveals a high conversion efficiency of about 0.74%, corresponding to cladodes dyes extract (Ganta et al., 2017). This is attributed to the adhesion of chlorophyll dye to the TiO_2 layer resulting in better charge transfer. Interestingly, a side-by-side alignment of the two dyes, which was reported to reduce the mixing of dyes, demonstrated a 0.50% conversion efficiency (Ganta et al., 2017).

In contrast, two different betalain sources (*Opuntia ficus indica* and *Beta vulgaris*) displayed low conversion efficiency compared to *Hylocereus undatus*, the source of anthocyanin dye (Suganya & Jaisankar, 2019). Purushothamreddy et al. (2020) extracted the betalain from *Opuntia ficus indica* grown in Western Ghats Mountain in the southern part of Taminadu, India. They characterized the prickly pear fruit extract for its optical properties using UV-Vis and FTIR to confirm the presence of betacyanin and explore its promising characteristics as a photosensitizer for use in DSSC (Purushothamreddy et al., 2020). They further fabricated a DSSC with a conversion efficiency (η) of 0.56% with the highest fill factor (FF) of 0.85, open-circuit voltage (Voc) of 0.56 V, and short circuit-current density (Jsc) with 1.17 mA/cm^2.

7 DSSC Stability Challenge

DSSCs are of great interest due to their fabrication simplicity, eco-friendliness, flexible design with a good energy conversion efficiency. They also open a new commercial window for a sustainable, cheap, and useful product that can compete with other types of solar cells. However, the main problem with this type of solar cell is the stability issues and purification process. DSSCs show less stability than the synthetic inorganic-complex-based cells, i.e., natural DSSCs show less efficiency in contrast with the artificial ones, which is mainly attributed to the weak binding with the TiO_2 semiconductor layer, wherein the dye structure impact the cell performance (Ammar et al., 2019). Some natural dye structures may reduce contact with the semiconductor layer and efficiently inhibit the array of the molecules on the semiconductor layer. This negatively affects the number of electrons reaching the conduction band in the TiO_2 layer, decreasing the light absorption intensity, and hence the solar cell's performance. The stability of DSSC is based on its components, such as the dye sensitizer, semiconductor layer, counter electrode, electrolyte, and the working electrode (Sharma et al., 2018). This is in addition to other parameters such as the semiconductor layer thickness, extraction solvent, the electrolyte, and the active area ratio (Ammar et al., 2019). Enhancing the long term stability of the DSSC is one of the exciting topics for motivating this new type of solar cell. The DSSC cell should be stable and at an acceptable performance level for around 20 years. However, the natural dyes degrade upon exposure to UV radiation. UV filters can cover the outer anode as an initial step for protection and filtration of the UV radiation to enhance the stability.

The stability of the redox electrolyte is also an essential parameter in the DSSC performance. Preventing the decomposition of the redox couple will enhance DSSC stability. Even the extraction solvent for the natural dye could impact the light absorption and stability of the DSSC (Aduloju et al., 2011). Besides, the effect of a fast injection and intense light absorption for DSSC performance enhancement has been reported (Aduloju et al., 2011). All these variable parameters are concerned with the stability issues of the DSSC and represent a real research challenge for its industrial applications.

8 Conclusion

Natural dyes are promising alternatives to synthetic dyes considering their natural origin and economic value. The low-cost production, simple preparation techniques, eco-friendliness, and availability of natural dyes are important features. Among different tested natural dyes, betalain revealed a high potential efficiency in DSSC, whereas *Opuntia* spp. is the most promising betalain source. Although the natural dyes' efficiency in the DSSC looks promising, low stability is one of the major issues for this type of technology.

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References

Abdel-Latif, M. S., El-Agez, T. M., Taya, S. A., Batniji, A. Y., & El-Ghamri, H. S. (2013). Plant seeds-based dye-sensitized solar cells. *Materials Sciences and Applications, 4*(9), 516–520.

Abdin, Z., Alim, M. A., Saidur, R., Islam, M. R., Rashmi, W., Mekhilef, S., & Wadi, A. (2013). Solar energy harvesting with the application of nanotechnology. *Renewable and Sustainable Energy Reviews, 26*, 837–852. https://doi.org/10.1016/j.rser.2013.06.023

Abdulrazzaq, O. A., Saini, V., Bourdo, S., Dervishi, E., & Biris, A. S. (2013). Organic solar cells: A review of materials, limitations, and possibilities for improvement. *Particulate Science and Technology, 31*(5), 427–442.

Adedokun, O., Titilope, K., & Awodugba, A. O. (2016). Review on natural dye-sensitized solar cells (DSSCs). *International Journal of Engineering Technologies, 2*(2), 34. https://doi.org/10.19072/ijet.96456

Aduloju, K. A., Shitta, M. B., & Justus, S. (2011). Effect of extracting solvents on the stability and performances of dye-sensitized solar cell prepared using extract from Lawsonia Inermis. *Fundamental Journal of Modern Physics, 1*(2), 261–268.

Ammar, A. M., Mohamed, H. S. H., Yousef, M. M. K., Abdel-Hafez, G. M., Hassanien, A. S., & Khalil, A. S. G. (2019). Dye-sensitized solar cells (DSSCs) based on extracted natural dyes. *Journal of Nanomaterials, 2019*, 1–10. https://doi.org/10.1155/2019/1867271

Arof, A. K., & Ping, T. L. (2017). *Chlorophyll as photosensitizer in dye-sensitized solar cells*. InTech. https://doi.org/10.5772/67955

Atli, A., Atilgan, A., Altinkaya, C., Ozel, K., & Yildiz, A. (2019). St. Lucie cherry, yellow jasmine, and madder berries as novel natural sensitizers for dye-sensitized solar cells. *International Journal of Energy Research, 43*, 3914–3922.

Azeredo, H. M. C. (2009). Betalains: Properties, sources, applications, and stability—a review. *International Journal of Food Science & Technology, 44*(12), 2365–2376.

Bauer, C., Boschloo, G., Mukhtar, E., & Hagfeldt, A. (2002). Interfacial electron-transfer dynamics in Ru(tcterpy)(NCS)3-sensitized TiO_2 nanocrystalline solar cells. *Journal of Physical Chemistry B, 106*(49), 12693–12704.

Buscaino, R., Baiocchi, C., Barolo, C., Medana, C., Grätzel, M., Nazeeruddin, M. K., & Viscardi, G. (2008). A mass spectrometric analysis of sensitizer solution used for dye-sensitized solar cell. *Inorganica Chimica Acta, 361*(3), 798–805.

Calogero, G., Di Marco, G., Cazzanti, S., Caramori, S., Argazzi, R., Di Carlo, A., & Bignozzi, C. A. (2010). Efficient dye-sensitized solar cells using red turnip and purple wild Sicilian prickly pear fruits. *International Journal of Molecular Sciences, 11*(1), 254–267.

Calogero, G., Yum, J. H., Sinopoli, A., Di Marco, G., Grätzel, M., & Nazeeruddin, M. K. (2012). Anthocyanins and betalains as light-harvesting pigments for dye-sensitized solar cells. *Solar Energy, 86*(5), 1563–1575.

Calogero, G., Sinopoli, A., Citro, I., Di Marco, G., Petrov, V., Diniz, A. M., Parola, A. J., & Pina, F. (2013). Synthetic analogues of anthocyanins as sensitizers for dye-sensitized solar cells. *Photochemical and Photobiological Sciences, 12*(5), 883–894.

Calogero, G., Bartolotta, A., Di Marco, G., Di Carlo, A., & Bonaccorso, F. (2015). Vegetable-based dye-sensitized solar cells. *Chemical Society Reviews, 44*(10), 3244–3294.

Cao, W., & Xue, J. (2014). Recent progress in organic photovoltaics: Device architecture and optical design. *Energy and Environmental Science, 7*(7), 2123–2144.

Castellar, M. R., Obón, J. M., Alacid, M., & Fernández-López, J. A. (2008). Fermentation of *Opuntia stricta* (haw.) fruits for betalains concentration. *Journal of Agricultural and Food Chemistry, 56*(11), 4253–4257.

Clement, J. S., Mabry, T. J., Wyler, H., & Dreiding, A. S. (1994). Chemical review and evolutionary significance of the betalains. In Caryophyllales (pp. 247–261). Springer, Berlin, Heidelberg.

Dang, C., Labie, R., Simoen, E., & Poortmans, J. (2018). Detailed structural and electrical characterization of plated crystalline silicon solar cells. *Solar Energy Materials and Solar Cells, 184*, 57–66.

Duan, S., Zhou, Q., Li, A., Wang, X., Sasaki, S., & Tamiaki, H. (2020). *Semisynthetic chlorophyll derivatives toward solar energy applications* (p. 2000162). Solar RRL. https://doi.org/10.1002/solr.202000162

Fung, A. K. M., Chiu, B. K. W., & Lam, M. H. W. (2003). Surface modification of TiO2 by a ruthenium(II) polypyridyl complex via silyl-linkage for the sensitized photocatalytic degradation of carbon tetrachloride by visible irradiation. *Water Research, 37*(8), 1939–1947.

Gandía-Herrero, F., Escribano, J., & García-Carmona, F. (2016). Biological activities of plant pigments betalains. *Critical Reviews in Food Science and Nutrition, 56*(6), 937–945.

Ganta, D., Jara, J., & Villanueva, R. (2017). Dye-sensitized solar cells using *Aloe Vera* and cladode of cactus extracts as natural sensitizers. *Chemical Physics Letters, 679*, 97–101.

García-Salinas, M. J., & Ariza, M. J. (2019). Optimizing a simple natural dye production method for dye-sensitized solar cells: Examples for betalain (Bougainvillea and beetroot extracts) and anthocyanin dyes. *Applied Sciences, 9*, 2515.

Ghann, W., Kang, H., Sheikh, T., Yadav, S., Chavez-Gil, T., Nesbitt, F., & Uddin, J. (2017). Fabrication, optimization and characterization of natural dye sensitized solar cell. *Scientific Reports, 7*(1), 1–12.

Godibo, D. J., Anshebo, S. T., & Anshebo, T. Y. (2015). Dye sensitized solar cells using natural pigments from five plants and quasi-solid state electrolyte. *Journal of the Brazilian Chemical Society, 26*(1), 92–101.

Gokilamani, N., Muthukumarasamy, N., Thambidurai, M., Ranjitha, A., & Velauthapillai, D. (2015). *Basella alba* rubra spinach pigment-sensitized TiO_2 thin film-based solar cells. *Applied Nanoscience, 5*(3), 297–303.

Gorlov, M., & Kloo, L. (2008). Ionic liquid electrolytes for dye-sensitized solar cells. *Dalton Transactions, (20)*, 2655–2666.

Gunn, G. (2013). Platinum-group metals. In *Critical metals handbook*. https://doi.org/10.1002/9781118755341.ch12

Hagberg, D. P., Yum, J. H., Lee, H. J., De Angelis, F., Marinado, T., Karlsson, K. M., Humphry-Baker, R., Sun, L., Hagfeldt, A., Grätzel, M., & Nazeeruddin, M. K. (2008). Molecular engineering of organic sensitizers for dye-sensitized solar cell applications. *Journal of the American Chemical Society, 130*(19), 6259–6266.

Hernandez-Martinez, A. R., Estevez, M., Vargas, S., Quintanilla, F., & Rodriguez, R. (2011). New dye-sensitized solar cells obtained from extracted bracts of *Bougainvillea glabra* and spectabilis betalain pigments by different purification processes. *International Journal of Molecular Sciences, 12*(9), 5565–5576.

Hernández-Martínez, A. R., Estevez, M., Vargas, S., Quintanilla, F., & Rodríguez, R. (2012). Natural pigment-based dye-sensitized solar cells. *Journal of Applied Research and Technology, 10*(1), 38–47.

Hug, H., Bader, M., Mair, P., & Glatzel, T. (2014). Biophotovoltaics: Natural pigments in dye-sensitized solar cells. *Applied Energy, 115*, 216–225.

Isah, K. U., Ahmadu, U., Idris, A., Kimpa, M. I., Uno, U. E., Ndamitso, M. M., & Alu, N. (2015). Betalain pigments as natural photosensitizers for dye-sensitized solar cells: The effect of dye pH on the photoelectric parameters. *Materials for Renewable and Sustainable Energy, 4*(1), 5–9.

Ishak, N., Salleh, H., Rahman, S. A., Dagang, A. N., Kamarulzaman, N. H., Ahmad, Z., Abd Majid, S. N., & Ghazali, S. M. (2020). Application of conjugated chlorophyll from natural dye

(*Imperata cylindrica*) to apply in hybrid DSSC as third generation solar energy. *Solid State Phenomena, 301*, 135–144.

Jamalullail, N., Mohamad, I. S., Norizan, M. N., Baharum, N. A., & Mahmed, N. (2018). Short review: Natural pigments photosensitizer for dye-sensitized solar cell (DSSC). In *IEEE Student Conference on Research and Development: Inspiring Technology for Humanity, SCOReD 2017—Proceedings* (pp. 344–349).

Jose, R., Kumar, A., Thavasi, V., & Ramakrishna, S. (2008). Conversion efficiency versus sensitizer for electrospun TiO_2 nanorod electrodes in dyesensitized solar cells. *Nanotechnology, 19*(42), 424004.

Kabir, F., Sakib, S. N., & Matin, N. (2019). Stability study of natural green dye based DSSC. *Optik, 181*, 458–464.

Kippelen, B., & Brédas, J. L. (2009). Organic photovoltaics. *Energy and Environmental Science, 2*(3), 251–261.

Kour, N., & Mehra, R. (2017). Recent advances in photovoltaic technology based on perovskite solar cell—A review. *International Research Journal of Engineering and Technology, 4*(7), 1284–1296.

Kumar, K. A., Subalakshmi, K., & Senthilselvan, J. (2016). Effect of mixed valence state of titanium on reduced recombination for natural dye-sensitized solar cell applications. *Journal of Solid State Electrochemistry, 20*(7), 1921–1932.

Lee, J. K., & Yang, M. (2011). Progress in light harvesting and charge injection of dye-sensitized solar cells. *Materials Science and Engineering B: Solid-State Materials for Advanced Technology: B, 176*(15), 1142–1160.

Ludin, N. A., Al-Alwani Mahmoud, A. M., Bakar Mohamad, A., Kadhum, A. A. H., Sopian, K., & Abdul Karim, N. S. (2014). Review on the development of natural dye photosensitizer for dye-sensitized solar cells. *Renewable and Sustainable Energy Reviews, 31*, 386–396.

Mansour, R. (2018). Natural dyes and pigments: Extraction and applications. In *Handbook of renewable materials for coloration and finishing* (pp. 75–102). https://doi.org/10.1002/9781119407850.ch5

Mazzio, K. A., & Luscombe, C. K. (2015). The future of organic photovoltaics. *Chemical Society Reviews, 44*(1), 78–90.

Miguel, M. G. (2018). Betalains in some species of the Amaranthaceae family: A review. *Antioxidants, 7*(4), 53.

Narayan, M. R. (2012). Review: Dye sensitized solar cells based on natural photosensitizers. *Renewable and Sustainable Energy Reviews, 16*(1), 208–215.

Neale, N. R., Kopidakis, N., Van De Lagemaat, J., Grätzel, M., & Frank, A. J. (2005). Effect of a coadsorbent on the performance of dye-sensitized TiO_2 solar cells: Shielding versus band-edge movement. *Journal of Physical Chemistry B, 109*(49), 23183–23189.

Onah, E. O., Offiah, S. U., Chime, U. K., Whyte, G. M., Obodo, R. M., Ekechukwu, O. V., Ahmad, I., Ugwuoke, P. E., & Ezema, F. I. (2020). Comparative photo-response performances of dye sensitized solar cells using dyes from selected plants. *Surfaces and Interfaces, 20*, 100619. https://doi.org/10.1016/j.surfin.2020.100619

O'regan, B., Grätzel, M. (1991). A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films. *Nature, 353*(6346), 737–740.

Osman, O. I. (2017). DFT study of the structure, reactivity, natural bond orbital and hyperpolarizability of thiazole azo dyes. *International Journal of Molecular Sciences, 18*(2), 239. https://doi.org/10.3390/ijms18020239

Purushothamreddy, N., Dileep, R. K., Veerappan, G., Kovendhan, M., & Joseph, D. P. (2020). Prickly pear fruit extract as photosensitizer for dye-sensitized solar cell. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 228*, 117686. https://doi.org/10.1016/j.saa.2019.117686

Qin, Y., & Peng, Q. (2012). Ruthenium sensitizers and their applications in dye-sensitized solar cells. *International Journal of Photoenergy, 2012*, 291579. https://doi.org/10.1155/2012/291579

Ramamoorthy, R., Radha, N., Maheswari, G., Anandan, S., Manoharan, S., & Victor Williams, R. (2016). Betalain and anthocyanin dye-sensitized solar cells. *Journal of Applied Electrochemistry, 46*(9), 929–941.

Rodriguez-Amaya, D. B. (2018). Betalains. In Encyclopedia of food chemistry. https://doi.org/10.1016/B978-0-08-100596-5.21607-7

Sabagh, S., Izadyar, M., & Arkan, F. (2020). Photovoltaic properties of the flavonoid-based photosensitizers: Molecular-scale perspective on the natural dye solar cells. *International Journal of Quantum Chemistry, 120*(10), e26171. https://doi.org/10.1002/qua.26171

Sandquist, C., & McHale, J. L. (2011). Improved efficiency of betanin-based dye-sensitized solar cells. *Journal of Photochemistry and Photobiology A: Chemistry, 221*(1), 90–97.

Scharber, M. C., & Sariciftci, N. S. (2013). Efficiency of bulk-heterojunction organic solar cells. *Progress in Polymer Science, 38*(12), 1929–1940.

Schindler, F., Fell, A., Müller, R., Benick, J., Richter, A., Feldmann, F., Krenckel, P., Riepe, S., Schubert, M. C., & Glunz, S. W. (2018). Towards the efficiency limits of multicrystalline silicon solar cells. *Solar Energy Materials and Solar Cells, 185*, 198–204. https://doi.org/10.1016/j.solmat.2018.05.006

Sharma, K., Sharma, V., & Sharma, S. S. (2018). Dye-sensitized solar cells: Fundamentals and current status. *Nanoscale Research Letters, 13*, 381. https://doi.org/10.1186/s11671-018-2760-6

Sreeja, S. S., & Pesala, B. (2019). Performance enhancement of betanin solar cells co-sensitized with indigo and lawsone: A comparative study. *ACS Omega, 4*(19), 18023–18034.

Steim, R., Kogler, F. R., & Brabec, C. J. (2010). Interface materials for organic solar cells. *Journal of Materials Chemistry, 20*(13), 2499–2512.

Suganya, N., & Jaisankar, V. (2019). A study on the effect of dye and polymer nanocomposite electrolyte on the performance of natural dye sensitized solar cells. *Materials Today: Proceedings, 14*, 471–481.

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.

Wink, M. (1997). Compartmentation of secondary metabolites and xenobiotics in plant vacuoles. *Advances in Botanical Research, 25*, 141–169.

Zaban, A., Ferrere, S., & Gregg, B. A. (1998). Relative energetics at the semiconductor/sensitizing dye/electrolyte interface. *Journal of Physical Chemistry B, 102*(2), 452–460.

Zhang, D., Lanier, S. M., Downing, J. A., Avent, J. L., Lum, J., & McHale, J. L. (2008). Betalain pigments for dye-sensitized solar cells. *Journal of Photochemistry and Photobiology A: Chemistry, 195*(1), 72–80.

Zhang, C., Zhao, W., Sasaki, S., Tamiaki, H., & Wang, X.-F. (2020). A chlorophyll derivative-based bio-solar energy conversion and storage device. *Electrochimica Acta, 347*, 136283. https://doi.org/10.1016/j.electacta.2020.136283