



Recent advances in anthocyanin dyes extracted from plants for dye sensitized solar cell

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Abstract

Dye-sensitized solar cells (DSSCs) are under extensive research works due to their appealing features such as low production costs. The production costs and energy conversion efficiency of DSSCs is strongly influenced by the types of dyes used to harvest photons. Natural dyes extracted from different sources are emerged as a potential candidates to synthetic photosensitizers due to their merit properties including low cost, complete biodegradability, availability and less environmental concern. In order to improve the energy conversion efficiency of natural photosensitizers, blending of different dyes, co-pigmentation of dyes, acidifying of dyes and other approaches have been conducted by researchers, resulting in appreciable performance. This paper reviews the factors affecting the stability of anthocyanin pigments and also the solvents needed for efficient extraction of anthocyanins. Moreover, the potential application of anthocyanin dyes as photosensitizers for DSSC along with the work done over the years is covered.

Keywords Dye sensitized solar cell · Sensitizer · Anthocyanin dyes · Extraction · Purification · Stability of dye

Introduction

Dye-sensitized solar cells (DSSCs) got attentions of researchers as a promising low-cost solar cell technology since their discovery in 1991 [1–6] due to their simple preparation procedure, eco-friendly [7], good performance under diffuse light conditions, reasonably good power conversion efficiency [8, 9], colorful natures, and low production cost [11–12]. DSSCs are based on the sensitizing nanocrystalline metal oxide films to visible light through the adsorption of regenerative dyes [13]. The first manufactured DSSC was found to absorb visible light up to about 800 nm and the energy conversion efficiency reached 7.1% [15–16]. Following its discovery, research on the DSSCs has made remarkable progress and, by using nanostructured semiconductor electrodes, the conversion efficiency was boosted to 11.4%

in 2001 [18–19]. Recent findings have found that perovskite sensitized solar cells have achieved an efficiency of approximately 15% in power conversion 21.60% (certified at 21.52% by Newport) [20]. In a DSSC, unlike conventional solar cells, semiconductors and electrolytes are used to transport electrons and holes respectively, and because of this, recombination chances in the cell are low. Upon illumination, the dye molecule adsorbed on TiO₂ films absorbs photons of wavelength corresponding to the energy difference between its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [8, 21]. Numerous dyes extracted from different inorganic and organic sources are utilized as sensitizers [13, 14, 22]. Due to their advantages such as high efficiency, excellent stability, wide absorption bands in the visible region, excellent electron injection and efficient metal-to-ligand charge transfer, ruthenium-based complexes are considered to be the most efficient sensitizers [24–25]. Despite their advantages, Ru-based colorants are upset by their preparation procedures and chromatographic methods that take time [26]. Moreover, the use of expensive ruthenium metals from relatively scarce natural resources is a relatively heavy environmental burden [28–29].

Recently, organic dyes synthesized from various natural sources are intensively investigated due to their large

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absorption coefficients, high light-harvesting efficiency, biodegradability, low production cost, and easily processability. Natural dyes extracted from fruits, flowers, seeds, roots or leaves of plants have been employed as photosensitizers for DSSC [29, 30]. Anthocyanins, found in strongly colored fruits as well as flowers and leaves of plants, are the most extensively investigated photosensitizers [14, 29, 31]. The strongly colored extracts of natural sources have been confirmed to have high concentrations of anthocyanins, mainly cyanidin and its derivatives, such as cyanidin-3-glucoside and cyanidin-3, 5-diglucoside.

In the following sections, the anthocyanin extraction temperatures, solvents and pH values as well as light and co-pigmentation effects on pigment stability have been reviewed for efficient anthocyanin dye extraction. In view of this in extracting anthocyanin pigments from plant parts, suitable extractions and storage parameters are expected to be maintained especially for dye sensitized solar cell application. This paper gives an overall glimpse of accomplishments recorded over the years in this exciting area of sensitized solar cells based on anthocyanin dyes along with the parts of plants used as sources of anthocyanin pigments.

Anthocyanin dyes

Anthocyanins, belonging to the flavonoid class, are natural pigments used mainly as natural colorants [12, 32]. The genetic and environmental factors influence the concentration as well as the composition of anthocyanin pigments found in fruits and vegetables [33]. These pigments are dominantly responsible for the different visible colors including shiny orange, pink, red, violet and blue colors in different parts of plants and fruits, which explains their name, in Greek, anthos means flower and kyanose means blue [35–36]. The anthocyanidins are the basic structures of the anthocyanins [29, 37]. As could be seen in Fig. 1, anthocyanidins (or aglycons) are basically composed of an aromatic ring (A) bonded to a heterocyclic ring (C) that contains oxygen, and these also bonded by a carbon–carbon bond to a second aromatic ring (B) [38]. Anthocyanidins are anthocyanins, when they are found in their glycoside form (bonded to a sugar moiety) [37, 39]. According to Pauling, who explained the color displayed by anthocyanin initially, the resonant structure of the flavylium ion is responsible for color intensity [40]. There are different varieties of anthocyanins spread in nature.

Anthocyanins differ based on the number of hydroxylated groups, the number of sugars bonded to their structure, the aliphatic or aromatic acids bonded to sugar in the molecule, and the position of these bonds [41, 42]. It is estimated that there are more than 500 different anthocyanins [43] and 23 anthocyanidins [44] based on several reviews to date,

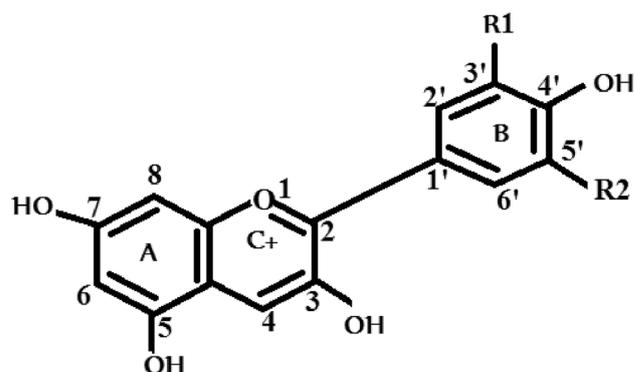


Fig. 1 General structure of anthocyanin: **a** aromatic hydrocarbon, **b** aromatic hydrocarbon, heterocyclic ring (c)

of which only six are the most common in vascular plants, pelargonidin, peonidin, cyanidin, malvidin, petunidin and delphinidin [45]. The most commonly found anthocyanins in nature are the glycoside derivatives of cyanidin, delphinidin, and pelargonidin [46]. Anthocyanins are replaced in cactus, beets, and amaranth by betalain pigment [37].

Anthocyanin pigments are assembled in plants from two different streams of chemical raw materials in the cell: both from the photosynthesis-derived C2 unit acetate (or acetic acid) [37]. One stream involves the pathway of shikimic acid to produce phenylalanine amino acid [37]. The other stream (the pathway of acetic acid) produces three molecules of malonyl-coenzyme A, a unit of C3 [37]. The enzyme chalcone synthase (CHS), which forms an intermediate chalcone via a polyketide folding mechanism commonly found in plants, meets these streams and is coupled together [37]. The chalcone is then isomerized to the prototype pigment naringenin by the enzyme chalcone isomerase (CHI), which is subsequently oxidized to yield the final anthocyanins by enzymes such as flavonoid hydroxylase and coupled with sugar molecules by enzymes such as UDP-O-glucosyl transferase [37]. Therefore, synthesizing these pigments requires more than five enzymes, each working in concert [37].

Stability of anthocyanins

Anthocyanins are known to be unstable under different environmental conditions as a natural water-soluble pigment [48]. Anthocyanin stability may be influenced by various factors. These factors may affect anthocyanin's stability either chemically or physically through structural modifications with hydroxyl, methoxyl, glycosyl and acyl groups, or through environmental factors such as anthocyanin structure, pH, temperature, light, oxygen, and a number of other factors, resulting in color change and degradation [39, 49]. The isolated anthocyanins are highly unstable and very susceptible to degradation [50].

Effect of pH on the stability and color of anthocyanin

pH value potentially affects the stability and color of anthocyanin pigments. The most notable anthocyanin phenomenon in a pH gradient is the color change caused by changing chemical forms. Structural transformations of anthocyanins occur with changes in pH which have a dramatic effect on color [51], i.e. anthocyanins can be found in different chemical forms depending on the solution's pH [53–55]. At a pH below 3, anthocyanins predominantly exist in the form of red flavylium cation, carrying the positive charge of oxygen [51]. The quinonoidal blue species predominate when pH values rise between 2 and 4, rapid deprotonation occurs in groups of oxygen and skeleton hydroxyl to form quinonoidal bases. There are colorless species as the pH values rise between 5 and 7; a carbinol pseudo base and a yellowish chalcone. The reason for this is due to the hydration reaction at C-2, producing the pseudo-base of colorless carbinol and the light yellow chalcones.

Depending on their substituent groups, the anthocyanin pigments are degraded if the solution's pH values are greater than 7. The four structural forms of anthocyanins, namely flavylium cation, anhydrous quinoid base, colorless carbinol base and pale yellow chalcone, coexist when the pH value ranges from 4 to 6. The red flavylium ion under more acidic conditions is the predominant species [56]. Additional hydroxyl or methoxyl groups and ring B substituents affect anthocyanidin stability, reducing aglycone stability in neutral media [53].

On the other hand, because of the sugar molecules preventing the degradation of unstable intermediaries into phenolic acid and aldehyde compounds, monoglycosides and mostly diglycoside derivatives are more stable under neutral pH conditions [53]. Research on stability and color variation with pH concludes that changes in anthocyanin color are more significant due to their instability in the alkaline region [57]. Generally, only in extremely acidic conditions, flavylium salts are stable. These salts are missing the proton at higher pH and reworked into the quinoid base, which is associated with unstable pigment, directly binding to water and forming colorless compound called chromenol. The more intense and stable the color is for many anthocyanins, the lower the pH. As the pH increases, at the expense of stability, the anthocyanins are missing intensity and falling bluer [36, 58].

Effect of temperature on stability of anthocyanin

Since anthocyanins are thermally susceptible compounds, temperature affects the anthocyanin molecular structure [59]. The degree of anthocyanin destruction is increasing with an increase in temperature. The rapid destruction of anthocyanin at higher temperatures may be caused by

hydrolyzing the 3-glycoside structure, which has a protective effect in unstable anthocyanin. Generally, heat introduced in processing and storage plays a major role in accelerating chalcones transformation, and eventually decomposing anthocyanins into benzoic acid derivatives, resulting in color loss. Researchers have studied the effect of temperature on anthocyanin stability and have shown that pigment destruction is significantly accelerated by an increase in storage temperature [60].

Effect of light on the stability of anthocyanin

Light also affects the stability of anthocyanin pigments [59, 61]. Researchers studied the impact of light on anthocyanin stability in grape juice and demonstrated that light exposure of anthocyanin pigments accelerates its destruction [62]. Their experiments showed that nearly 30% of pigments were destroyed after placing the anthocyanin containing juice samples in dark at 20 °C for 135 days, but placing the same samples at the same temperature and time in the presence of light destroyed over 50% of total pigments.

Co-pigmentation on anthocyanin color enhancement

The co-pigmentation reactions between anthocyanin pigments and other compounds including metallic ions enhances and stabilizes the color of anthocyanins through blocking the hydration of chromophores in the pigments [63]. Depending up on the acidic conditions of the solutions, the co-pigments stabilize anthocyanin pigments via either a hyperchromic effect or a bathochromic shift in the absorption spectra (UV–Vis region) when mixed with anthocyanins [51]. The co-pigments could bind with the electron deficient structural forms of anthocyanins through their delocalized π -electron systems [64]. Different compounds including flavonoids, alkaloids, amino acids, organic acids, nucleotides, polysaccharides, metallic ions, and anthocyanins themselves (self-association) are investigated as co-pigments by different research groups [51, 64]. Researchers have stated that the co-pigmentation reactions required to strengthen and shift the color of anthocyanin pigments could occur either through inter-molecular or intra-molecular interactions depending upon the nature of the co-pigments [65]. According to the findings being reported, the anthocyanin dyes and co-pigments are interacting with a π – π interactions through a vertical stacking between the planar structure of anthocyanin chromophores and the co-pigment molecules in the inter-molecular interaction reactions whereas the anthocyanin dyes and the co-pigments are covalently linked in a more effective way in addition to a π – π interactions in an intra-molecular co-pigmentation processes [64]. Both the interaction systems are crucial to protect the nucleophilic

attack of water at position 2 of the flavylum nucleus and thus preventing the formation of carbinol pseudobase.

Extraction of anthocyanins

Extraction is a very important step in isolating, identifying and using plant pigments such as anthocyanin compounds and no single, standard method of extraction is available. Fruits, vegetables, flowers, and leaves may be ground, dried, or lyophilized, and some fresh plants may be soaked to extract phenolic compounds with subsequent extraction of solvent [66]. These methodologies of extraction result in the co-extraction of non-phenolic substances such as sugars, organic acids and proteins, requiring subsequent purification processes such as the extraction of solid phase [67].

Chemical/conventional/extraction

Since anthocyanins are polar molecules, aqueous mixtures of ethanol, methanol, acetone, water and their water mixtures with or without acid are the most commonly used solvents in extractions [68, 69]. Solvent polarity plays a key role in enhancing solubility of phenols [68]. Solvents with high polarity such as water or low polarity such as hexane are unable to efficiently extract anthocyanins [70]. Because anthocyanins are not stable in neutral or alkaline solutions, acidic aqueous solvents were used as extraction solvents to disrupt cell membranes while facilitating anthocyanin solubilization [71]. Compared to other extractants for the extraction of anthocyanin pigments, acidified methanol or ethanol is the most effective extractant [70]. The effect of acidic conditions on the extraction processes of anthocyanin pigments was experimented by different research groups using different acids [73–77]. Researchers confirmed that methanol as an extracting solvents of anthocyanin pigments from grape pomace was more efficient than ethanol and water when used separately [78]. Additionally, acidified methanol as an extracting solvent of anthocyanin dyes was mentioned to be twice more efficient than the aqueous acetone solvents [79]. Even though acidification of the solvents for efficient anthocyanin extraction is vital, it may potentially destruct the anthocyanin pigments due to acid concentrations. In order to avoid such destructions, weak organic acids and strong acids with low concentrations such as trifluoroacetic acid (0.5–3.0%) and hydrochloric acid (<1.0%), are strongly recommended [71, 80, 81].

High temperatures are reported to improve extraction efficiency due to increased diffusion rate and analyte solubility in solvents [82, 83]. However, high temperatures of extraction and concentration can simultaneously increase the rate of degradation of anthocyanin. Typically, conventional anthocyanin extraction and concentration is performed

at temperatures between 20 and 50 °C [71, 84]. Rapid anthocyanin and color degradation were shown at temperatures > 70 °C [85]. The anthocyanin degradation rate depends on time and temperature. High-temperature, short-term extraction conditions and processing treatments have therefore been successfully used to delay fruit degradation of anthocyanin [86].

Physical/modern/extraction

Several new extraction techniques such as ultrasound-assisted extraction, microwave-assisted extraction, supercritical fluid extraction and high hydrostatic pressure extraction have been developed in recent years to extract phytochemicals from plants as alternatives to conventional extraction that can take long extraction times.

Purification of anthocyanins

Anthocyanin extraction is non-selective and normally results in a mixture of pigments and impurities due to the co-extraction of non-phenolic substances such as sugars, organic acids and proteins (R). Therefore, purification becomes one of the most important stages in the recovery of high purity anthocyanins after the extraction process. A wide range of techniques have been investigated, ranging from solid-phase (SPE) and liquid–liquid (LLE) extractions to the use of sophisticated chromatographic techniques such as counter-current chromatography [87, 88], medium-pressure liquid chromatography (MPLC) and HPLC [89]. HPLC with UV–Vis or photodiode array (PDA) detectors is the most common method used to separate anthocyanin [67].

Anthocyanin dyes as photosensitizers in dye sensitized solar cells

Dye molecules are expected to meet certain criteria that will be used in DSSCs as an efficient photosensitizer as the sensitizer is a very critical part of the DSSC. Ideally, photons in all visible and near-IR regions should be intensively absorbed. The photosensitizer should also be strongly adsorbed through the attachment groups such as carboxylates, sulfonates, carbonyl, hydroxyl, phosphates and so on through chemisorption to the wide band gap semiconductor surface. The dye molecules' attachment groups ensure that when the oxide film is exposed to a dye solution, it spontaneously assembles as a molecular layer. For efficient electron injection into the semiconductor, the excited state energy level (LUMO) of the dye molecule should be higher than that of the semiconductor conductive band edge. The oxidized state of the dye must be more positive in potential than

that of the redox electrolyte in order to effectively regenerate the dye. In addition, the dye should be regenerated quickly by the mediator layer to avoid processes of electron recombination and should not form aggregates, but should be chemically stable, thermally stable and photostable as well. Many different compounds were investigated for the sensitization of semiconductors, including synthetic and natural dyes. Transition metal complexes have been the best among the photosensitizers investigated so far [90]. Ruthenium-complex sensitizers, which possess many desirable optical and electronic properties such as a wide absorption spectrum in visible and near IR regions, suitable excited and ground-state energy levels and good chemical stability [16, 91, 92], have a maximum conversion efficiency of more than 11%. Compared to other dyes, these sensitizers achieved the highest energy conversion efficiency which might be due to their intrinsic properties such as their optical and electronic properties. On the other hand, organic dyes such as coumarin dyes, indoline dyes, triarylamine dyes and others, which are cheaper and more ecofriendly than transition metal complexes, are well designed to fabricate photosensitizers [94–96] (Fig. 2).

Alternatively, natural dyes extracted from plant fruits, vegetables, seeds, flowers and leaves have become increasingly important in recent days, exhibiting different colors and containing several pigments that can be easily extracted and used as sensitizers in DSSC [97]. The advantages of these natural colorants as DSSC photosensitizers are due to their high coefficients of absorption in the visible region, relative abundance, ease of preparation, complete

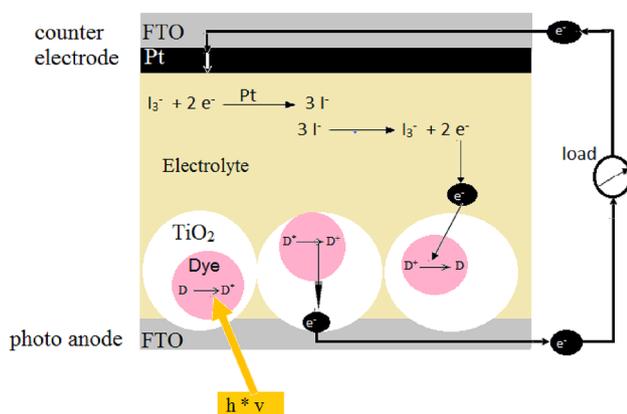
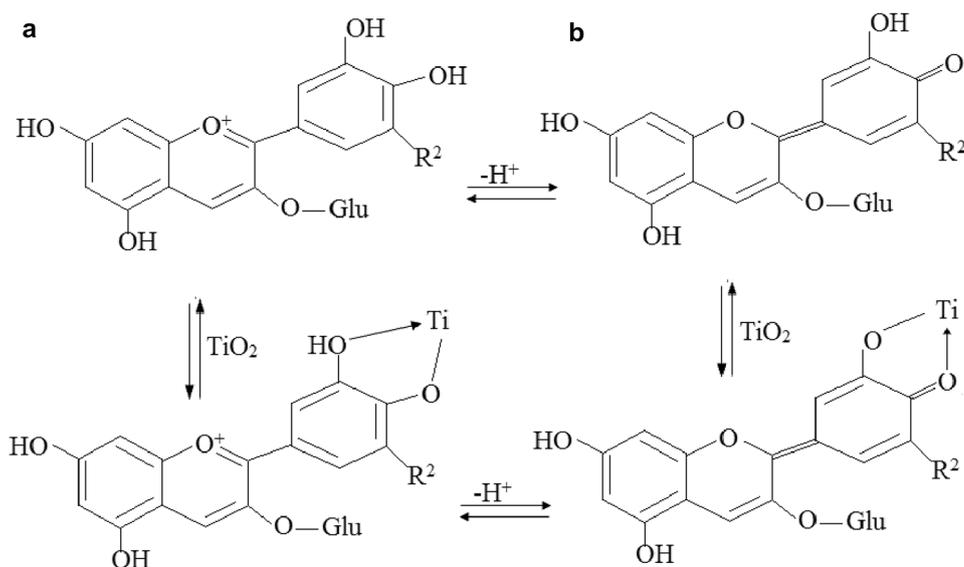


Fig. 2 Schematic illustration of a dye sensitized solar cell. The photo-anode and counter-electrode are based on glass coated with fluorine-doped tin oxide (FTO). The illumination ($h\nu$) of a dye sensitized solar cell initiates a cascade of reactions leading to an electrical current. Photons excite the ground-state (D) dye molecule to its electronically excited (D^*) state. The electronically excited dye molecule then injects an electron (e^-) into the TiO_2 semiconductor conductive band and becomes an oxidized dye (D^+) which will be reduced by iodide (I^-) in the electrolyte

biodegradation and eco-friendly [98, 99]. Most importantly, the natural dye-based DSSC synthesis route is cost-effective. These plant pigments have an electronic structure that interacts with sunlight and alters the wavelengths that the plant tissue either transmits or reflects. This process leads to the occurrence of plant pigmentation and each pigment is described from the maximum absorption wavelength (λ_{max}) and human perceived color [100]. Natural pigments include chlorophyll, carotenoid, betalines and anthocyanin, compared to synthetic colors, are relatively easy to extract from natural products [101].

Anthocyanins, which are responsible for various colorations of plants, are most extensively investigated as photosensitizers due to their excellent ability to chelate to TiO_2 and the ability to convert light energy to electrical energy. Anthocyanin pigment is a well-known visible-light trapper that undergoes charge excitation and a charge-transfer process with a metal oxide semiconductor like TiO_2 after complexation. The anthocyanin charging-transfer mechanism is primarily ligand-centric. This is due to the presence of TiO_2 complexing O and OH sites. It is generally accepted that the anthocyanins' chemical adsorption is reported as the result of their alcohol-bound protons condensing with the hydroxyl groups present on the thin films of the TiO_2 nanostructured surface, as shown in Fig. 3. A chelating contribution to the Ti (IV) ions can also enhance the attachment. There is an increased charge density of anthocyanin molecule after complexation with Ti^{4+} ion and thus allows for electronic coupling for charge injection. The chemical attachment affects the energy levels of the highest occupied molecular level (HOMO) and the dye molecule's lowest unoccupied molecular level (LUMO), which eventually affects the band gap of these materials and results in a shift in the absorption band of the absorption spectrum. In the visible region of the spectrum, anthocyanin compounds exhibit a broad band absorption with the maximum absorption spectrum ranging from 450 to 580 nm depending on the plant or solvent used, ascribed to charging transitions [102]. The visible band is assigned to a $\pi-\pi^*$ charge transfer transition, resulting in a shift of the electronic load density from the chromenium portion to the anthocyanin molecule's catechol end. The anthocyanin absorption band is also sensitive to pH, showing the acidic red flavylium form and the purple deprotonated quinonoidal form as pH increases. Adsorption from raw acidic aqueous dye extracts was found to give more intensely colored photoanodes than those obtained from non-acidified dye solutions in the presence of 0.1 M HCl. This is most likely due to the predominance of (protonated) flavylium cations, which is initially able to coordinate more effectively with Ti^{4+} sites. Compared to the absorption spectrum of the free dye solution, its absorption band is extended and the maximum absorption peak will be shifted to longer or shorter wavelength when chemically adsorbed

Fig. 3 Schematic representation of attachment of cyanidine-3-glucoside (anthocyanin) onto TiO₂ **a** flavylium, **b** quinonoidal form and upon adsorption onto TiO₂ the equilibrium between the forms is believed to shift towards the quinonoidal form, consistent with the purple coloration of the electrodes



on a semiconductor surface such as TiO₂ due to complexation with metal ions. This might be due to the fact that the metal ions compete with the protons that displace them and move flavylium-quinonoidal equilibrium to the quinonoidal or flavylium shape.

The anthocyanin pigments in natural sources could be found in different chemical forms, i.e., quinonoidal base, cation of flavylium, carbinol or pseudobase, and chalcone and also its chemical structure could be transformed depending upon the extraction conditions. Principally, anthocyanins exist as red-colored flavylium cations, while quinonoidal base is blue. The anthocyanin dyes exist as colorless pigment in Carbinol form but in chalcone form, they exhibit pale yellow color. The balance between the quinonoidal bases and carbinol must be achieved through the cation of flavylium. The flavylium cation is therefore the stable form of anthocyanin, and the flavylium form oxonium ion is said to assist in photon absorption in the visible range.

Since plants may have either one type of anthocyanin (dianthus, petunia) or mixtures of different anthocyanins (pink, tulip, grapes, etc.), different plant anthocyanins give different sensitizing performance. It must also be considered that it is important to achieve efficient sensitization to the extraction conditions of natural dyes. The mixture of anthocyanin pigments with different absorption characteristics would give synergistic effect to the sensitizing pigments, meaning the pigment absorption spectrum combined to increase light absorption in different regions as different colors promote light harvesting in different wavelengths and have particular quantity injection of electrons leading to an increase in photocurrent and photovoltage. Researchers evaluated the synergetic effect of sensitizers by producing cells in a ratio of 1:1:1 using raspberry, hibiscus, lemon leaves chlorophyll and their mixtures [29]. DSSC sensitized

with the dyes mixture (raspberry, hibiscus, chlorophyll) was reported to have shown the highest solar energy conversion efficiency value compared to the rest of the prepared solar cells, yielding 3.04% efficiency.

As explained above, anthocyanin pigment acidification causes the anthocyanins to undergo transformation from one form to the other—to lose their color. It therefore affects the performance of DSSCs based on anthocyanin. DSSC based on anthocyanin was manufactured using anthocyanin pigments extracted from *Melastoma malabathricum*'s flower petals and the effect of anthocyanin acidification on the performance of the built DSSC was investigated [103]. It has been reported that the performance of the built DSSC has been further enhanced by anthocyanin pigment acidification. With acidified anthocyanin as the sensitizer in DSSCs, the overall efficiency was increased from 0.64% to 0.84% with short-circuit current density (J_{sc}) ranging from 2.76 mA/cm² to 3.39 mA/cm² and open-circuit voltage (V_{oc}) from 0.394 to 0.41 V. The absorption peak that emerged when HCl was added to the anthocyanin resulted in a new level of HOMO formed near the middle of the TiO₂ band gap facilitating more efficient electron transfer to the TiO₂ conductive band, which could be due to DSSC's increased efficiency using acidified anthocyanin pigment.

The photoanode sintering process also affects DSSC performance as the sintering process plays a significant role in enhancing charge collection efficiency by promoting both faster transportation of electron and slower recombination of charge. Electron diffusion through the semiconductor such as TiO₂ film depends on the degree of crystallinity [104, 105], phase composition [105, 106] and particle connectivity [106, 107]. Higher crystallinity and improved particle connectivity result in faster electron diffusion through the photoanode resulting in higher current density in the

cell. Semiconducting film porosity is known to be related to the duration and temperature of sintering, which affects the density of the photocurrent and the amount of adsorbed dye. For the process of photoanode calcination, the gradual sintering and continuous sintering processes are used. In this regard, the gradual sintering process results in better conversion efficiency than that of continuous sintering since the thin film layer made in the step-wise sintering process is more homogeneous than in the rapid and continuous sintering process, leading to the cracking of films that could be easily peeled from the TCO substratum along with the anthocyanin pigment.

Studies on the effect of sintering process have been conducted by fabricating DSSC based on FTO substrate covered with a TiO₂ film that was sintered in a furnace by raising the temperature gradually from 60 to 180 °C. The sample was stabilized at 180 °C for 10 min. and then the temperature raised from 180 to 320 °C. The sample also stabilized at 320 °C for 10 min and finally raised the temperature to 450 °C for another 10 min, gradual sintering process [108]. On the other hand, another DSSC sample made from FTO substratum covered with TiO₂ film was continuously sintered for 30 min from 60 to 450 °C. Following the cooling and immersion with the same procedure of the gradual and continuous sintered electrodes in the anthocyanin dye solution extracted from rapa and allium cepa, it was reported that the gradually sintered cells for both dyes show a significant improvement in the density and efficiency of the current short circuit compared to the continuously sintered ones. The open-circuit current density (J_{sc}) increases 2.39 to 2.69 mA/cm² for allium cepa sensitized DSSCs and 2.88 to 3.43 mA/cm² for rapa sensitized. In addition, the efficiency of these cells increased due to gradual sintering from 0.70 to 0.75% for allium cepa dye and from 0.82 to 0.99% for rapa.

In general, natural dyes such as anthocyanins tested so far suffer from low V_{oc} values, which may be due to possible efficient recombination pathways of electron/dye cation and the environment of acid dye adsorption. In fact, to obtain a satisfactory dye coverage of the semiconductor surface and H⁺, an acidic environment is necessary to be potential determining ions for TiO₂ resulting in a positive shift of the semiconductor Fermi level and limiting the maximum photovoltage that the cells could deliver.

Researchers manufactured DSSCs using anthocyanin pigments extracted from sour and sweet grenade [110] and reported a short-circuit current density (J_{sc}) of 0.50 mA/cm² and 0.61 mA/cm², an open-circuit voltage (V_{oc}) of 2.97 V and 4.60 V, a filling factor (FF) of 0.49 and 0.55 and a power conversion efficiency of 0.73% and 1.50% respectively for sour and sweet grenade. It has been reported that the sweet grenade has the best effect of photosensitization. This was attributed to the improved interaction between the anthocyanin molecule carbonyl and hydroxyl groups present in

the sweet pomegranate extract with the porous TiO₂ film surface.

The efficiency of DSSC sensitized with anthocyanin pigments extracted from Hibiscus sabdariffa and Ribes nigra was 3.16% and 2.97% respectively [120].

DSSCs manufactured using anthocyanin dye solutions extracted from Melastoma malabathricum leaves and flower petals showed better performance of anthocyanin pigment extracted from the flower petals, resulting in a remarkable short-circuit current density (J_{sc}) of 2.76 mA/cm², 0.394 V open-circuit voltage (V_{oc}) and 0.64% efficiency [103].

Grape pigment coloring (malvidin-3-fructoside) [121] was used as a sensitizer in DSSC, resulting in short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}) and fill factor (FF) of 4.06 mA/cm², 0.43 V and 0.33 respectively with a conversion efficiency of 0.55%.

Natural dye-based DSSCs were manufactured using anthocyanin pigments isolated from raspberries, shamberrries, grapes, hibiscus green leaves and chlorophyll pigment extracted from young green lemon leaves, resulting in short-circuit current density (J_{sc}) ranging from 0.017 to 0.269 mA/cm², open-circuit voltage (V_{oc}) from 0.255 V to 0.429 V, fill factor (FF) from 0.541 to 0.648, and conversion efficiency from 0.04 to 1.50% [29]. Raspberries have been reported to have the best effect of photosensitization among all these sensitizers. This was attributed to the better interaction between the carbonyl and hydroxyl groups of anthocyanin molecule present in the raspberry extract with the surface of TiO₂ porous film and also a higher concentration of anthocyanin it contains.

Researchers constructed DSSCs using anthocyanin pigments extracted from more than 35 native plants and evaluated its performance [122]. Among these plants, Melastoma malabathricum (fruit pulp), Hibiscus rosa-sinensis (flower), and Codiaeum variegatum (leaves) showed the highest absorption peaks and were selected to determine anthocyanin content and stability based on the impacts of storage temperature and also to be employed as natural photosensitizers. Of all these sensitizers, the highest efficiency around 1.16% was obtained from DSSC sensitized with M. malabathricum fruit pulp extract with the open circuit voltage (V_{oc} = 0.383 V), short circuit current density (J_{sc} = 6.17 mA/cm²), and fill factor (FF = 0.44). These results could be attributed to the highest anthocyanin content (8.43 mg/L) compared to others and the carbonyl and hydroxyl groups of anthocyanin molecules present that favors photoelectric conversion as it allows effective binding with the surface of TiO₂ porous film. The impact of storage temperature on the stability of extracted anthocyanin pigments was also studied by storing the extracts at three different storage temperatures, namely, 4 °C, -20 °C, and 25 °C, evaluated by half-life periods. It was reported that the storage temperature had a strong influence on the degradation of anthocyanins

extracted from all three plants. The result showed that significantly greater stability of anthocyanins in all three species was achieved when stored at 4 °C while storage at 25 °C resulted in much faster degradation of anthocyanin. They also pointed out that frozen anthocyanin extracts maintained at –20 °C also ensured a good stability over a period of three months though the best storage temperature was still 4 °C.

DSSCs were fabricated using dye solutions extracted from dry seeds of ten different plants [108]. Among these extracts, allium cepa (Onion) extract was reported to have the best performance resulted in a short circuit current density of 2.6 mA/cm², open circuit voltage of 0.635 V and efficiency of 0.875%. Furthermore, the rapa and lepidium sativum extracts showed interesting performance respectively, with short-circuit current density of 2.9 mA/cm² and 1.72 mA/cm², open circuit voltage of 0.63 V and 0.65 V and conversion efficiency of 0.86% and 0.575% respectively using TiO₂ as a wide band gap semiconductor. These results were compared with DSSCs sensitized with allium cepa (Onion), rapa and lepidium sativum extracts using ZnO as wide band gap semiconductor and the value for the conversion efficiencies declined to 0.19%, 0.035% and 0.07% for allium cepa (Onion), rapa and lepidium sativum extracts respectively, which might be attributed to TiO₂ could effectively retard charge recombination and achieve longer electron lifetime than ZnO; as a result, the DSSCs composed of TiO₂ exhibit higher performance than those of ZnO.

Researchers constructed natural dye based DSSCs by extracting the natural dyes from rosella, blue pea flowers and a mixture of these extracts and studied the synergetic effect of the mixture of rosella and blue pea flower dyes on the photovoltaic performance. It was confirmed that the mixed extract does not show synergetic light absorption and photosensitization effect when compared to the individual extracts. The power conversion efficiency of DSSCs sensitized with dyes extracted from rosella, blue pea flowers and a mixture of these extracts was reported to be 0.37%, 0.05% and 0.15%, respectively. The power conversion efficiency of rosella dye sensitized cells was improved from 0.37 to 0.7% when the pH value and extraction temperature decreased [111].

The photovoltaic performance of natural dye based DSSCs was investigated using anthocyanin pigments extracted from jaboticaba and calafate. It was reported that DSSCs sensitized with jaboticaba extracts exhibited a short circuit current density of 9.0 mA/cm², an open circuit voltage of 0.59 V, maximum power of 1.9 mW/cm² and a fill factor of 0.54. while that of calafate extracts exhibited a short circuit current density of 6.2 mA/cm², an open circuit voltage of 0.47 V, maximum power of 1.1 mW/cm² and fill factor of 0.36 [123].

The photovoltaic performance of anthocyanin sensitized DSSCs was studied by employing gold nanoparticles as a

Schottky barrier on a TiO₂ electrode with the aqueous electrolyte of Ce^{4+/3+} system. According to the research work being conducted, promising efficiency based on natural dye in water based DSSCs was achieved, resulting in 1.49% power conversion efficiency [124].

Natural pigments were extracted from tropical flowers and their performance as photosensitizers in a DSSC was investigated. It was observed that the prepared cells resulted in 1.1 to 5.4 mA cm⁻², 0.39 to 0.41 V, 0.53 to 0.64 and 0.20% to 1.14% of short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (η) respectively. The highest power conversion was achieved with the magenta-colored *H. surattensis* extracts due to high content of delphinidin-derived anthocyanins and flavonol-glycosides. Both *Sesbania grandiflora* and *Hibiscus rosa sinensis* extracts possess a variable amount of flavonol-glycosides, achieving a power conversion efficiency of 1.02%. [125].

Anthocyanin dyes were extracted from black rice, capsicum, *Erythrina variegata* flower and *Rosa xanthina* and their photovoltaic performance was studied in a DSSC. The prepared cells exhibited 1.142 mA to 0.225 mA, 0.551 V to 0.412 V, 0.52 to 0.63, and 58 μ W to 327 μ W of short circuit current (I_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and maximum power respectively. It was confirmed that the black rice extract performed the best photosensitized effect as compared to other extracts, which could be attributed to the better interaction between the carbonyl and hydroxyl groups of anthocyanin molecule on black rice extract and the surface of TiO₂ porous film.

A photo electrochemical cell was fabricated using anthocyanin dyes extracted from blackberries and achieved power conversion efficiency of 0.56%, open-circuit voltages (V_{oc}) of 0.4–0.5 V and short-circuit photocurrents density (J_{sc}) of 1.5–2.2 mA/cm² [126].

Ahmed M. Ammar et al. prepared natural dye based DSSCs and investigated their performance as well as the degradation in the power conversion efficiencies over a week. The onion peels and red cabbage anthocyanin pigment based DSSCs resulted in 0.24 mA cm⁻² open circuit current density (J_{sc}), 0.48 V open circuit voltage (V_{oc}), 46.631% fill factor (FF), 0.064% power conversion efficiency (η) and 0.21 mA cm⁻² open circuit current density (J_{sc}), 0.51 V open circuit voltage (V_{oc}), 46.610% fill factor (FF), 0.060% power conversion efficiency (η) respectively. The power conversion efficiencies of the prepared DSSCs were observed to degrade from day to day in a week. The deterioration of the PV performance was proposed mainly due to leakage or solvent evaporation of the liquid electrolyte and also due to the detachment of the dye from the TiO₂ surface. Additionally, the investigators studied the effect of the TiO₂ mesoporous layers on the efficiency of DSSC by varying TiO₂ concentration in the mesoporous

layer from 4 to 10%. They confirmed that the efficiency of DSSC increases with increasing the concentration of TiO₂ mesoporous layers. The short-circuit current and open-circuit voltage of 10% TiO₂ were much greater than the other concentrations [4].

The photovoltaic performances of unpurified natural extracts was studied in a DSSC application by extracting the pigments from the bark of eggplant twigs and leaves, showing an efficiency of 1%. The researchers also studied the thermal stability of eggplant pigments anchored on TiO₂ nanoparticles and confirmed natural pigments from not edible eggplant parts, thermally stable at least up to 65 °C, as appropriate dyes in totally sealed DSSC [127].

Researchers studied the effect of natural dye extraction processes on the DSSC performance by constructing anthocyanin based DSSCs where the anthocyanin pigments were extracted from cornelian cherry fruit using three different extraction methods (acidic solvent extraction, mechanical extraction and ultrasonic-assisted extraction). It was confirmed that varying the extraction methods caused all parameters to be altered indicating the extraction methods have a strong impact on the photovoltaic performance. The value of short circuit current density (J_{sc}) was remarkably changed with varying extraction method and resulted in improved power conversion efficiency (η), while the value of open circuit voltage (V_{oc}) was similar with all representative devices. The highest performance, short circuit current density (J_{sc}) of 7.89 mA cm⁻² and power conversion efficiency (η) of 0.98%, was achieved with acidic extraction method [128].

The natural pigments extracted from the skin of *Canarium odontophyllum* were used for dye sensitized solar cells (DSSCs) exploring. The extracted pigments were detected to be consisted of three main groups of flavonoid pigments namely aurone (maritimein), anthocyanidin (pelargonidin) and anthocyanidin (cyanidin derivatives) exhibiting different UV–Vis absorption properties, and hence showing different light harvesting capabilities. When tested in DSSC, the highest conversion efficiency of 1.43% was exhibited by cyanidin derivatives, and this was followed by conversion efficiencies of 0.51% and 0.79% for aurone and pelargonidin, respectively. Additionally, the researchers confirmed that individual pigments, like cyanidin derivatives and pelargonidin, exhibited higher power conversion efficiency when compared to that of *C. odontophyllum* skin pigment mixture power conversion efficiency (0.68%), depicting the masking effects of the pigments when used as a mixture [129].

Researchers constructed anthocyanin co-pigmented with caffeine based DSSCs and investigated the effect of co-pigmentation of anthocyanin dyes on the energy-conversion efficiency of DSSCs. It was reported that a co-pigmentation with caffeine increased the efficiency. Moreover, the cells with co-pigmented dyes were observed to be more stable than the cells with pure anthocyanin, i.e. they showed a

Table 1 Structural identification of the six common anthocyanidins [47]

Name	Substitution pattern		Color (pH=1)	λ_{max} (nm)
	R1	R2		
Cyanidin	OH	H	Orange–red	510
Delphinidin	OH	OH	Blue–red	522
Malvidin	OCH ₃	OCH ₃	Blue–red	520
Pelargonidin	H	H	Orange	505
Peonidin	OCH ₃	H	Orange–red	532
Petunidin	OCH ₃	OH	Blue–red	546

smaller drop of efficiency during the observation period [130].

Researchers investigated the effect of solvents such as water, acidified water, ethanol, acidified ethanol and citric acid in the extraction and stability of anthocyanin for DSSC applications.

It was experimented that citric acid solvent improved the anthocyanin content and color intensity in the extract solution compared to other solvents as confirmed by the absorption spectra of various solvents, showing a maximum intensity of absorbance for citric acid. The sensitization effect of different solvents extracts with TiO₂ nanorods were shown by the absorbance spectra which signified the advantage of using citric acid as solvent in extracting anthocyanin. The sensitized TiO₂ film using citric acid extracts have shown higher photovoltaic performance of efficiency 0.83% compared to other solvent extracts [131].

The photo catalytic activity of photo electrodes for enhancing the efficiency of anthocyanin based dye sensitized solar cells was investigated by doping TiO₂ film with calcium (1%, 2%, 3%). The researchers aimed to maintain and increase the performance of DSSCs by minimizing the photo catalytic activity with a passivation layer on the surface of TiO₂. It was confirmed that calcium doped nanorods passivate the free electrons on the TiO₂ surface, thereby minimizing the photo catalytic activity in the film. The 3% calcium doped TiO₂ nanorods exhibited higher resistance to photo catalytic activity when compared with the undoped TiO₂ photo electrode. This increased the photovoltaic conversion efficiency of rose dye sensitized DSSC to 2.32%. On the other hand, it was observed that the surface trap density linearly increases that contributes for the enhanced conduction in the film with increase in photo catalytic activity when the dopant concentration (4% calcium doped TiO₂) was increased, leading to high degradation rate compared to 2% and 3% dopant concentration mainly due to the coalescence of nanorods that reduce the device performance [132].

Researchers studied the photovoltaic performance of DSSC which was sensitized with pomegranate and berry fruit extracts. It was reported that the power conversion

Table 2 Photoelectrochemical parameters of the DSSC's sensitized with different anthocyanin dye sources extracted from leaves, seeds, flowers, fruits, vegetables and tree barks

Dye solution	Photos	Semiconductor electrode	Electrolyte	Pigment used	λ_{max} (nm)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	η (%)	References
Rosella (<i>Hibiscus sabdariffa</i> L.)		TiO ₂	Γ/II_3^-	Anthocyanin	520	1.63	0.40	0.57	0.37	[109]
Sour pomegranate		TiO ₂	Γ/II_3^-	Anthocyanin	511	0.50	2.97	0.49	0.73	[110]
Sweet pomegranate		TiO ₂	Γ/II_3^-	Anthocyanin	529	0.61	4.60	0.55	1.50	[110]
Hibiscus surattensis		TiO ₂	Γ/II_3^-	Anthocyanin	545	5.45	0.39	0.54	1.14	[111]
Citrusinensis (Redscilian)		TiO ₂	Γ/II_3^-	Anthocyanin	515	3.84	0.34	0.50	–	[112]
Hylocereus costaricensis (Dragon fruit)		TiO ₂	Γ/II_3^-	Anthocyanin	535	0.20	0.22	0.30	0.22	[113]
Brassica oleracea (Redcabbage)		TiO ₂	Γ/II_3^-	Anthocyanin	537	0.50	0.37	0.54	0.13	[114]
Lawsonia inermis(Henna)		TiO ₂	Γ/II_3^-	Anthocyanin	518	1.87	0.61	0.58	0.66	[115]
Sumac/Rhus		TiO ₂	PEO	Anthocyanin	650	0.93	0.39	0.41	1.5	[116]

Table 2 (continued)

Dye solution	Photos	Semiconductor electrode	Electrolyte	Pigment used	λ_{\max} (nm)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	η (%)	References
Morinda lucida		TiO ₂	Γ/I_3^-	Anthocyanin	440	1.15	0.35	0.63	0.25	[117]
Black carrot (Daucus carota L.)		TiO ₂	Γ/I_3^-	Anthocyanin	540	1.3	0.4	0.47	0.25	[118]
Begonia		TiO ₂	Γ/I_3^-	Anthocyanin	540	0.63	0.537	0.72	0.24	[119]
Rhododendron		TiO ₂	Γ/I_3^-	Anthocyanin	540	1.61	0.585	0.609	0.57	[119]
Violet		TiO ₂	Γ/I_3^-	Anthocyanin	546	1.02	0.498	0.645	0.33	[119]

efficiency of the prepared pomegranate sensitized solar cell was 2.0%, and fill factor (FF) of 0.41 with the short circuit current density (J_{sc}) and open circuit voltage (V_{oc}) being 12.2 mA/cm² and 0.39 V respectively. The excellent photovoltaic performance of the solar cell could be attributed to the high concentration of anthocyanin present in pomegranate dye used in the sensitization of the nanocrystalline TiO₂ [12].

Anthocyanin pigments extracted from *Lawsonia inermis* plants using ethanol and mixture of ethanol and water as extracting solvents in the ratio 4:1 by volume were used as photosensitizers. A promising efficiency of 0.66% with short current density (J_{sc}) of 1.87 mA/cm² and open circuit voltage (V_{oc}) of 0.61 V for ethanol as extracting solvent and efficiency of 0.52% with short current density (J_{sc}) of 1.35 mA/cm² and open circuit voltage (V_{oc}) of 0.59 V for mixture of ethanol and water as extracting solvent were reported [133]. Better efficiency was recorded with ethanol as a solvent extraction which could be due to the fact that anthocyanin is more soluble in ethanol than in a mixture of ethanol and water, resulting in higher amounts of dye being adsorbed to the TiO₂ surface. It was reported that the cell sensitized with ethanol extract showed poor stability compared to cells sensitized with a mixture of ethanol and water extract that may be due to TiO₂ photocatalytic decomposition of anthocyanin in the presence of ethanol [125] although the conversion efficiency for ethanol extract was higher.

Irén Juhász Junger et al. [134] studied the influence of caffeine as a co-pigmentation of anthocyanin on the energy conversion efficiency of anthocyanin based DSSCs. They stated that the efficiency of anthocyanin based DSSCs when co-pigmented with caffeine is dependent upon the pH contents of the solution due to either hyperchromic or hypochromic effects. It was reported that for pH ≥ 2, the efficiency of cells with caffeine was higher than the efficiency of cells with pure anthocyanins as a result of the hyperchromic effect in presence of caffeine. On the other hand, for pH = 1, the efficiency of cells with pure dye was higher than the efficiency of cells with copigmented dye corresponding to the hypochromic effect observed for pH = 1.

Conclusion and future prospectives

Effects of the different factors on the stability of anthocyanin dyes are discussed with aid of literature reports available. It is evidenced from the literature reports that the acidic contents of the solution, light and temperature used for extraction processes have significant influence on the stability of anthocyanins, degradation or structural transformation of anthocyanins takes place. Additionally, the influence of the types of solvents used for efficient extraction of anthocyanin dyes has been well explained.

Moreover, the energy conversion efficiency of the anthocyanin dye based DSSCs have been analyzed. It was found that the energy conversion efficiency of anthocyanin photosensitizers is unsatisfactory for technological applications. In fact, in terms of performance/cost ratio, anthocyanin-based DSSCs have a potential advantage over synthetic dye based DSSCs. But to make anthocyanin dyes a solution of choice for DSSC technology, intensive researches are needed to be conducted on hindering dye aggregation on the semiconductor lay using suitable additives, selecting suitable electrolyte additives, reducing the back electron injection from the TiO₂ to the oxidized dye by creating interfaces between the dye and the semiconductor—for example using a Schottky barrier, exploiting functional groups to improve the charge transfer between the anthocyanin dye and electrolyte mediator and from the anthocyanin dye to the semiconductor layer surface—for example incorporating graphene in the anthocyanin dye mixture and the subsequent co-adsorption onto the titanium nanoparticles reduce the dark current, increasing of the anthocyanin dye photo-stability—for example using co-pigmentation and/or the additives linking the dye with the semiconductor layer without affecting the photoelectrochemical properties and other critical issues (Tables 1 and 2).

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