Asian Journal of Chemistry; Vol. 37, No. 5 (2025), 985-996

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2025.33078

REVIEW

Anthocyanin-Based Photosensitizers: A Comparative Study of Natural Dyes in Enhancing Third-Generation Solar Cell Efficiency

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Received: 1 December 2024; *Accepted*: 6 March 2025; *Published online*: 30 April 2025; AJC-21961

This review examines third-generation dye-sensitized solar cells (DSSCs), focusing on natural dyes due to their sustainability, non-toxicity and cost-effectiveness. It explores key natural dyes–chlorophyll and anthocyanin–alongside others like betalain, sepia melanin, lawsone, curcumin, clathrin and carminic acid. The extraction techniques from plant and animal sources, along with variables like pH, temperature, solvent selection and the source of extraction that affect dye adherence on the photoanode are also examined, evaluating the effects of dye concentration and the optimum conditions for dye application. The benefits and limitations of natural dyes in DSSCs for solar energy applications also addressed.

Keywords: Sensitizer molecule, Dye composite, Dye efficiency, Photoanode, Redox couple electrolyte, Conducting electrode.

INTRODUCTION

Solar cells, also known as photovoltaic (PV) cells, convert light energy into electrical energy through the photovoltaic effect. They are primarily classified into three generations. First-generation solar cells are silicon-based, including mono- and polycrystalline variants, offering high efficiency but at higher costs [1]. Second-generation cells utilize thin-film technologies, such as amorphous silicon, cadmium telluride and copper indium gallium selenide (CIGS), offering lower efficiency but reduced production costs [2]. Third-generation solar cells include emerging technologies like organic photovoltaic cells (OPVs), perovskite solar cells and dye-sensitized solar cells (DSSCs), which aim for greater flexibility, cost-efficiency and improved performance through novel materials and processes [3].

As Albert Einstein once remarked, "The true value of a scientific theory is not the effect it has on the understanding of the phenomena, but the way it enables us to control the phenomena". This insight is reflected in the development of solar cells, where the ability to harness sunlight–an abundant, renewable resource–is paramount [4]. The principle of a solar cell is grounded in the photovoltaic effect, where light energy is directly converted into electrical energy [5]. When light photons strike the surface of a semi-conductor material, typically silicon, they transfer their energy to electrons in the material, exciting them into higher energy states. These excited electrons are then liberated from their atoms, creating electron-hole pairs. An electric field, typically generated by a p-n junction, directs these free electrons toward the negative terminal and the holes toward the positive terminal, thus generating a flow of electric current [6]. In a typical silicon-based solar cell, the p-n junction creates an internal electric field that separates and directs the electrons and holes [7]. The resultant current is then captured by external circuitry, providing usable electrical energy. As solar cell technology evolves, advancements in materials like perovskites, organic semiconductors and dye-sensitized cells are being explored to enhance efficiency, lower costs and expand applicability, offering a sustainable solution for global energy needs [8].

Third-generation solar cells represent the forefront of photovoltaic technology, focusing on the novel materials and innovative designs to surpass the limitations of traditional silicon-based cells. These include dye-sensitized solar cells (DSSCs), perovskite solar cells and organic photovoltaic cells (OPVs) [9]. Unlike first- and second-generation cells, which rely on silicon or thin films, third-generation cells leverage materials like organic polymers, perovskite crystals and natural dyes, offering advantages such as lower production costs, flexibility and potential for higher efficiency [10]. They aim to address the scalability, cost-efficiency and environmental sustainability issues, providing a promising alternative for large-scale solar energy harvesting [11].

A typical third-generation solar cell works on the basic principle of the photovoltaic effect, utilizing sunlight as the source for generating current within the solar cell [12]. The third-generation solar cell is composed of a dye as a photosensitizer molecule embedded/coated onto the TiO_2 photoanode, a Pt conducting electrode and the two electrodes connected exter-nally. The circuit is completed with the redox couple electrolyte [13]. Upon absorption of sunlight by the TiO_2 photoanode, the dye coated on it becomes excited, leading to the release of electrons. These electrons then traverse to the Pt counter-electrode through the external circuit. To complete the circuit, once the electrons reach the Pt-counter electrode, they are then transferred back to the photoanode by the redox couple elect-rolyte, thus regenerating the oxidized dye [14].

Dyes are the organic compounds that absorb specific wavelengths of light and reflect others, giving substances their characteristic colour. They are broadly classified into synthetic and natural dyes. Synthetic dyes are chemically engineered for specific applications, while natural dyes are derived from plant, animal, or mineral sources. In solar energy technology, dyes play a crucial role in dye-sensitized solar cells (DSSCs), where they act as photosensitizers to absorb light and convert it into electrical energy [15,16]. The preference for dyes in solar energy applications stems from their ability to absorb a wide spectrum of light, particularly visible and ultraviolet light, making them efficient for harnessing solar energy [17]. Natural dyes, in particular, are gaining attention due to their eco-friendliness, abundance and low toxicity. In plants, pigments like chlorophyll capture sunlight to produce energy. Similarly, in solar cells, natural dyes can capture light and facilitate energy conversion [18]. Interestingly, dyes used in textile industries, known for their vibrant colour and stability, are effective in solar cells due to their light-absorbing properties. Similar to their role in imparting colour to fabrics, they effectively absorb light in the DSSCs, emulating the energy capturing function of pigments in photosynthesis [19]. The transformation of these dyes from decorative to functional agents illustrates the interaction between nature and technology, wherein the intrinsic qualities of natural compounds are utilized to enhance the energy conversion in solar cells [20].

Photosynthesis is fundamental to the life cycle of plants and chlorophyll, the primary pigment responsible for this process exists in two forms *viz*. chlorophyll-a and chlorophyll-b. In order to maintain the plant's fundamental processes, both are essential [21]. The vibrant colours of fruits and flowers are caused by a combination of chlorophyll and other pigments found in plants, such as anthocyanins and betalains [22]. But why are these pigments valuable as dye photosensitizers for third-generation solar cells?

Dyes extracted from plants have been used for centuries in various applications, from textiles to food and are increasingly being explored for their potential in dye-sensitized solar cells. Plant-derived dyes, such as anthocyanins (from berries), chlorophyll (from leaves), curcumin (from turmeric) and betalains (from beets), are naturally occurring pigments with the ability to absorb light across a wide spectrum [23]. These dyes are not only abundant and biodegradable but also sustainable, aligning with the growing demand for eco-friendly technologies. Chlorophyll and anthocyanin are particularly well-suited for use in photosensitizer molecules, essential components in the fabrication of third-generation solar cells [24]. The performance of these solar cells largely depends on the effectiveness of the photosensitizer. These natural pigments are excellent absorbers of both UV and visible light, making them highly efficient for light harvesting [16,25]. Third generation solar cells function by absorbing light and transferring charge carriers from the dye to a wide band-gap material, providing a sustainable, eco-friendly alternative to synthetic dyes [26]. The use of plant-based dyes like chlorophyll and anthocyanin thus enhances both the performance and environmental appeal of solar energy technology [27,28].

In DSSCs, the plant dyes function as photosensitizers, absorbing photons from sunlight and transferring the energy to the semiconductor material to generate the electrical current [29]. For instance, chlorophyll, the molecule responsible for photosynthesis in plants, is known for its ability to efficiently capture sunlight and convert it into chemical energy [30]. This mimicking of natural photosynthesis processes offers a direct analogy for harnessing solar energy, making plant-derived dyes ideal candidates for improving the efficiency and sustainability of solar cells [31]. Unlike plant-based dyes, animal-derived dyes typically offer rich, vibrant colour and unique colourfastness properties [32,33]. For instance, carminic acid, derived from cochineal insects, has demonstrated promising light absorption properties, making it an effective candidate for DSSCs [34]. Similarly, sepia melanin, a pigment found in cuttlefish, has been studied for its unique ability to interact with light and its stability in various environmental conditions [35,36]. The fundamental component to fabricate these solar cells is the photosensitizer molecules made from dye components either synthetically or from natural sources, the former prevailing over the latter in terms of high efficiency and *vice versa* when it comes to sustainability and eco-friendly nature [37,38].

This review extensively elaborates on the wide range of natural dyes used in the manufacturing of third-generation solar cells. It covers the extraction and purification of dyes alongside the experimental parameters required to be maintained for making the photosensitizer molecules from such dyes. The dye sensitizer molecules have been thoroughly characterized and the most likely settings for making photosensitizer molecules useful in solar cell production are discussed.

The natural dyes that are the most discussed are chlorophyll and anthocyanin dyes due to their robust light absorption capability, making them a good light-harvesting pigment. Other dyes namely betalain, melanin, carminic acid, lawsone, lupeol, curcumin, santalin and clathrin are also explored. A meticulous examination has been made of the composites specifically, nanoparticles and polymer composites that can be used in fabricating dye sensitizers, electrodes and electrolytes.

Different parameters like solvent choice, pH and dye concentration have been evaluated. Individually and when blended, these two are also considered while examining dye extracts for their overall solar cell performance. Furthermore, a comparative analysis based on the solar cell performance and efficiency has been made by incorporating certain characterization tools namely cyclic voltammetry, I-V curve measurements, incident photon-to-current efficiency (IPCE) and solar cell efficiency, impedance measurements, UV-Vis spectrophotometry and FTIR spectroscopy.

A. Anthocyanin dye as a photosensitizer molecule: A study on solar cell performance and comparative analysis of anthocyanin dye and the blend with other natural dyes

Anthocyanin dyes exhibit strong light absorption properties and when combined with other natural dyes, their light absorption capacity can potentially increase several fold. However, such enhancements are typically observed only in select cases. Each dye molecule used to synthesize photosensitizers is evaluated for incident photon-to-current efficiency (IPCE) using UV-Vis spectroscopy. Lim *et al*. [39] developed a blend of anthocyanin and betalain dyes for this purpose and showed that it outperformed the components. A robust and durable photoanode was developed to assess the efficacy of this dye blend using cyclic voltammetry. The current-voltage (I-V) curve revealed a significant higher peaks in open-circuit voltage and short-circuit current for the individual dyes compared to the dye blend. The results obtained from the I-V measurements were further corroborated through electrochemical impedance spectroscopy, which confirmed that the photoanode coated with anthocyanin dye extracted from the Ixora plant species exhibited superior solar cell performance. In contrast, the dye blend demonstrated intermediate performance. Furthermore, anthocyanin dye extracted from dragon fruit and applied to a TiO_2 nanoparticle-based photoanode also resulted in admirable solar cell performance as reported by Ali & Nayan [40]. Similarly, Lai *et al*. [41] also extracted dyes from *Bougainvillea brasiliensis* Raeusch, *Garcinia subelliptica*, *Ficus retusa* Linn and *Rheo spathacea* Stearn, which were subsequently adsorbed onto a water-based dye-sensitized solar cell. The dye behaved as a good adsorber onto the photoanode due to the formation of a Schottky barrier. Solvents also play a critical role in enhancing the efficiency of the dye as a photosensitizer.

Reda *et al.* [42] extracted anthocyanin dye from mulberry fruit and akenchira flower using different solvents and varied pH conditions. Their study was focused on the conditions with which an effective dye sensitizer molecule could most likely be fabricated without the use of making a composite. Sub-nanosecond laser spectroscopy, DFT and TDDFT calculations showed that photosensitizers made from selected chlorophyll derivatives, raw anthocyanin, and betalain extracts had high monochromatic photon-to-current conversion efficiency and performed well in solar cells. A photosensitizer made from ethanolic extract of mulberry fruit and akenchira flower works best.

A new type of blend consisting of anthocyanin and chlorophyll dyes, extracted from flame tree flowers and pawpaw leaves was used as DSSCs as reported by Kimpa *et al.* [43]. The conversion efficiency of the dye-sensitized solar cell from the mixed solution could achieve a maximum of 0.27%, while the individual one reaches 0.20% only. Thus, the composite dye demonstrates enhanced conversion efficiency compared to dyes sourced from flame tree flower or pawpaw leaf extracts.

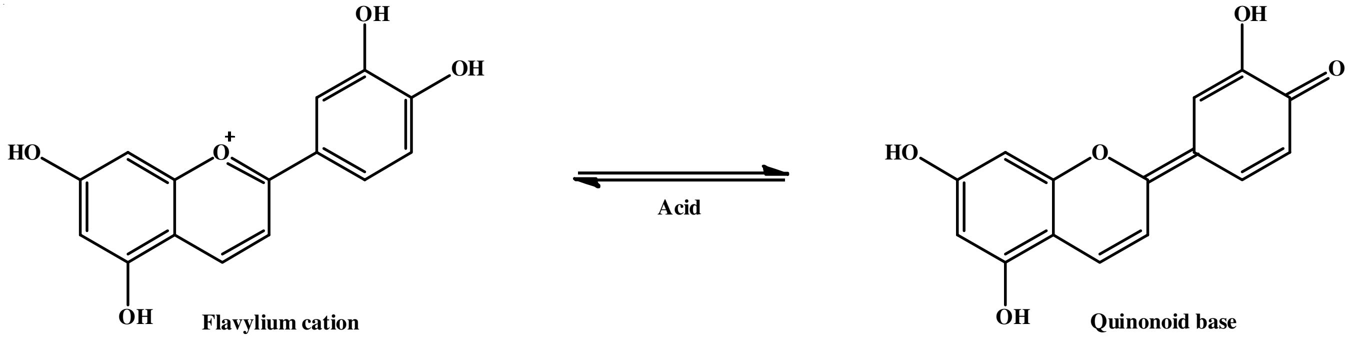
On comparing the data obtained from this experiment with the data obtained from the experiment conducted previously by Lim *et al*. [39], it was duly observed that the dye blend prepared from anthocyanin and chlorophyll exhibited superior activity over the dye blend prepared from anthocyanin and betalain. Furthermore, the blend dye (anthocyanin and chlorophyll) showed better performance than its counterparts. In case of the blend dye (anthocyanin and betalain), anthocyanin dye outperformed the blend dye and betalain dye. This could be attributed to the molecular structure differences among the corresponding blended dyes.

Another example of making a blend dye that resembled superior performance over its corresponding individual dye is, the purple chrysanthemum flower and jatropha leaves dye extract solutions, good sources of anthocyanin and chlorophyll dye, as reported by Tahir *et al.* [44]. Similar to previous works, ethanol was proved to be the best-extracting solvent, with I^-/I^{3-} as an electrolyte and ITO/TCO (transparent conductive oxide) glass as the conducting electrode.

Vinutha *et al*. [45] developed various concentrations of anthocyanin dye extracted from strawberry fruit and utilizing ethanol as solvent. Their research was focused on developing a robust photoanode that would provide the dye molecule with an adequate surface area. The doctor blade method was incorporated in making the TiO_2 photoanode, which was coated with FTO. The porosity of the photoanode was improved, when TiO_2 nanopowder was incorporated instead of regular TiO_2 powder.

In a plant's life cycle, a seed serves a vital role contributing to processes like dispersal, reproduction and new plant growth. Adapted specifically to their functions within each plant species, seed characteristics vary widely. Thus, seeds, just like other parts of plant, can be used in dye processing and the synthesis of photosensitizer molecules. For example, Taya *et al*. [46] used seeds of *Raphnus rapphanistrum*, *Lepidium sativum* and *Dianthus barbatus* as a source to extract anthocyanin dye. They carefully analyzed the seed among the three that would yield the best results and found that the photosensitizer molecule synthesized from the dye extracted from the *Dianthus barbatus* seed had superior activity. The superior activity of *D. barbatus* extract was attributed to the stability of anthocyanin dye in the acidic pH range. This was observed in the I-V measurements as well where the higher current production was solely dependent on the reduced pH range. Moreover, this reduced pH range enhanced the flavylium ion, a stable form of anthocyanin dye, whereas increased pH levels lead to ion hydration to quinonoid bases (**Scheme-I**). Thus, a higher pH range of the anthocyanin dye would give superior activity over its counter pH range.

The strong binding of dye to the oxide layer of photoanode to form a stable complex allows a photosensitizer molecule absorb light. The stability may be compromised if the dye clusters



Scheme-I: Chemical structure of the stable forms of anthocyanin dye

at the interaction site; therefore, to minimize dye clustering, additives are used. Cole *et al.* [47] reviewed cholic acid as additive acted as a spacer in binding the ethanolic dye extract to the TiO_2 surface, thereby prevent dye aggregation and excited state-quenching. It facilitated the open circuit voltage of the solar cell while preserving the integrity of dye. Similar works were reported by Tadesse *et al.* [48] wherein the *Syzgium guineese* plant, a water berry or wild plum found in regions across Africa, was exploited to extract anthocyanin dye. Different solvents *viz.* ethanol, methanol, water and ethyl acetate were used and the solvent-solvent extraction techniques were used to purify the respective dye extracts.

The results obtained coincided with the works of Reda *et al.* [42] that under an acidic pH range, the ethanolic anthocyanin dye extract showed the superior results over other dye extracts. The dye is extracted from mulberry fruit, other similar works were performed on the anthocyanin dye extracted from water berry fruit. A negative solvatochromism in the absorption peaks in the UV-Vis spectral analysis showed the presence of anthocyanin molecules as the solvent polarity increased. While altering pH, the equilibrium between flavylium and quinonoid forms of anthocyanin shifted, indicating that the photosensitizer works best when the dye molecule is extracted with ethanol and maintained at a low pH, improving solar cell performance [49]. Munawaroh *et al.* [50] extracted the anthocyanin dye from *Mangosteen pericarp* were prepared by adding some additives namely malic acid and ascorbic acid. The additives were added specifically to enhance the colour of the dye extract so that the dye molecule could be stabilized. The additives are generally used to prevent dye aggregationand their application is not restricted solely to the interaction between dye and photoanode. Ghosh *et al.* [51] employed the co-pigmentation method to stabilize the dye molecule isolated from *M. pericarp*, enhancing its efficacy as a photosensitizer molecule. It was determined that the degradation of methylene blue dye by mangosteen dye extract coated on TiO_2 photoanode occurs only at optimized dosages.

Polo & Murakami [52] extracted blue-violet anthocyanin dye from jaboticaba fruit and calafate berries. In comparison with other dye extracts used in the experimentation, jaboticaba and calafate showed the superior activity. *Kopsia flavida* fruit dye extract is another example which is a widely used source of anthocyanin dye and gives superior results when extracted using ethanol solvent as reported by Nishantha *et al.* [53]. In a study conducted by Ghann *et al.* [54], the TiO_2 photoanode was analyzed for its performance on better light absorption by coating it with pomegranate and blueberry dye extracts, respectively. Several spectroscopic techniques like UV-Vis, Raman, FTIR, AFM and FESEM, were employed to characterized the as-synthesized TiO_2 photoanode material prepared *via* the spin coating approach. The results indicated that the efficiency of pomegranate dye extract surpassed other dye extracts.

Wattananate *et al.* [55] extracted the anthocyanin and betalain dyes from the variety of fruits like pomegranate, concord grape, Virginia creeper, beetroot, purple yam, black rice, dried pomegranate and butterfly pea. A high IPCE was achieved when dye extracts were derived from purple yam, pomegranate and concord grape juice, as demonstrated by experimental data from UV-Vis spectral analysis and oxygen radical absorption capacity. The *Saraca asoca* flower, another flowering plant, renowned for its vibrant and ecstatic look, is another source of anthocyanin dye. As reported by Maurya *et al.* [56], the anthocyanin dye extract, prepared from the raw anthocyanin present in the core of *Saraca asoca* flower, showed a highly strong chelating effect on the TiO_2 photoanode. The experimental data obtained from UV-Vis, FTIR, I-V measurements, fill factor and the photocurrent action spectra (IPCE *vs.* wavelength curve) were in agreement with the results obtained.

Atli *et al.* [57] synthesized various dye extracts from Yellow jasmine, St. Lucie cherry and madder berries, flowers, and fruits, and each dye extract was evaluated for its efficacy in total solar cell performance. Yellow jasmine consists of apigeninidin, whereas madder berries contain malvidin, both of which are anthocyanin derivatives. St. Lucie cherry also consist of variety of anthocyanin derivatives *viz.* cyanidin, delphinidin, petunidin and peonidin. Among the studied materials, the St. Lucie cherry dye extract exhibited improved performance, as evidenced by electrochemical impedance spectroscopy data, which demonstrated reduced charge transfer resistance and elevated recombination resistance values. The enhanced light absorption onto the TiO_2 photoanode and the resulting higher currents are thought to be caused by the presence of delphinidinm, which may have a derivative molecular structure. In the same manner, Hamadanian *et al.* [58] also extracted the anthocyanin dye from *Reseda luteola*, *Berberis integerrima* , *Punica granatum* Pleniflora, *Consolida orientalis*, *Reseda gredensis*, *Clematis orientalis*, *Adonis flammea*, *Salvia sclarea* and *Consolida ajacis*. Based on the UV-Vis spectral analysis, a large portion of visible light absorption was observed when *Consolida ajacis* dye extract was analyzed as this dye extract consisted of delphinidin showed broader and larger solar light absorption, which led to the generation of higher currents across the circuit.

Third-generation solar cells: The main objectives of the third-generation solar cells are to improve power conversion efficiency and lower the manufacturing costs. The most common electrolyte sources used are redox couple of iodide/triiodide systems in these cells. Nonetheless, to enhance the efficiency of electron-charge transfer, modifications to the electrolyte system are possible. One approach to achieve this is by employing chitosan as composite to enhance the support of electrolyte. Although chitosan is not a dye by itself, it serves effectively as a dye-fixing agent and mordant, enhancing both the colour and durability of the dye.

Chawla *et al.* [59] developed an electrolyte system using the LiI:I_2 redox couple, with chitosan serving as host polymer. The synthesized photoanode consisted of TiO_2 enhanced with WO_3, with TiO_2 serving as a filler component. The altered photoanode received a coating of anthocyanin dye extract and the overall circuit performance was based on the comparative analysis between chitosan-Li:I_2 electrolyte and liquid electrolyte systems. Based on the detailed experimentation, it was found that chitosan-based electrolytes and TiO_2-WO_3 photoanodes sensitized with anthocyanin dye gave superior overall solar cell performance as compared to liquid electrolyte cells. The main advantage of this chitosan-based electrolytes compared to liquid electrolytes lies in their ability to maintain stability for as long as ten weeks without any leakage or vaporization.

Anthocyanin dye is the most stable under the acidic pH range and the solar cells work best under acidic conditions. Kim *et al.* [60] investigated the optimal intensity of acid required to enhance the adsorption capacity of anthocyanin dye by using various acid reagents for the extraction of dye. The treatment of dye extracts with acetic acid resulted in enhanced performance of solar cells, as indicated by the results from the UV spectral analysis and photoelectrochemical measurements. Ayelew & Ayele [61] also conducted similar research on the optimum conditions of acid content in the dye extract, using anthocyanin dye extracted from *Euphorbia cotinifolia* leaves and *Acanthus sennii chiovenda* flowers. The UV-Vis spectra showed higher absorbance when lower acid concentrations were used. It was determined that the *Acanthus sennii chiovenda* flower dye extract yielded optimal results when extracted using ethanol solvent with 1% HCl acid.

Cassia fistula, a Thailand's national flower, serves as a valuable source of anthocyanin dyes, most specifically, rhein, kaempferol and leucopelarrgonidi. Maurya *et al.* [62] prepared a photosensitizer from *Cassia fistula* dye extract and ethanol as the extracting solvent. On thorough investigation of the dye extracts, it was concluded that rhein dye gave the best results over the other derivatives, which is attributed to the higher electron donor capability of the dye extract. Surana *et al.* [63] extracted the anthocyanin dye extract from jamun fruit to evaluate its effectiveness in comparison to the synthetic N719 dye. The dye extract, when combined with rGO-TiO_2 and gel-polymer electrolyte, yielded better results comparable to the synthetic N719 dye. Anthocyanin dye extracted from the spin coating method showed promising results in overall solar cell performance as observed by Ghann *et al.* [54]. Similar work was reported by Madnasri [64], whereby ITO glass substrate was incorporated into ZnO photoanode and the resulting *Musa acuminata* bracts dye extract showed superior results, attributed to the technique used in preparing the dye extract that enabled higher dye adsorption on the photoanode surface.

The synthesis of a photosensitizer molecule is dependent upon the degree to which dye aggregation on the photoanode can be reduced, in addition to the dye source and preparation technique. For this, various co-pigments, mordants, additives, and surfactants can be integrated. Yuvapragasam *et al*. [65] synthesized TiO_2 nanorods as photoanode synthesized through the hydrothermal method using potash alum as surfactant. The grown TiO_2 nanorods had been sensitized using the flowers of *Sesbania grandiflora*, leaves of *Camellia sinensis* and roots of *Rubia tinctorum*. The results showed that the dye extract from *C. sinensis* leaves showed better results as compared to others.

Red cabbage and blue peas serve as significant sources for the extraction of anthocyanins, particularly recognized for their delphinidin pigment, a derivative of anthocyanin. Saelim *et al*. [66] prepared a photoanode was made up of TiO_2/bentonite (clay). Based on the results, red cabbage dye extract coated onto the benzoyl chloride-modified TiO_2/bentonite clay electrode showed superior results as it facilitated improved current generation in the solar cell. Similarly, Wongcharee *et al*. [67] fabricated using natural dyes extracted from rosella, blue pea and the mixture of these dye extracts. Based on results, the rosella extract has higher photosensitized performance as compared to the pea blue extract. Park *et al*. [68] also studied the effect of extracted anthocyanin from gardenia yellow flower as evidenced by the adsorption kinetics data and impedance analysis.

Additional sources of anthocyanin and its derivatives including, but not limited to, coffee, marigold, rose, lily, scoparia herb, China loropetalum, flowery knotweed, mangosteen pericarp, bithospermum and bauhinia were also investigated. Zhou *et al*. [69] studied the efficiency of DSSCs using 20 natural dyes extracted from natural materials such as flowers, leaves, fruits, traditional Chinese medicines and beverages. Among the studied material, *M. pericarp* dye extract outperformed the other dye extracts. Furthermore, it can work under acidic conditions and when blended with chlorophyll, it gives improved quality as a photosensitizer.

B. Chlorophyll dye as a photosensitizer molecule: A study on solar cell performance and comparative analysis of chlorophyll and the blend with other natural dyes

The green pigment found in plants, algae and cyanobacteria is essential for the process of photosynthesis, where these organisms convert light energy into chemical energy. Many cyclic and non-cyclic photosynthesis processes depend on chlorophyll [70]. In an electron microscope, chlorophyll appears as a series of interconnected buds, each linked by weaks bonds, forming several pockets of these small compartments [71]. These small pockets help process food by harvesting sunlight, thus turning it into essential nutrients vital for the sustenance of a plant in its life cycle. This plant pigment is also used to fabricate photosensitizer molecules in third-generation solar cells.

Chlorophyll can absorb light from red, blue and violet wavelengths and obtains its colour by reflecting the green wavelength [72]. A typical chlorophyll structure contains a porphyrin head and a phytol tail. Chlorophyll can be categorized as chlorophyll-a and chlorophyll-b depending on whether the R group on the II ring of the porphyrin head is a -CH_3 group or an -CHO group [73]. One of the reasons that makes chlorophyll a highly efficient dye, similar to anthocyanin, is the molecular structure of chlorophyll. Just like anthocyanin, several chlorophyll derivatives can be used in fabricating an efficient sensitizer for the third-generation solar cell [74].

Al-Alwani *et al*. [75] obtained the chlorophyll dye extract from pandan leaves, utilizing various solvents such as ethanol, acetonitrile, chloroform, ethyl ether and methanol to prepare the dye concentration extract. Through extensive experimentation, it was proven that the chlorophyll dye extracted using ethanol as a solvent showed better results than other dye extract solutions. A study by Chang *et al.* [76] investigated a combination of dye extracts from spinach leaves and the ipomoea flowering plant as well as the individual extracts. These were extracted using ethanol solvent and analyzed for their impact on the overall performance of solar cells. The careful research and experimental findings obtained through UV-Vis spectrometry and FESEM demonstrated that chlorophyll dye extracted from ipomoea leaves with ethanol as the solvent yielded superior results.

Chlorophyll-a and chlorophyll-b can at times be found in the peel of an avocado fruit. When compared with other dyes like anthocyanin, betalain and other flavonoids, chlorophyll-a and chlorophyll-b are bound to stand superior, one of the reasons could be its molecular structure consisting of methyl and aldehyde groups, respectively. This performance of chlorophyll pigment over the other pigments was tested in a study conducted by Hamid *et al*. [77], who used pomegranate, blueberries and avocado peel as the source to extract flavonoids, anthocyanin and chlorophyll dyes. They concluded that the ethanolic extract prepared from avocado peel showed superior overall solar cell performance as compared to blueberry and pomegranate dye extracts. This finding was associated with the chlorophyll pigment, which demonstrated a high IPCE and closely resembled the anthocyanin pigment present in pomegranate fruit. On comparing the light absorption capability of anthocyanin and chlorophyll dye, it is confirmed that the two dyes work equally efficiently due to their comparable colour and/or composition, observed as per absorption peak wavelengths in UV-Vis spectral analysis. On the contrary, the blend of these two dyes would surpass their component and other dye extracts reviewed so far.

Indigo dye is primarily recognized for its application in the textile industry, as well as in the production of inks and paints. Synthetically refurnished, this dye originates from the *Indigofera tinctoria* plant, located in tropical and subtropical regions. Various old and new technologies can be incorporated to extract dyes like chlorophyll, flavonoids, anthocyanins, *etc.* from this plant source. Rajan & Cindrella [78] evaluated the optimal method for extracting indigo dye from its natural source. Three distinct procedures were employed *viz.* simple cold extraction, Soxhlet extraction and fermentation, applied to dried and fresh indigo leaves, respectively. Among the produced extracts, the cold extraction method exhibited superior solar cell performance. This was attributed to an elevated concentration of chlorophyll pigments in the dye extract which enabled the three solar cell functioning parameters namely short-circuit current, open-circuit voltage and solar cell efficiency to be at their maximum. Furtheranalysis on this method suggested that an acidified solution of cold methanolic extract or even Soxhlet extraction led to a decrease in photovoltaic parameters as they led to the degradation of chlorophyll pigments, altering the extract's colour significantly. The data obtained from electrochemical impedance spectroscopy also showed identical results, thus signifying that out of the three methods to extract dye from the indigo plant, the simple cold extraction technique using methanol as a solvent without acidifying the solution gives superior overall solar cell performance.

Plants like copperpod (*Peltophorum pterocarpum*), also known as yellow flame and chenille plant, also known as red hot cat's tail (*Acalypha amentacea*) were also used as chlorophyll dye sources as reported by Sanjay *et al*. [79]. In their work, rod-shaped ZnO nanoparticles were synthesized to be used as the photoanode. It was concluded that the dye extract made using dye from *P. pterocarpum* and using ethanol solvent showed superior results. Similarly, Abdel-Latif *et al.* [80] generated TiO_2 nanocrystalline thin films to construct the photoanode, applying various color extracts from olive roots, Lycium shawii roots and Ziziphus leaves. It was found that the samples synthesized with bases such as NaOH and NH_3 exhibited desorption from the photoanode surface, while the dye extracts synthesized with acetic acid demonstrated strong adsorption to the photoanode. The reason is attributed to the chemical bonding occurs during the adsorption and physical or van der Waals adsorption.

C. Other natural dyes as a photosensitizer molecule

Marine culture: Sepia melanin is a pigment most commonly found in cuttlefish. These exquisite sea animals are recognized for their anatomical structure and ink production, which can vary in colour from brown to deep black. This dye has been particularly utilized in the development of third-generation solar cells due to its exceptional capacity for high absorbance and improved molecular interaction with the photoanode surface, as stated by Mbonyiryivuze *et al*. [81], who highlighted that sepia melanin dye extract has significantly emerged as a key component in solar cell technology.

Insects: Carminic acid and santalin are the pigments found in the cochineal insects and red sandalwood, respectively. Indigenous to Mexico and South America, carminic acid, a vivid red coloured pigment, serves as a natural defense mechanism in female cochineal arthropods. Red sandalwood, on the other hand, is a tropical hardwood tree native to southern India. It is quite surprising that the two dyes are made to be compared with such extreme sides of origin. One logical reason could be attributed to the reddish colour that the two dyes exhibit in common, the former being used as a defense mechanism whereas the latter serves in old Ayurveda traditional practices [82-84]. The overall solar cell performance of the third-generation solar cells was tested by coating the photo-anode with dye extracts namely carminic acid and santalin and comparing the same with LEG-4, an organic sensitizer [85]. These dyes were dissolved in a low-volatile solvent, 3-methoxy-propionitrile. Coadsorbers namely 3-phenyl propionic acid and chenodeoxycholic acid were used to prevent unwanted dye degradation. Through a meticulous examination, it was concluded that the carminic acid and santalin dye extracts would show nearly equal performance as LEG-4 so long as strong coadsorbers are mixed with them.

Polypeptide: Clathrin, a protein involved in the complicated construction of transport vesicle membranes in eukaryotic cells, is also used as a dye indirectly [86]. Trihutomo *et al*. [87] used this colourful component to make a photosensitizer. Different concentrations of this dye extract were prepared and tested for its adsorption capability onto the photoanode. The dye being a protein molecule, itself serves as an electrolyte, therefore, a higher concentration of this dye extract would lead to decreased porosity in the photoanode, in other words, it helps fill the cavity in the photoanode. The molecules present in this dye extract served as a bridge for higher electron transport to the anode. The existence of this bridge could reduce the recombination, thus increasing the overall solar cell performance.

Natural spices: In recent years, turmeric has emerged as a subject of scientific interest for its potential as an effective photosensitizer. Turmeric's inherent properties, coupled with its photoactive properties, make it a compelling candidate for fabricating third-generation solar cells [88,89]. Ruhane *et al.* [90] synthesized photosensitizer using curcumin dye extracted from dry and raw turmeric. The spectral analysis data and eZAF smart quant analysis concluded that using methanol solvent under acidic conditions, with a dye loading period of 60 min, gave superior overall solar cell performance. Besides its remarkable lightabsorbing properties, curcumin is also highly sensitive to light and its activity can change drastically under dark conditions as reported by Hossain *et al*. [91]. Under optimal conditions, the activity of curcumin dye in dark conditions demonstrated that the photovoltaic response was significantly influenced by the light sensitivity of the curcumin dye.

Lawsone dye: Lawsone dye originates from the henna plant, cultivated in North Africa, the Middle East and South Asia and is well-renowned for its reddish-brown colour. It is a primary colouring agent in the henna plant and exhibits photovoltaic properties. Ananth *et al*. [92] prepared a photosensitizer from Lawsone dye through the sol-gel technique. They found that the photosensitizer prepared from lawsone dye through sol-gel technique showed superior results, which allows the limited dye aggregation and thereby opened a path for maximum dye adsorption onto the photoanode. Jasim [93], explored the probability of the henna plant being the best source by comparing the dye extract solution made from this source with other dye extract sources namely Bahraini, pomegranate, cherries and raspberries. It was found that the blend of henna plant extract with all the other extracts showed the superior overall solar cell performance over the individual dyes. Similar studies were reported by Sathyajyoti *et al.* [94], in which photosensitizer molecules were synthesized using extracts from beetroot and henna plants. The photoanode was fabricated from TiO_2 nanopowder by the sol-gel method, and it was determined that henna plant extract applied to the TiO_2 nanopowder photoanode exhibited superior performance compared to other dye extracts.

Lupeol dye: A photosensitizer was synthesized utilizing lupeol dye extract as reported by Abodunrin *et al*. [95]. The colour extract was most effective when methanol served as the extracting solvent. The significant aspect of this work was that lupeol dye deteriorated at moderately increased temperatures and under acidic pH conditions. However, SEM studies highlighted the possibility of mango leaves as superior dye sensitizers, even if there were obstacles such as lupeol dye degradation, which resulted in a tiny band gap and low fill factor.

Betalain dye: Available from natural sources namely the areca catchu plant, a yellow-greenish flower, rich in betalain pigment, is widely cultivated in native to Southeast Asia. Najm *et al*. [96] prepared different betalain dye extracts using ethanol, acetonitrile and methanol solvents. Based on the results, the betalain dye extracted from methanol and ethanol solvents showed superior results.

Factors that makes anthocyanin dye as superior for third-generation solar cell efficiency than other dyes

Research indicates that the solar cells operate most efficiently under acidic conditions. In typical first-generation solar cells, the acidic conditions have been demonstrated to improve the interface between silicon and carbon nanotubes. This improved interfacial contact facilitates increased charge carrier mobility, creating additional conductive pathways for the carriers to exit the cell, thereby enhancing the generation of external current [97]. Although most dyes are susceptible to degradation in acidic environments, anthocyanin dye is an exception, exhibiting stability within an acidic pH range. The acidic environment is the exclusive pH range in which anthocyanin maintains stability, due to the stability of flavylium cation within this specific pH range.

In a comparative analysis of the two dye extracts, anthocyanin and chlorophyll, the UV-Vis spectral analysis reveals similar absorption wavelengths for anthocyanin and chlorophyll, suggesting that both dyes could potentially serve as effective light harvesters in DSSCs, it is important to observe that only anthocyanin performs effectively under optimal pH conditions. Chlorophyll, in contrast, degrades in the acidic pH range, whereas anthocyanin remains stable and functional within this pH environment. Thus, based on pH studies, anthocyanin outperforms chlorophyll as a dye in DSSCs. A similar comparison can be made between anthocyanin and lupeol dyes, as the latter also degrades under acidic conditions, further solidifying anthocyanin as the superior choice. The same results holds when comparing anthocyanin to alizarin dye, with anthocyanin demonstrating greater stability and efficacy under acidic conditions, thereby establishing it as the dominant option.

Another distinction between the two lies in the molecular composition of anthocyanin, which contains aromatic benzene rings that undergo resonance to attain maximal stability. This resonance gives rise to two highly stable canonical forms like the flavylium cation and the quinonoid base. Furthermore, anthocyanin is characterized by an abundance of hydroxyl and carbonyl functional groups within its structure. Chlorophyll, in contrast, consists of aromatic porphyrin rings with a divalent magnesium cation at its core. The structure is divided into a porphyrin head and a phytol tail. The porphyrin head contains a ketonic carbonyl group and an ester group, while the phytol tail features an ester group, along with various alkyl groups integrated throughout the entire molecular framework.

Both anthocyanin and betalain are dyes that function effectively within an acidic pH range. The pH range for anthocyanin typically spans from 4 to 6, while betalain operates within a slightly broader range of 3.5 to 7 [98]. To determine which dye is superior, one must consider the number of stable canonical forms in resonance [99]. Anthocyanin exhibits two stable canonical structures under acidic conditions, whereas betalain stabilizes only a single structure [100]. Another key distinction lies in the carbon framework of the two dyes as anthocyanin features a core structure consisting of a naphthalene ring fused with an aromatic ring at the β-position of naphthalene and this framework is further functionalized with several alkyl and hydroxyl groups [101]. These structural elements contribute to its stability and functionality, particularly in acidic environments.

Similarly, in other aspects, the flavylium cation carries a positive charge on the oxygen atom, an electronegative species, which enhances its basicity. Under acidic conditions, this positive charge is neutralized, leading to a structural transformation where a previously absent ketone oxygen is incorporated, thereby yielding a corresponding canonical form [102]. In contrast, the carbon framework of betalain incorporates an amino acid side chain but lacks an aromatic ring, which precludes it from participating in resonance. The ability to form multiple canonical structures is a significant factor influencing the stability of aromatic ring systems [103]. Additionally, the presence of both positive and negative charges on the carbon ring, as well as other heteroatoms within the ring structure, further contributes to the overall stability of the system [104]. Based on these considerations, it can be concluded that anthocyanin dye outperforms betalain in terms of stability and functionality.

Mechanism of surface conjugation of TiO_2 with dyes: The potential for a molecule to undergo conjugation with TiO_2 is determined by the spatial arrangement of the carbonyl and hydroxyl groups within its structure. As in anthocyanin and chlorophyll, the ketonic carbonyl group adjacent to the fourth porphyrin aromatic ring emerges as the preferred site for conjugation with titanium. In contrast, the ester group is not favoured as a conjugation site.

For anthocyanin, the most favourable sites for conjugation are those where two hydroxyl groups are positioned adjacent to one another or where a ketone and a hydroxyl group are adjacent [105]. When comparing this observation to other dyes such as carminic acid, lawsone, curcumin and santalin, this trend holds. In all cases, conjugation with the titanium metal cation predominantly occurs at adjacent sites containing either a combination of one ketone and one hydroxyl group or two hydroxyl groups [106].

In contrast, lupeol and betalain exhibit the ability to bind with titanium without requiring adjacent functional groups. In case of lupeol, a steroidal compound, the hydroxyl group located on ring A of the steroid structure is likely to serve as a linker group, facilitating the interaction with titanium through its potential to form bonds with other moieties. As for betalain, a dye derived from an amino acid side chain, the carboxyl group within its molecular framework is the most plausible site for titanium attachment, given its inherent reactivity and capacity to form coordination bonds.

Anthocyanin is most stable when its two classical forms, the flavylium cation and the quinonoid base, are in equilibrium, which usually occurs in acidic conditions. The two forms differ in hydroxyl group position and ketonic and hydroxyl group arrangement. These functional groups are the most likely conjugation sites and also balance each other dynamically. In other words, the shift from one molecular structure to another doesn't make any difference to the bonding of titanium as conjugation complex formed after the attack of titanium is found to remain in equilibrium just like the former two canonical structures of anthocyanin.

In contrast, chlorophyll does not exhibit distinct canonical structures like anthocyanin. It functions optimally under basic conditions, as acidic environments lead to the degradation of the dye. The interactions between TiO_2 surfaces and dye molecules, particularly the anthocyanin and chlorophyll dyes, can be better understood through the coordination chemistry. Titanium, particularly in its +4-oxidation state (as TiO_2 or other titanium complexes), can coordinate to various functional groups that contain lone pairs of electrons. The ketone group (-C=O) has a polar carbonyl group (C=O), where the oxygen atom has a lone pair of electrons. This lone pair can interact with metal ions like titanium, facilitating the coordination [107].

In case of chlorophyll, the carbonyl oxygen is a good ligand, since it can donate electron density to the titanium center, forming a stable complex. The ketone group in chlorophyll (especially in its porphyrin-like structure) is part of a conjugated system with alternating single and double bonds. This conjugation helps stabilize the interaction between titanium and the carbonyl group of chlorophyll. The conjugated system can also affect the electron density distribution, making the oxygen of the ketone more nucleophilic and hence more capable of binding to a titanium atom [108].

In case of anthocyanin, the ketone and hydroxyl groups can work together to bind to titanium through their ability to coordinate with titanium metal centres, particularly in TiO_2. When looking at the coordination of the hydroxyl group with titanium, the oxygen atom in the hydroxyl group bears lone pairs of electrons, which makes it capable of acting as a ligand for titanium ions. The lone pairs on the oxygen atom coordinate with the titanium center like how other oxygen-containing ligands (like carboxylates or carbonyls) bind to metal centers [109]. In addition to direct coordination, hydroxyl groups can also form hydrogen bonds with surface hydroxyl groups on TiO_2. This non-covalent interaction can help stabilize the attachment of anthocyanins to the titanium surface, assisting in the binding process. The carbonyl group (C=O) in the ketone functions similarly to the hydroxyl group but with slightly different electronic properties. The oxygen atom in the carbonyl group has lone pairs of electrons that can be donated to coordinate with the titanium metal center [110,111] and makes them an ideal choice for the synthesis of photosensitizer molecules.

Future prospects and challenges

The primary advantage of employing natural dyes over synthetic alternatives is their considerably lower toxicity, making them safer for both human health and ecological systems [112]. Their inherent biodegradability ensures that they break down naturally without posing long-term environmental risks. Furthermore, their environmental compatibility facilitates more sustainable disposal practices, contributing to a reduction in pollution and aligning with broader sustainability goals [113].

The pivotal factor influencing cell performance is the precise control of adsorption conditions, encompassing pH maintenance (favouring an acidic environment, as solar cells tend to work efficiently in this range), optimization of pH, temperature, solvent and dye concentration upkeep. Dye-sensitized solar cells utilizing natural dyes offer a sustainable alternative with a wide range of potential applications, though they also present certain challenges. The primary problem is the availability of the dye extract, which may be plentiful in certain cases but limited in others. Moreover, the efficacy of the dye extract is significantly dependent on its source, with variations in quality and effectiveness based on the material's unique origin. This suggests that only those dyes, typically derived from specific flowers or fruits known for their high performance, can be effectively utilized from the vast array of potential sources. Even if less conventional natural sources are explored, achieving the necessary optimization of the dye extract would present significant challenges, as replicating the complex processes of nature in a controlled laboratory environment is inherently difficult [114].

The second significant challenge pertains to the dye aggregation. To minimize or prevent aggregation in these dye extracts, various mordants, additives and surfactants are employed. Several studies have demonstrated that incorporating polymers and nanocomposites into the redox couple electrolyte and the electrodes can significantly reduce dye aggregation [115,116]. However, further research is needed to improve and identify more effective alternatives to these natural-based composites, as they alone may not be sufficient to fully address the issue. While synthetic mordants or additives could potentially be used to minimize aggregation, their inclusion would undermine the sustainability objectives of natural dye-sensitized solar cells (DSSCs) [117]. Another challenge is the extraction of dyes on a large scale and the production of these solar cells at that scale [118].

Conclusion

Anthocyanin, a flavonoid pigment present in the fruits, flowers and seeds of flowering plants, imparts a striking and vibrant colour to these plant structures. In the realm of energy technology, anthocyanin plays a crucial role as an efficient light harvester, owing to its exceptional light absorption properties. Derivatives of anthocyanin, notably rhein and anthraquinone derivatives, have demonstrated significant light-harvesting efficacy. Moreover, certain dye combinations have shown promising performance, with the pairing of anthocyanin and chlorophyll exhibiting particularly favourable results. In contrast, blends of anthocyanin with betalain, anthocyanin with carminic acid and anthocyanin with carotenoids have yielded sub-optimal outcomes. When employed either in isolation or in conjunction with other dyes, particularly chlorophyll, anthocyanin proves to be an exceptional photosensitizer, particularly when extracted using ethanol as a solvent and under acidic pH conditions. This specific pH range is crucial for maintaining the equilibrium between the two stable forms of anthocyanin *viz.* the flavylium cation and the quinonoid base. The performance of the photoanode can be improved by adding benzoyl chloride during the fabrication of the metal oxide electrode, which has demonstrated effectiveness. This reagent is recognized for diminishing the porosity of the photoanode, thus enhancing its dye adsorption capacity. Moreover, the performance of the photoanode is significantly enhanced when the spin coating technique is employed, particularly when the photoanode is constructed from a nanostructured thin film or nanopowder. Furthermore, the electrolyte systems comprising host polymer composites, gel-polymer electrolytes and electrolytes derived from coupling polymer composites, demonstrated superior performance compared to conventional redox couple electrolytes.

ACKNOWLEDGEMENTS

The author extend their deepest gratitude to Department of Chemistry, Jai Hind College (Autonomous) Mumbai for their undying encouragement, advice and assistanceship.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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