

Harnessing the potential of selected plant pigments in dye-sensitized solar cells: the current status

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Abstract

Dye-sensitized solar cells (DSSC) represent the third generation of solar cells which have revolutionized sustainable energy research owing to the fact that they act as a renewable energy source integrated with employment of environmentally benign light-harvesting pigments as sensitizers and cost-effective materials for manufacture. This review compiles the exploration of plant pigments with a potential for use as photosensitizers in solar cells, focusing on their isolation and the factors that affect their physicochemical properties to identify those pigments providing the optimum performance. Newly reported considerations of flavonoids, anthocyanins, carotenoids, betalains, and chlorophyll, as light-harvesting pigments are summarized. Further, outcomes of the solar cell efficiency obtained by various semiconductors and types of electrolytes are compared and discussed. The main goal of this review is to highlight the significance of naturally obtained light-harvesting pigments, which will be used as the promising class of sensitizers in DSSC.

Keywords: photovoltaics; flavonoids; anthocyanins; carotenoids; betalains; chlorophyll

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1. INTRODUCTION

It is a well-known fact that the daily energy utilization is about 17.4 TW worldwide of which 80% is gained from natural gas, fossil fuels, and coal. To find a sustainable energy source which is environmentally friendly and cheap, scientists suggest the use of solar power. Solar radiation is about 3.8 million exajoules per year, namely 10,000 times more than humanity needs [1]. In addition, solar power represents renewable source of energy that could be applied as one-time investment and, during the photovoltaic transformation, harmful gases are not released [2]. Since the production of electric energy by illumination of certain organic molecules was disclosed in the 1960s [3], dye-sensitized solar cells (DSSCs) have revolutionized sustainable energy research [2]. Due to eco-friendly preparation methods that require the use of cost-effective materials [2], DSSCs have been extensively studied.

According to their architecture and the type of implemented materials, all solar cells are generally classified into four main categories termed generations [2,4-6].

1) First generation

- Crystalline Si
 - Monocrystalline Si
 - Polycrystalline (multicrystalline) Si
- III-V Single-junction solar cells

2) Second generation

- Amorphous Si (a-Si)
- Microcrystalline Si (μ c-Si)
- Chalcogenides
 - Copper-Indium-Gallium-Selenide (CIGS)
 - Cadmium-Telluride (CdTe)
 - Cadmium-Sulphide (CdS)
 - Others

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- 3) Third generation
 - Dye-sensitized solar cells (DSSC)
 - Perovskite solar cells (PSC)
 - Quantum dot-sensitized solar cells (QDSSC)
 - Organic and polymer materials (OPV)
 - III-V Multi-junction solar cells
- 4) Fourth generation
 - Graphene and its derivatives
 - Carbon nanotubes
 - Metal nanoparticles and metal oxides.

The conventional structure/design of a DSSC (proposed by O'Regan and Gratzel) consists of four fundamental parts:

1. a photoanode—mesoporous metal oxide (usually TiO_2) adsorbed on the transparent conductive oxide (TCO; usually fluorine-doped tin oxide (FTO) or indium tin oxide (ITO)) of a glass substrate,
2. a sensitizer—a dye molecule,
3. an electrolyte—usually a I_3^-/I^- redox couple in aprotic polar organic solvent, and
4. a photocathode—photocatalytic material adsorbed onto TCO of a glass substrate [7].

To address the challenges associated with the application of synthetic dyes as sensitizers in DSSCs, such as a high cost, propensity to degradation and employment of toxic substances, biocompatible natural sensitizers have been applied. These natural sensitizers contain various pigments managing the absorption of light and insert of charges to the conduction band of TiO_2 [7].

It was demonstrated in literature [8] that a DSSC containing a mixture of anthocyanin pigment, more precisely, a mixture of cyanin-3-glycoside and cyanin-3-rutinoside, as a sensitizer for TiO_2 , can produce a conversion efficiency of $\eta = 0.56\%$, the open-circuit voltages in the range of $V_{oc} = 0.4$ to 0.5 V, and short-circuit currents in the range of $J_{sc} = 1.5$ to 2.2 mA cm^{-2} . Additionally, the maximum current of 4 mA, the maximum voltage of 300 mV and the overall efficiency of 1% were obtained by using a blackberry extract to sensitize TiO_2 [9]. Garcia and coworkers revealed that employment of natural dyes extracted from chaste tree fruit, mulberry and cabbage-palm as TiO_2 sensitizers, produce a short-circuit current and open-circuit voltage close to those of conventional dyes [10]. Inspired by these results, this review compiles the performance of natural dye based DSSCs coupled with different biocompatible plant pigments extracted from diverse natural products and implemented in solar cells. Recent explorations of plant pigments are coupled with data about their chemical stability, extraction, and purification methods. In addition, a comparative study based on the findings of various research groups related to natural dye-sensitized solar cells is also described. The main goal of this review is to highlight the application potential of natural pigments as sensitizers for the future development of solar cells with promising performance.

2. CLASSIFICATION OF LIGHT-HARVESTING PIGMENTS AND APPLICATION-BASED FUTURE PERSPECTIVES

Pigments occurring in plants represent one of the most important natural components for absorption of solar radiation and generation of electrons. To ensure the optimal performance of DSSCs, two conditions should be fulfilled: a greater number of so-called light-harvesting pigments extracted from different parts of plants and the existence of anchoring groups (*e.g.* hydroxyl, carbonyl group) for chemisorption of the dye molecule on semiconductor's surface [2]. In accordance with this, an efficient light-harvesting pigment should fulfil the following:

1. broad absorption in the visible and near-infrared part of the solar spectrum, providing a high molar attenuation coefficient,
2. a strong interaction with the semiconductor's surface through the anchoring groups, in order to provide the efficient injection of photoexcited electrons from the LUMO (lowest unoccupied molecular orbital) of the dye to the conduction band (CB) of the semiconductor,
3. faster injection rate of photoexcited electrons compared to the rate of decomposition of the dye,
4. a value of the LUMO energy level of the dye higher than the value of CB energy level of the semiconductor to enable injection of photoexcited electrons,

5. a value of the HOMO (highest occupied molecular orbital) energy level of the dye lower than the value of the redox couple energy level to enable efficient reduction of the oxidized dye molecule/regeneration of the oxidized dye molecule [1].

A literature review indicates that plant compounds such as flavonoids, anthocyanins, carotenoids, betalains and chlorophyll, meet these criteria and possess advantages including: large absorption coefficients, high light-harvesting efficiencies, biodegradability, low production costs and easy processability [2,11].

In recent years, there has been a growing number of papers and patents dealing with application of natural pigments in DSSCs [12-15]. Here, we provide a new perspective on their selection with the emphasis on molecular scaffolds and functional groups that influence, among others, the following properties: the pigment stability, light absorption and the electron injection efficiency. In this context, the classification of natural pigments is presented in detail together with their sourcing. A key insight from this review is the structural variety of natural pigments, which offers guidelines for optimizing their properties to improve the DSSC efficiency and operational stability.

2. 1. Flavonoids

In the 1930s, a new compound isolated from oranges was recognized as a vitamin family member and was named vitamin P. It was later discovered that it was the unique antioxidant flavonoid (rutin, citrus flavonoid glycoside) [16]. Flavonoids comprise different polyphenolic compounds found in plants. The core structure of these polyphenolics is built of a 15-carbon phenyl-benzopyrone skeleton (C6-C3-C6 system), which consists of a benzene ring (designated as B) associated to a benzo-gamma-pyrone structure (condensed fragments A and C) (Figure 1) [17-19].

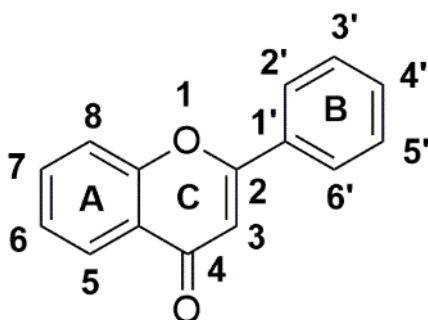


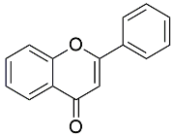
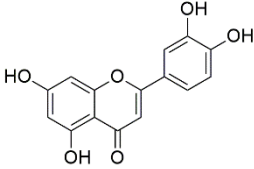
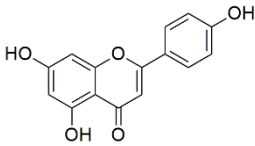
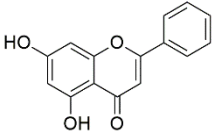
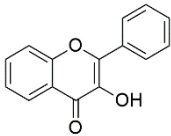
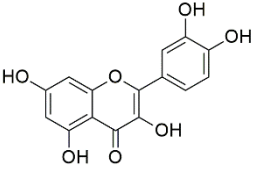
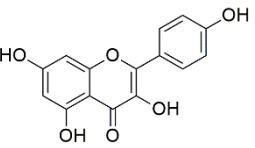
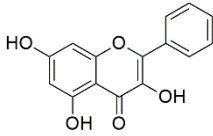
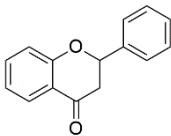
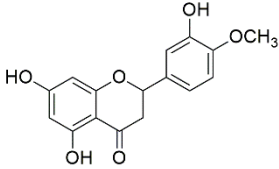
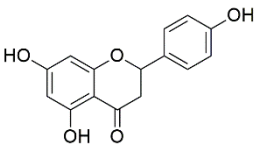
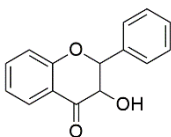
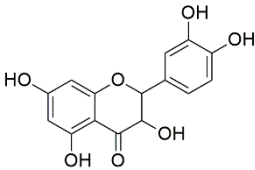
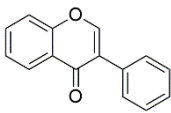
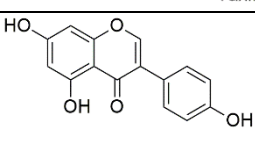
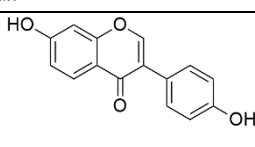
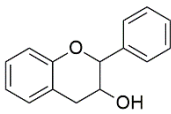
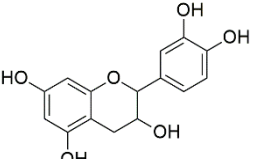
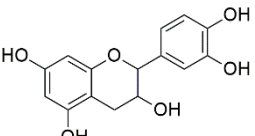
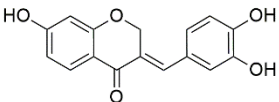
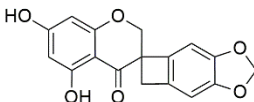
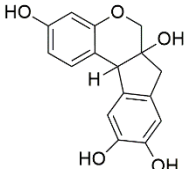
Figure 1. General structure of flavonoids

Flavonoids are present in plants as both aglycones (free form) and *O*-glycosidic (rarely *C*-glycosidic) conjugates that is the most frequent form; other altered forms exist as well [19,20]. *O*-glycosides are less reactive, but more polar and their transport across cell membranes is improved [19,20]. In the *O*-glycosidic form, at least one hydroxyl group is connected with a sugar moiety (*e.g.* glucose, galactose, rhamnose, xylose *etc.*) *via* the acid-labile acetal bond in the following way: the hydroxyl group at C7 in flavones, flavanones and isoflavones, the hydroxyl group at C3 and C7 in flavonols and flavanols and the hydroxyl group at C3 and C5 in flavonoid-related anthocyanidins [20].

Flavonoid compounds are very abundant natural plant pigments secreted as secondary metabolites. In times of stress, plants often release secondary metabolites as a defensive response. These flavonoid phytochemicals can serve as signal molecules, UV-filters and scavengers for reactive oxygen species (ROS) and have essential roles in enhancing tolerance to drought, heat, and freezing conditions [17,20,21]. Among the flavonoid family, there are various subclasses such as flavones, flavonols, flavanones, flavanonols, isoflavones, flavanols, anthocyanidins and others (*e.g.* chalcones and aurones) [16,20]. The general structures and examples of some typical flavonoid subclasses are shown in Table 1. In this review, anthocyanidins are especially highlighted because of their great importance among the light-harvesting plant pigments; they are not bundled with the rest of flavonoids. According to unsaturation and oxidation degree of the central heterocyclic ring C (Figure 1), most of flavonoids are divided into flavones and flavonols (possess the benzo-gamma-pyrone moiety) and their dihydro derivatives. Flavan-3-ols are somewhat different from the rest, because they do not possess a carbonyl group in the heterocyclic moiety. The position of the benzenoid substituent classifies them into flavonoids (2-position) and isoflavonoids (3-position) [16,20]. There are also homoisoflavonoids, an infrequent

flavonoid subclass, with a core structure similar to isoflavonoids, but with a 16-carbon skeleton (e.g. sappanin-type homoisoflavonoids bear a 3-benzylchroman-4-one key unit) [22,23].

Table 1. General structures and examples of some typical flavonoid subclasses

Subclass of flavonoid	General structure	Examples
Flavones		 Luteolin  Apigenin  Chrysin
Flavonols		 Quercetin  Kaempferol  Galangin
Flavanones		 Hesperetin  Naringenin
Flavanonols		 Taxifolin
Isoflavones		 Genistein  Daidzein
Flavan-3-ols		 Catechin  Epicatechin
Homoiso-flavonoids	Five basic scaffolds	 Sappanone A  Scillascillin  Brazilin

The wide application of flavonoids in the various branches of industry implies the existence of various methods for their extraction. The polarity of flavonoid molecules is crucial for the solvent selection. For example, highly alkylated

aglycones are extracted using ethyl acetate, while the more hydroxylated aglycones are extracted using acetone, alcohol, water of their mixtures [17].

Using flavonoids and betacyanins (water-soluble, nitrogen-containing pigments) extracted from *Nerium Oleander*, *Tecomastan*, and *Bougainvillea* as light-harvesting pigments, and TiO_2 nanoparticles as semiconductor implied on a FTO glass plate, Devi and coworkers fabricated DSSC with V_{oc} in the range of 132 to 554 mV, J_{sc} in the range of 3.22 to 15.22 mA cm^{-2} , and η in the range of 0.30-0.68 % [24]. Results of an optical analysis indicated that the observed efficient sensitizing behaviour of the pigments can be related to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions in the heterocyclic moieties of flavonoids and betacyanins [24]. Homoisoflavonoids isolated from *Caesalpinia sappan* represent interesting optically active pigments because, upon excitation at 383 nm, they produce emission at 563 nm, while the results of a current-voltage analysis indicate good photovoltaic performances as follows: $V_{oc} = 487$ mV, $J_{sc} = 0.10$ mA cm^{-2} and a fill factor (FF) of 87.6 % [25]. In another study, it was demonstrated that a DSSC containing chokeberry (*Aronia melanocarpa*) juice pigments as sensitizers had the photovoltaic parameters similar to those of the Ru(II) complex N719 as a reference dye [26]. By using hybrid nanostructures like TiO_2 hollow spheres of tetragonal form as semiconductor, and natural pigments isolated from *Punica granatum* and *Acacia catechu*, a DSSC was fabricated with a higher power conversion efficiency (PCE) of 0.26, V_{oc} of 530 mV and a fill factor of 85 % [27]. At the same time, in another research it was denoted that cells built from crude plant extracts containing mixtures of alkaloids, carotenoids, flavonoids and anthraquinones, with TiO_2 as semiconductor, produce a respectable V_{oc} and very low J_{sc} compared to the standard cell containing the N719 dye. Among them, the highest performance exhibited a cell containing extract isolated from *Sorghum bicolor*, with a maximum power of $P_{max} = 0.18$ mW/cm^2 , which can be attributed to a high anthocyanin content [28]. By using extracts from *Trifolium pratense*, *Mirabilis jalapa* and *Bassia scoparia*, Muhammad and coworkers constructed a DSSC with the efficiency of 0.15, 0.05 and 0.18 %, respectively [29]. According to the fluorescence spectroscopy analysis, chlorophyll extracted from *Bassia scoparia* displayed the highest light absorption, photon emission and stacking capability with TiO_2 semiconductor [29]. Spectral properties of flavonoids isolated from red/yellow gambier fruits suggest that these pigments have a high application potential as natural light-harvesting pigments in solar cells. Also, *I-V* measurements showed that the DSSC efficiency linearly correlated with their concentration. An efficiency of 3.248 % was reached in a DSSC with the concentration of yellow gambier fruit pigment of 70 %, while the efficiency of 0.72 % was reached in a DSSC with the concentration of red gambier fruit pigment of 30 % [30]. A DSSC was manufactured by using TiO_2 nanostructures and fruit extracts originated from grape, pineapple, and orange (G- TiO_2 , P- TiO_2 and O- TiO_2 , respectively) as reducing agents (or electron donors) and using flavonoids isolated from *Murraya koenigii* as a natural sensitizer [31]. Owing to a light scattering ability and a strengthened electron transfer related to the above-mentioned analogs, the DSSC constituted of G- TiO_2 exerted the best photovoltaic parameters: $V_{oc} = 628$ mV, $J_{sc} = 4.88$ mA cm^{-2} , FF = 58 % and $\eta = 1.78$ % [31]. DSSCs were made using flavonoids, isolated from *Argemone mexicana* flower, as photosensitizer and fabricated by employing microwave processing to anneal a TiO_2 layer. The optimum photovoltaic parameters were obtained for microwave annealed solar cells with a blocking layer and irradiation time of 7 min. The observed photovoltaic parameters were: $V_{oc} = 472$ mV, $J_{sc} = 2.73$ mA cm^{-2} , FF = 0.54 % and $\eta = 0.69$ % [32]. A broad absorption maximum of these pigments at 359 nm, and fast adsorption on the TiO_2 surface qualified these flavonoids as appropriate sensitizers for solar cell applications [32]. By using natural pigment scopoletin isolated from *Malva sylvestris*, Karoui and coworkers fabricated a DSSC with a short-circuit density of 0.69 mA cm^{-2} and very stable performance under illumination [33]. To enhance the efficiency of DSSCs containing natural light-harvesting pigments extracted from *Cytisus*, *Aleurosea*, and *Roselle*, zinc oxide quantum dots (ZnO-QDs) were applied manufactured through co-precipitation in an ethanolic solution. Results of transmission electron microscopy (TEM), dynamic light scattering (DLS), and photoluminescence (PL) revealed that ZnO-QDs 3 nm in size and a maximum emission intensity in the range 1550 to 520 nm improved the efficiency of the DSSC by 17 % [34]. Table 2 shows the corresponding photovoltaic parameters of DSSCs sensitized with flavonoids, flavonoid-related anthocyanins and other pigments.

Table 2. Photovoltaic parameters of DSSCs sensitized with flavonoids, flavonoid-related anthocyanins and other pigments

No.	Name of plant	Class/name of pigment	Semi-conductor	Electrolyte	Photovoltaic parameters				Ref.
					V_{oc} / mV	$J_{sc} / \text{mA cm}^{-2}$	FF, %	$\eta / \%$	
1	Pink <i>Plumeria rubra</i>	Flavonoid	TiO ₂	I ⁻ /I ₃ ⁻	310	0.55	0.30	0.05	[28]
2	Yellow <i>Plumeria rubra</i>	Flavonoid	TiO ₂	I ⁻ /I ₃ ⁻	420	1.12	0.32	0.15	[28]
3	<i>Nerium oleander</i>	Flavonoid	Nano-TiO ₂	NaI/I ₂	358	7.41	0.20	0.54	[24]
4	<i>Nerium oleander</i>	Flavonoid	Nano-TiO ₂	KI/I ₂	544	3.22	0.39	0.68	[24]
5	<i>Tecoma stan</i>	Flavonoid	Nano-TiO ₂	NaI/I ₂	413	3.56	0.20	0.30	[24]
6	<i>Tecoma stan</i>	Flavonoid	Nano-TiO ₂	KI/I ₂	439	3.69	0.23	0.38	[24]
7	<i>Terminalia chebula</i>	Flavonoid	TiO ₂	I ⁻ /I ₃ ⁻	470	0.11	0.40	0.24	[27]
8	Yellow gambier fruit	Flavonoid	TiO ₂	KI/I ₂	649	1.11	0.43	3.25	[30]
9	Red gambier fruit	Flavonoid	TiO ₂	KI/I ₂	442	0.76	0.21	0.72	[30]
10	<i>Murraya koenigii</i>	Flavonoid	Grape extract+TiO	I ⁻ /I ₃ ⁻	628	4.88	58	1.78	[31]
11	<i>Murraya koenigii</i>	Flavonoid	Pineapple extract+TiO ₂	I ⁻ /I ₃ ⁻	626	4.60	47	1.61	[31]
12	<i>Murraya koenigii</i>	Flavonoid	Orange extract+TiO ₂	I ⁻ /I ₃ ⁻	576	6.48	40	1.52	[31]
13	<i>Argemone mexicana</i>	Flavonoid	TiO ₂	I ⁻ /I ₃ ⁻	427	2.73	0.54	0.69	[32]
14	<i>Biancaea sappan</i>	Flavone and homoisoflavonoid	TiO ₂	I ⁻ /I ₃ ⁻	390	0.05	0.43	0.11	[27]
15	<i>Caesalpinia sappan</i>	Homoisoflavonoid	TiO ₂	I ⁻ /I ₃ ⁻	487	0.10	87.6	/	[25]
16	<i>Lawsonia inermis</i>	Lawsonone	TiO ₂	I ⁻ /I ₃ ⁻	470	0.66	0.50	0.16	[33]
17	<i>Malva sylvestris</i>	Scopoletin	TiO ₂	I ⁻ /I ₃ ⁻	600	0.69	0.55	0.21	[33]
18	<i>Cytisus scoparius</i>	Flavonoid and Anthocyanin	TiO ₂	I ⁻ /I ₃ ⁻	161	1.01	0.70	0.45	[34]
19	<i>Cytisus scoparius</i>	Flavonoid and Anthocyanin	TiO ₂ /ZnO-Qd ^a	I ⁻ /I ₃ ⁻	614	1.18	0.67	0.49	[34]
20	<i>Alcea rosea</i>	Flavonoid and Anthocyanin	TiO ₂	I ⁻ /I ₃ ⁻	621	1.91	0.68	0.80	[34]
21	<i>Alcea rosea</i>	Flavonoid and Anthocyanin	TiO ₂ /ZnO-Qd	I ⁻ /I ₃ ⁻	624	2.21	0.67	0.93	[34]
22	<i>Hibiscus sabdariffa</i>	Flavonoid and Anthocyanin	TiO ₂	I ⁻ /I ₃ ⁻	644	1.91	0.68	0.84	[34]
23	<i>Hibiscus sabdariffa</i>	Flavonoid and Anthocyanin	TiO ₂ /ZnO-Qd	I ⁻ /I ₃ ⁻	648	2.25	0.65	0.98	[34]
24	<i>Acacia catechu</i>	Catechin and epicatechin	TiO ₂	I ⁻ /I ₃ ⁻	580	0.20	0.84	1.15	[27]

^azinc oxide quantum dots (ZnO-Qd) applied on titanium dioxide (TiO₂) coating; entries 1, 2, 8, 9: indium tin oxide (ITO) glass counter electrode; entries 3-7, 10-24: fluorine-doped tin oxide (FTO) glass counter electrode

2. 2. Anthocyanins

Anthocyanins are polyphenolic water-soluble plant pigments that have been recognized as promising natural sensitizers for DSSCs application; furthermore, they are the most extensively investigated photosensitizers [11]. The resonant structure of the flavylium ion (Figure 2) plays a crucial role in determining the colour intensity of anthocyanins [11]. Aglycones of anthocyanins, anthocyanidins (Figure 2), are polyhydroxy and polymethoxy derivatives of flavylium salts [20,35]. A variety of anthocyanidins (Figure 2) are formed *via* hydroxylation of a flavylium cation backbone in various positions, typically on C3, C5, C6, C7, as well as C3', C4', and C5'; some hydroxyl groups may be further methylated (mainly at position 3' and 5') [11,35]. The basic chemical structure of anthocyanidins consists of an aromatic ring A fused with a pyrylium ring

C, which is further connected *via* a C-C bond to the second aromatic ring B [36]. Distinctive red to blue colour of flowers (tulips, roses and orchids), fruits (grapes, berries and apples), and vegetables (red cabbage and radishes) originate from high concentrations of water-soluble vacuolar pigments, known as anthocyanins [36].

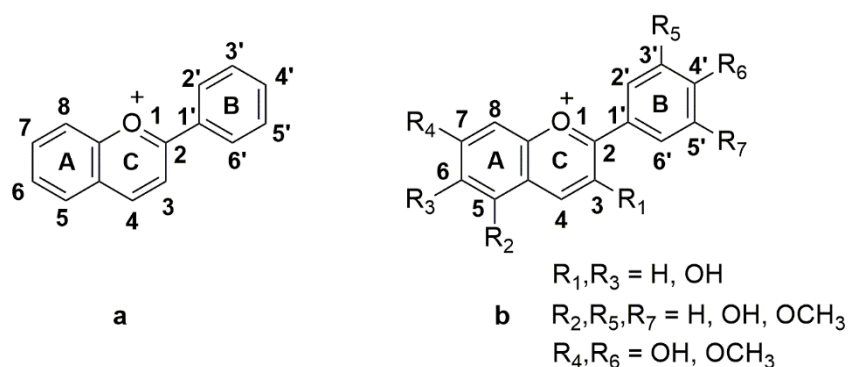


Figure 2. General structure of: flavylium cation (a), anthocyanidins (b)

O-Glycosylation of this polyphenol aromatic structure, which results in formation of appropriate anthocyanins, could take place on various hydroxyl moieties, among which the position 3 (Figure 3) is the most frequent.

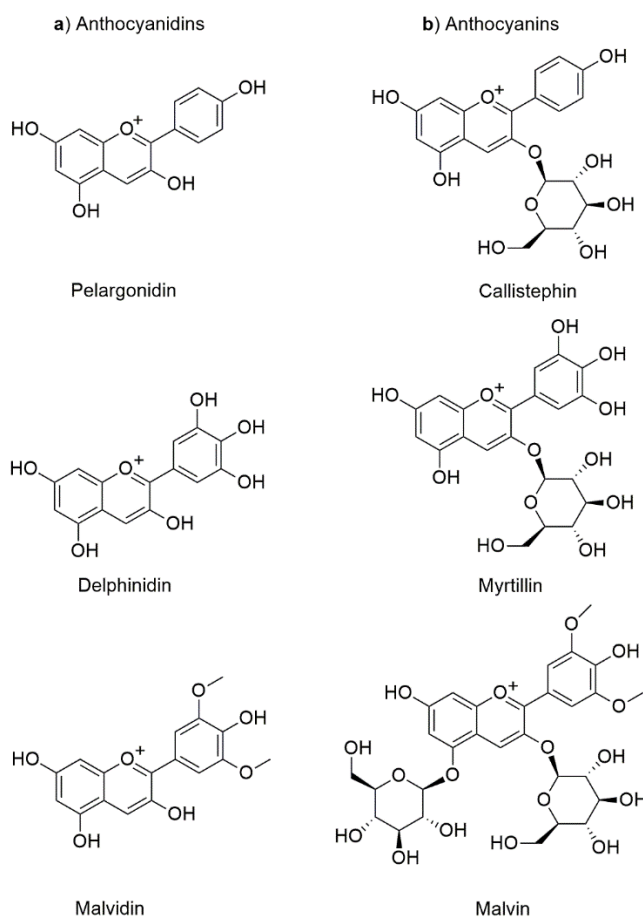


Figure 3. Chemical structure of some natural occurring anthocyanidins (a) and corresponding mono- or di-glycosides (anthocyanins) (b)

In carbohydrate-conjugated forms of anthocyanidins, the sugar residue might be glucose, xylose, galactose, arabinose, rhamnose or rutinose [37]. Although there is an enormous diversity of anthocyanins found in nature, only six of their aglycones (anthocyanidins) are predominant in vascular plants, namely: cyanidin, delphinidin, pelargonidin, peonidin, petunidin, and malvidin (Figure 3) [11,35]. Anthocyanins, which are most often found in nature, are glycosidic derivatives of cyanidin, delphinidin, and pelargonidin. Their chemical stability/colour is highly affected by many factors

including pH, storage temperature, concentration and chemical structure, oxygen, presence of enzymes (and other accompanying substances/metal ions), light and solvents [35,36].

Structural modifications of anthocyanins are correlated with changes in pH-values as follows (Figure 4) [35,36]:

1. at the pH 1, anthocyanins exist in the predominant equilibrium form of the red flavylum cation (A),
2. at a pH value in the range of 2–4, the blue quinonoidal species (B–D) are the most dominant,
3. at a pH value in the range of 5–6, a colourless carbinol pseudobase (E) and a chalcone (F), are the only two species that can be observed,
4. at a pH value greater than 7, anthocyanins are degraded, which is controlled by the substituent type.

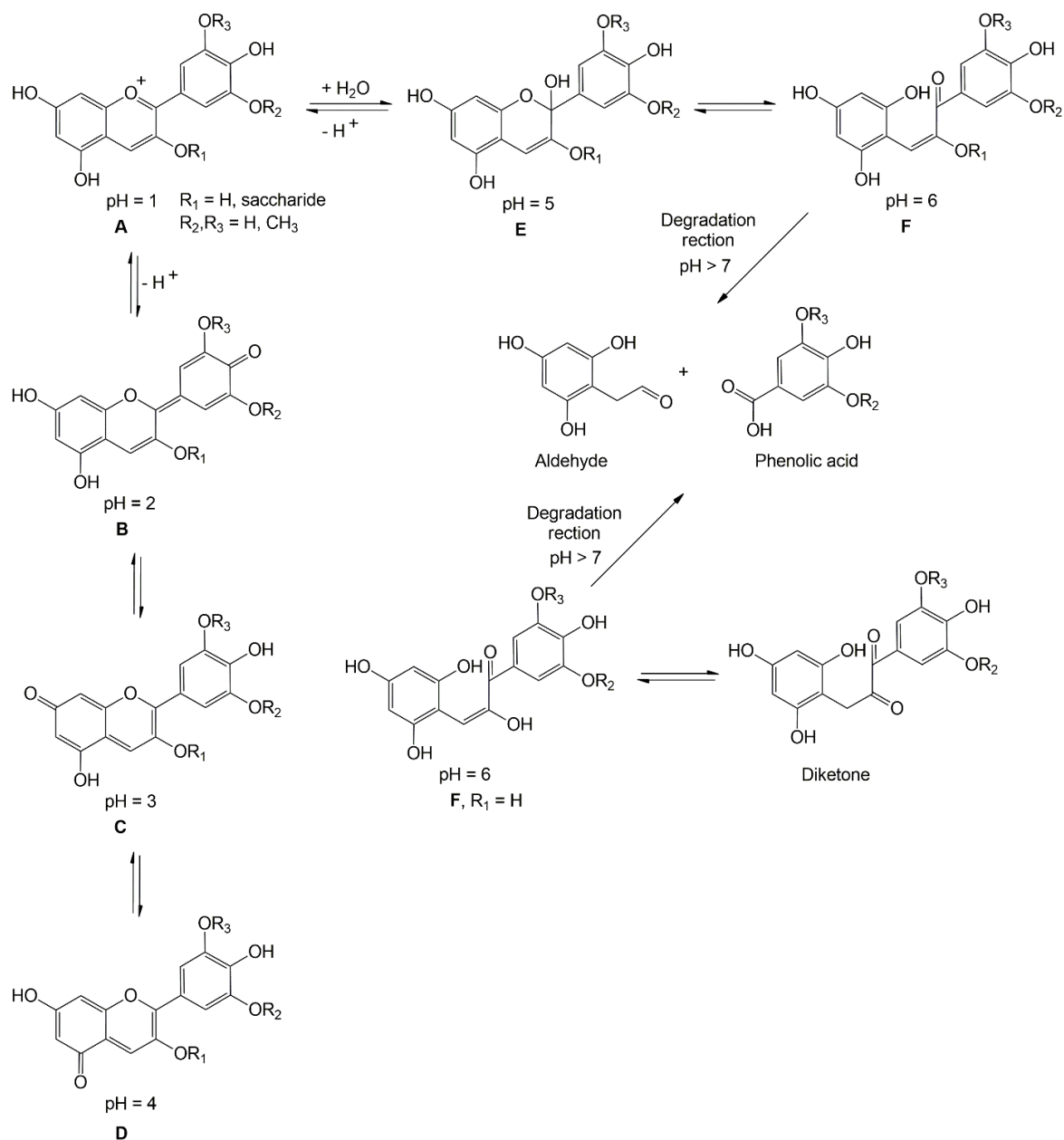


Figure 4. Chemical forms of anthocyanins depending on the pH and degradation reaction

As can be concluded from Figure 4 (structures D, A and E), the equilibrium between quinonoid bases and carbinol takes place through the flavylum cation, which is the predominant species in more acidic conditions (e.g. at a pH value in the range of 4 to 6, four structural forms exist at the same time: the red flavylum cation, the anhydrous blue quinonoid base, the colourless carbinol pseudobase, and the pale yellow chalcone). In addition, the anthocyanins stability is

controlled by the number of the hydroxyl/methoxy groups attached to the second aromatic ring B (Figure 2, structure b), because they decrease the aglycon stability in the neutral media [35,36].

One way to increase the stability of anthocyanins is to form co-pigments, systems rich in π -electrons and capable to interact with systems poor in π -electrons, like the flavylium cation. This inter/intramolecular interaction provides shielding of the flavylium cation (Figure 2) from the nucleophilic attack of the water molecule in position 2 and from peroxides and sulphur dioxide in position 4 [36]. Taking into account all the factors affecting the stability of anthocyanins, the best method for their extraction implies the use of acidified methanol or ethanol, at temperatures ranging from 20 to 50 °C, or the use of modern techniques including ultrasound-assisted extraction, microwave-assisted extraction, supercritical fluid extraction, and high-hydrostatic pressure extraction [11].

It was demonstrated in literature that a DSSC containing acidified anthocyanin extracted from *Syzygium cumini* achieved better performances compared to the original pigment previously utilized [38]. This is due to the interaction of light-harvesting pigment with concentrated hydrochloric acid which results in breaking-down of the flavylium cation O-glycosidic linkage and releasing the anthocyanidin. The optical analysis of the acidified anthocyanin indicates better delocalization of π -electrons within the pigment structure compared to the one not treated with acid and a smaller HOMO-LUMO energy gap [38]. Furthermore, a DSSC was constructed with a fill factor of 0.2 and overall efficiency of 1.33 % using an anthocyanin pigment extracted from *Eugenia claviflora*, and TiO₂/conjugated polymer poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) as semiconductor [39]. Erande and coworkers fabricated and investigated efficiency of DSSCs with pomegranate dye (specifically anthocyanin) treated TiO₂ thin films. The higher power conversion efficiency was succeeded for DSSCs fabricated by using anthocyanin than that of bare TiO₂ (η = 0.20 and 0.17 %, respectively) [40]. Photocatalytic activity of TiO₂ triggers degradation of natural pigments in DSSC, so Prabavathy and coworkers increased the anthocyanin performance by co-sensitizing it with astaxanthin isolated from *Haematococcus pluvialis* at the ratio 70:30. Fluorescence lifetime measurements indicated that astaxanthin reduces the degradation rate of anthocyanin without disturbing its band gap [41]. By employing anthocyanins isolated from *Canarium ovatum*, and TiO₂ nanoparticles accumulated on translucent ITO glass, Gasga and coworkers fabricated solar cells with the aim of determining the ideal TiO₂ film thickness and soaking time in dye. According to results obtained by using response surface methodology, the solar cells running at 55.249 μ m TiO₂ film thickness and soaked for 12 h gave the photovoltaic performances as follows: V_{oc} = 446 mV, J_{sc} = 6.29 mA cm⁻², FF = 0.60 % and η = 1.79 % [42]. The corresponding photovoltaic parameters of DSSCs sensitized with anthocyanins are shown in Table 3.

Table 3. Photovoltaic parameters of DSSCs sensitized with anthocyanins and with anthocyanin/carotenoid mixture

No.	Name of plant	Class/name of pigment	Semi-conductor	Counter electrode	Electrolyte	Photovoltaic parameters				Ref.
						V_{oc} / mV	J_{sc} / mA cm ⁻²	FF, %	η / %	
1	<i>Punica granatum</i>	Anthocyanin	TiO ₂	Pt paste coated on FTO glass	I ⁻ /I ₃ ⁻	520	0.34	0.65	0.12	[44]
2	<i>Punica granatum</i>	Anthocyanin	TiO ₂	FTO glass	I ⁻ /I ₃ ⁻	500	0.73	0.59	2.58	[27]
3	<i>Sorghum bicolor</i>	Anthocyanin	TiO ₂	ITO glass	I ⁻ /I ₃ ⁻	340	1.69	0.31	0.18	[28]
4	<i>Delonix regia</i>	Anthocyanin	TiO ₂	ITO glass	I ⁻ /I ₃ ⁻	420	0.81	0.29	0.10	[28]
5	<i>Syzygium cumini</i>	Anthocyanin	TiO ₂	Pt paste coated on FTO glass	I ⁻ /I ₃ ⁻	200	1.29	26.1	0.27	[38]
6	<i>Syzygium cumini</i> ^a	Anthocyanin	TiO ₂	Pt paste coated on FTO glass	I ⁻ /I ₃ ⁻	370	2.76	33.7	1.39	[38]
7	<i>Syzygium cumini</i>	Anthocyanin	TiO ₂ NP/TiNT ^b	FTO glass	I ⁻ /I ₃ ⁻	510	5.43	14.7	0.40	[45]
8	<i>Trifolium pratense</i>	Anthocyanin	TiO ₂	FTO glass	I ⁻ /I ₃ ⁻	0.58	0.34	0.75	0.15	[29]
9	<i>Eugenia claviflora</i>	Anthocyanin	TiO ₂ / conjugated polymer PEDOT:PSS ^c	ITO glass	I ⁻ /I ₃ ⁻	430	0.12	0.20	1.33	[39]

No.	Name of plant	Class/name of pigment	Semi-conductor	Counter electrode	Electrolyte	Photovoltaic parameters				Ref.
						V_{oc} / mV	J_{sc} / mA cm ⁻²	FF, %	η / %	
10	<i>Punica granatum</i>	Anthocyanin	TiO ₂	ITO glass	KI/I ₂ /EG	304	1.62	0.21	0.20	[40]
11	<i>Zea mays</i>	Anthocyanin	TiO ₂	Pt paste coated on FTO glass	TBAI/I ₂ ^d	586	0.88	0.59	0.31	[43]
12	<i>Brassica oleracea</i>	Anthocyanin	TiO ₂	FTO glass	I ⁻ /I ₃ ⁻	461	0.97	0.28	0.13	[33]
13	Rose / <i>H. pluvialis</i>	Anthocyanin: Astaxanthin = 70:30 ^e	TiO ₂	FTO glass	I ⁻ /I ₃ ⁻	740	8.6	0.70	2.82	[41]
14	<i>Canarium ovatum</i>	Anthocyanin	TiO ₂	ITO glass	I ⁻ /I ₃ ⁻	446	6.29	0.60	1.79	[42]
15	<i>Tropaeolum majus</i>	Anthocyanin and Carotenoid	TiO ₂	Pt paste coated on FTO glass	I ⁻ /I ₃ ⁻	502	0.70	0.62	0.22	[46]

^aacidified extract; ^bcomposite of TiO₂ nanoparticle/TiO₂ nanotube paste; ^cpoly(3,4-ethylenedioxythiophene):polystyrene sulfonate; ^d0.6 M of tetra-*n*-butylammonium iodide and 0.05 M of iodine in acetonitrile; ^evolume ratio

2. 3. Carotenoids

Research on carotenoids began with the isolation of an apocarotenoid from the crocin family (now known as crocetin) from saffron a little more than 200 years ago [47]. Later, a carrot pigment, carotene (today known as β -carotene), was isolated from carrot-juice [47,48]. In the 1930s, C40 structure of β -carotene and lycopene was described (Figure 5). Carotenoids, mostly 40-carbon skeleton isoprenoid natural pigments that can be synthesized by plants and microorganisms a la photosynthetic bacteria, fungi and algae, are responsible for the red, orange, and yellow colours of flowers, fruits, and vegetables. Together with chlorophylls, they are irreplaceable pigments in photosynthetic organs [49,50]. Even though there are several hundreds of naturally occurring carotenoids, only 50 of them have noteworthy pharmacological and industrial significance, particularly due to their provitamin A activity, antioxidant properties, potential as protective agents, and use as natural dyes [47,48,51].

According to the number of C atoms in their chemical structure, carotenoids can be divided into C30, C40, C45 and C50 carotenoids, while naturally most frequent are tetraterpene carotenoids (C40 compounds) with eight isoprene units [47]. Originally, they are mostly present as all-*E* geometric forms that undergo *E/Z*-isomerization [49,50]. Naturally occurring carotenoids can be primary classified as carotenes and xanthopylls. Carotenes consist of linear hydrocarbon chains, which can be cyclized at one/both ends, while xanthopylls represent the oxygenated derivatives of carotenes containing different functional groups such as hydroxyl, epoxy or keto (Figure 5) [47-49]. Some chemical modifications of carotenoids exist in nature. In addition to their free form, xanthopylls are also present in the form of fatty acid esters, glycosides, sulphates and complexes with proteins [47,49]. Allene and acetylene carotenoid structures are also examples of naturally occurring, chemically modified carotenoids [47,52].

In microorganisms and plants, tetraterpene carotenoids (C40 compounds) are the object of enzymatic (in the presence of carotenoid cleavage dioxygenases (CCDs) enzymes) and non-enzymatic (*via* singlet oxygen attack) oxidative cleavage resulting in wide variety of carotenoid-derived compounds called apocarotenoids [47,53,54]. For instance, biosynthesis of apocarotenoid bixin begins with the enzymatic oxidative cleavage of its precursor, lycopene, which produces bixin aldehyde that undergoes oxidation giving norbixin. Finally, bixin is formed by methylation of norbixin [53,55]. Both oxidation of bixin aldehyde and methylation of norbixin are also taking place in the presence of enzymes (dehydrogenase and methyltransferase, respectively).

There is a great interest in carotenoids as natural sensitizers for application in DSSCs due to their light-harvesting and photoprotecting function in plants [56]. Considering all-*E* long conjugated C=C system in carotenoid molecules, they absorb in the blue-green region of the electromagnetic spectrum. Orange-red pigments from apocarotenoid pigment group, bixin and norbixin, are promising natural dye photosensitizers for DSSCs application as well [57].

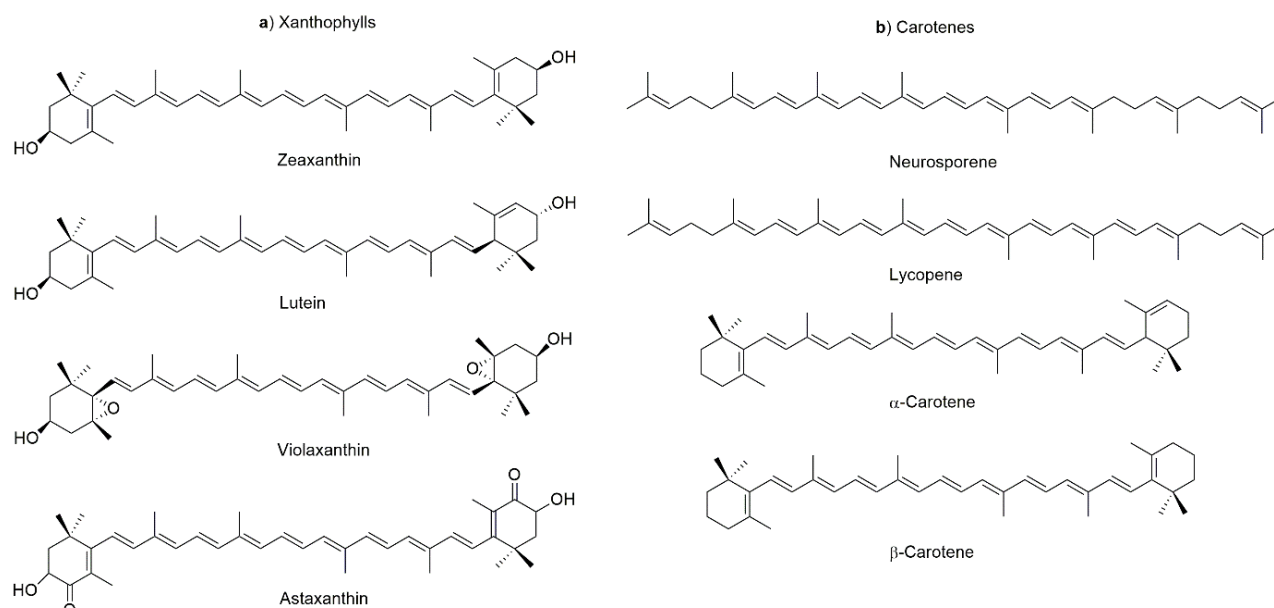


Figure 5. Carotenoid structure: a) Xanthophylls: zeaxanthin, lutein, violaxanthin and astaxanthin; b) Carotenes: neurosporene, lycopene, α -carotene and β -carotene

DSSCs assembled with two apocarotenoids indicated that the photocurrent conversion efficiency of norbixin ($\eta = 0.28\%$) is twice as high as that of bixin sensitized cells ($\eta = 0.12\%$). It was shown that the semiconductor TiO_2 can act as a catalyst for photodegradation process with a common mechanism with the formation of apocar radical cation [56]. DSSCs were also investigated using *Rauvolfia vomitoria* fruit extract rich in carotenoids as natural sensitizer of a TiO_2 thin film. Namely, a DSSC with $10\ \mu\text{m}$ TiO_2 film exhibited the best performances: $V_{\text{oc}} = 650\ \text{mV}$, $J_{\text{sc}} = 0.10\ \text{mA cm}^{-2}$, $\text{FF} = 0.65\%$ and $\eta = 0.05\%$. The short-circuit current density value increased directly with increasing the thickness of the TiO_2 film in the range of 5–10 nm which could be explained by the fact that a thicker electrode can absorb more photons, leading to a higher J_{sc} [58]. Relevant photovoltaic parameters of DSSCs sensitized with carotenoids and apocarotenoids are shown in Table 4.

Table 4. Photovoltaic parameters of DSSCs sensitized with carotenoids and apocarotenoids

No.	Name of plant	Class/name of pigment	Semi-conductor	Counter electrode	Electrolyte	Photovoltaic parameters				Ref.
						$V_{\text{oc}} / \text{mV}$	$J_{\text{sc}} / \text{mA cm}^{-2}$	FF, %	$\eta / \%$	
1	<i>Bixa orellana</i>	Bixin and Norbixin	TiO_2	ITO glass	I^-/I_3^-	350	1.28	0.35	0.16	[28]
2	<i>Tabebuia rosea</i>	Carotenoid	TiO_2	ITO glass	I^-/I_3^-	320	0.88	0.36	0.10	[28]
3	<i>Rauvolfia vomitoria</i>	Carotenoid	TiO_2	FTO glass	I^-/I_3^-	650	0.10	0.65	0.05	[58]
4	<i>Bixa orellana</i>	Bixin	TiO_2	Pt/ TiO_2 glass	I^-/I_3^-	410	0.65	46.7	0.12	[56]
5	<i>Bixa orellana</i>	Bixin	TiO_2	Pt paste coated on FTO glass	TBAI/ I_2	600	0.99	0.61	0.36	[43]
6	<i>Bixa orellana</i>	Bixin and Norbixin	TiO_2 NP/TiNT	FTO glass	I^-/I_3^-	630	6.19	18.9	0.74	[45]
7	<i>Bixa orellana</i>	Norbixin	TiO_2	Pt/ TiO_2 glass	I^-/I_3^-	500	1.13	48.6	0.28	[56]
8	<i>Tagetes</i>	Lutein	TiO_2	FTO glass	I^-/I_3^-	460	0.06	0.46	0.15	[27]

2. 4. Betalains

The best known pigments among betalains, betanin and indicaxanthin, were isolated and identified in the early 1960s. Indicaxanthin is a betaxanthin pigment from yellow-orange cactus pear (*Opuntia ficus-indica*), while betanin is a betacyanin pigment that is primarily responsible for the deep red colour of beet (*Beta vulgaris*) [59]. Betalains are natural hydrophilic, nitrogen-containing, Tyr-derived pigments, most frequently accumulated in epidermal/sub-

epidermal tissues of herbs belonging to the order *Caryophyllales* (red beet roots, graining/leafy amaranth, and coloured Swiss chard), and subfamilies of higher fungi including agaric *Amanita muscaria*, *Hydrocybe*, and *Hydrophorus* [60,61]. Even though betalains and anthocyanins differ both in their chemical structure and the biosynthetic pathway, they seem to have similar functions. Considering that those two pigments have never been found together in the same plant, it seems that they cannot exist together [60,61]. This is confirmed by the original name of betalain subgroups namely, betacyanins, which were labelled as “nitrogenous anthocyanins”, while the betaxanthins were labelled as flavonoids (Figure 6) [61]. Red beet containing roughly 75 to 95 % of betacyanins and 5 to 25 % of betaxanthins has been continually treated as the exclusive source of the betalains. The basic structure of all betalains is betalamic acid [4-(2-oxoethylidene)-1,2,3,4-tetrahydropyridine-2,6-dicarboxylic acid], which condensed with *cyclo*-DOPA [cyclo-L-(3,4-dihydroxyphenylalanine)] or its glycosyl derivatives builds red-violet betacyanins; hence, when condensed with various amino acids or amines, builds the yellow-orange immonium condensation products betaxanthins [61].

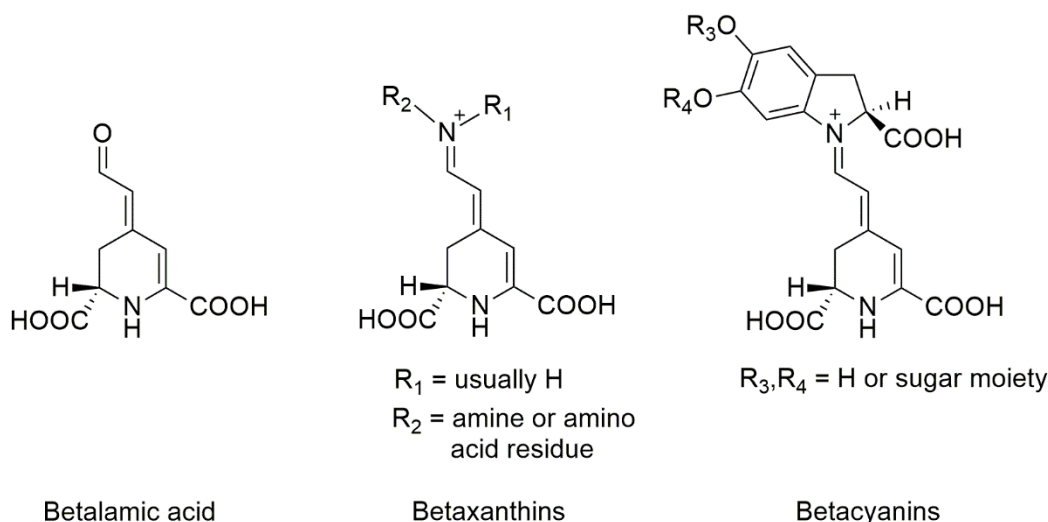


Figure 6. Structure of betalamic acid, betaxanthins and betacyanins

Generally speaking, the absorption properties of betalains are affected by both structural modifications/substituent effects and changing the acid-basic properties of the solvent used [60,62]. Owing to a strongly conjugated 1,7-diazheptamethine system, betalamic acid-derived moiety is the key chromophore of all betalains [60,63]. The visible region of absorption maximum for betaxanthins is between 460 and 475 nm, while betacyanins exhibit a shift of the absorbance maximum from 480 to 540 nm as a result of extended resonance (interaction of conjugated double bonds of 1,7-diazheptamethine system and aromatic ring of *cyclo*-DOPA) [63]. The second absorption maximum for betacyanins is in the UV region in the range of 270 to 280 nm due to *cyclo*-DOPA [61,62]. To provide the greatest stability of these hydrophilic pigments, the best method for their extraction represents the employment of water or 20 to 50 % methanol/ethanol solutions [62].

In addition to their charming colours, antioxidant activity and other biological properties such as anticancer, anti-inflammatory, chemopreventive *etc.*, betalain pigments have attracted the attention with their potential as natural sensitizers in DSSCs due to their 1,7-diazaheptamethine substructure [59,63].

Bharathi Devi and coworkers explored effects of microwave annealing on the performance of a DSSC assembled using betacyanins and betaxanthins extracted from *Beta vulgaris*. It was observed that the efficiency of microwave annealed DSSCs is much lower ($\eta = 0.16$ to 0.29 % depending on the irradiation time) than that of the conventionally annealed ones ($\eta = 1.11$ %) due to inefficient light scattering efficiency [64]. Analysis of the optical properties of a DSSC fabricated using betalain isolated from *Beta vulgaris* as a sensitizer, C, N, S co-doped TiO_2 (TU- TiO_2) as a semiconductor, and 75 % molar concentration of thiourea doped into TiO_2 nanoparticles, indicated a relative increase in the efficiency for 94 % and a decrease in the band gap making the solar cell more perceptive to visible light [65]. Table 5 shows the corresponding photovoltaic parameters of DSSCs sensitized with betalains.

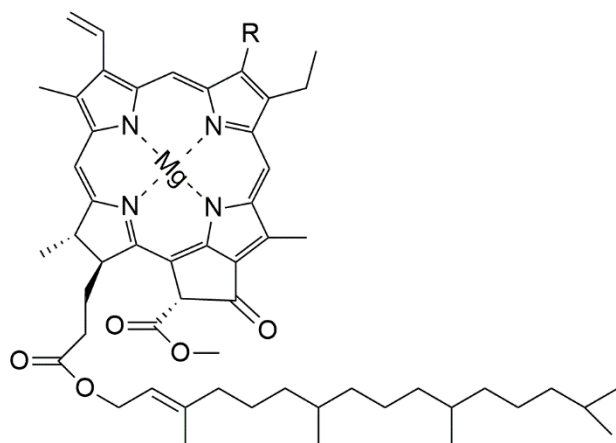
Table 5. Photovoltaic parameters of DSSCs sensitized with betalains

No.	Name of plant	Class/name of pigment	Semi-conductor	Counter electrode	Electrolyte	Photovoltaic parameters				Ref.
						V_{oc} / mV	J_{sc} / mA cm ⁻²	FF, %	η / %	
1	<i>Mirabilis jalapa</i>	Betalain	TiO ₂	FTO glass	I ⁻ /I ₃ ⁻	0.46	0.16	0.72	0.05	[29]
2	<i>Beta vulgaris</i>	Betalain	TiO ₂	FTO glass	I ⁻ /I ₃ ⁻	370	0.76	0.39	0.11	[33]
3	<i>Beta vulgaris</i>	Betalain	C,N,S co-doped TiO ₂ -(TU0.75) ^a	FTO glass	I ⁻ /I ₃ ⁻	350	0.42	0.61	0.36	[65]
4	<i>Bougainvillea</i>	Betacyanin	Nano-TiO ₂	FTO glass	NaI/I ₂	132	15.22	0.20	0.40	[24]
5	<i>Bougainvillea</i>	Betacyanin	Nano-TiO ₂	FTO glass	KI/I ₂	405	3.91	0.27	0.42	[24]
6	<i>Beta vulgaris</i>	Betacyanin and Betaxanthin (conventional extraction)	TiO ₂	FTO glass	KI/I ₂ /EG	310	7.47	0.48	1.11	[64]
7	<i>Beta vulgaris</i>	Betacyanin and Betaxanthin (5 min MW extraction)	TiO ₂	FTO glass	KI/I ₂ /EG	150	1.59	0.66	0.16	[64]

^acarbon-nitrogen-sulphur (C-N-S) co-doped titanium dioxide (TiO₂) nanoparticles containing 75 % of thiourea

2. 5. Chlorophyll

Energy for plant growth and further development is provided by natural complex green pigment molecules accumulated in plants, algae and some bacteria, known as chlorophylls (Chls) [66-68]. In 1818 Pelletier and Caventou [69] isolated Chls for the first time and coined this term meaning "green leaf" (translation from Greek). Three Nobel prizes were conferred to Willstätter R. in 1915 [70], Fischer H. in 1930 [71] and Woodward R. in 1965 [72], for their scientific contributions in elucidating the structure and chemical synthesis of Chls. There are five major chlorophyll (Chl) pigments (Chl *a*, *b*, *c*, *d* and *f*), varying mutually by a type of side chains linked to the tetrapyrrole moiety on the chlorin/porphyrin ring [67,68]. Chlorophylls *a* and *b* (Figure 7) are the key components of the photosynthetic systems in land plants and green algae. While Chl *b* is an antenna chlorophyll, Chl *a* is crucial in photochemistry and has a role both in light-harvesting and energy conversion [67,73].



Chlorophyll *a*, R = CH₃

Chlorophyll *b*, R = CHO

Figure 7. Structure of natural chlorophylls: chlorophyll *a* and chlorophyll *b*

Due to strongly conjugated tetrapyrrole moiety, Chls are capable to absorb light in the visible range. Chl *a* mostly exhibits visible light absorption in the red-orange region, while Chl *b* mostly absorbs in the blue-purple region of the electromagnetic spectrum [66]; poor absorption in the green spectral region is typical for both. Green appearance of Chls is due to their absorption features [67]. Natural Chls (Chl *a* and *b*) and Zn- or Cu-Chl derivatives (*i.e.* Zn- or Cu-chlorophyllins, pheophytins, pyropheophytins) are antioxidant, antimutagenic, antigenotoxic, anticancer, chemoprotective, and

antiobesogenic compounds with potential applications in medicine [67,68]. Chls and Chl-derivatives (various chlorophyllins) are in use as authorized food colorants E140 and E141 (food codes in the EU) [67,74]. Considering their advantageous light absorption properties, Chl pigments have the potential to serve as natural photosensitizers for DSSCs [75].

By using nanocomposite ZnO:TiO₂ (weight ratio 1:3) as a semiconductor material, and Chl extracted from broccoli, as a light-harvesting pigment, a DSSC was constructed with the efficiency of 0.171 % [76]. On the other hand, while using the same nanocomposite material, and the same natural pigment extracted from *Brassica rapa*, in another study a DSSC was produced exhibiting a slightly higher efficiency of 0.21 % [77]. When comparing the photovoltaic performances of DSSCs containing Chl and Chl:betalain mixture (volume ratio 1:1) as natural sensitizers, and the tetragonal TiO₂ nanoparticles as semiconductor, it was concluded that, cosensitization of light-harvesting pigments produces 5.5 times greater solar cell efficiency relative to a plain chlorophyll [78]. In this frame, Mensah-Darkwa and coworkers demonstrated that an increase in the efficiency of a DSSC based on a double-layer TiO₂/graphite oxide (GO) photoanodes compared to the one with a single-layer pristine TiO₂ photoanodes, might be a consequence of the rising GO content [78,79]. Siregar and coworkers investigated the significance of the annealing temperature of Mg-doped ZnO photoanode, of the manufactured DSSC containing natural light-harvesting pigment extracted from *Rhodomyrtus tomentosa*, which exhibits a strong absorption band at 610 nm. The maximum efficiency of $\eta = 3.53$ % was obtained in a DSSC with Mg-ZnO photoanode annealed at 500 °C [80]. When absorbed on TiO₂ nanoparticles, the absorption band of turmeric dye (containing up to 3 % curcumin as the active ingredient) is shifted to higher energy in the visible region. The broad absorption range indicates that the dye is effectively absorbed onto the TiO₂ nanoparticles, enabling it to harvest solar energy from a broader spectral range, which ultimately leads to a higher photocurrent. The overall efficiency $\eta = 0.22$ % was reached in a DSSC fabricated using turmeric dye [45]. Results of combined atomic force microscopy and photoluminescence analyses indicated that *Curcuma longa* dye thin films with a non-uniform granular structure absorbed in the range of 400 to 500 nm. The photoelectrochemical parameters determined by the finite element method simulation of a DSSC such as the short circuit current, the open-circuit voltage, and the fill factor were 0.13 mA cm⁻², 0.52 mV, and 0.83 %, respectively. The simulated DSSC based on *Curcuma longa* dye exhibited an efficiency about 0.86 % [81]. The corresponding photovoltaic parameters of DSSCs sensitized with Chls and other pigments are shown in Table 6.

Table 6. Photovoltaic parameters of DSSCs sensitized with Chl and other pigments

No.	Name of plant	Class/name of pigment	Semi-conductor	Counter electrode	Electrolyte	Photovoltaic parameters				Ref.
						V _{oc} / mV	J _{sc} / mA cm ⁻²	FF, %	H / %	
1	<i>Tridax procumbens</i>	Chlorophyll	TiO ₂	FTO glass	I ₂ /KI-lugol solution	170	0.31	0.40	0.02	[78]
2	<i>Tridax procumbens</i> / <i>Beta vulgaris</i>	Chlorophyll : Betalain = 1:1 ^a	TiO ₂	FTO glass	I ₂ /KI-lugol solution	270	1.16	0.34	0.11	[78]
3	<i>Brassia oleracea</i> var. <i>italica</i>	Chlorophyll	Nano-composite ZnO/TiO ₂ (1:3)	FTO glass	I ⁻ /I ₃ ⁻	0.55	/	/	0.17	[76]
4	<i>Mimosa pudica</i>	Chlorophyll	DL-0.71 wt.% GO ^b	Graphite	I ⁻ /I ₃ ⁻	284	0.016	0.035	0.1	[79]
5	<i>Malva verticillata</i>	Chlorophyll	TiO ₂		I ⁻ /I ₃ ⁻	540	1.42	55.4	1.70	[38]
6	<i>Brassica rapa</i>	Chlorophyll	Nano-composite ZnO/TiO ₂ (1:1)	Pt paste coated on FTO glass	PEO:KI/I ₂	0.333	/	/	0.076	[77]
7	<i>Brassica rapa</i>	Chlorophyll	Nano-composite ZnO/TiO ₂ (1:2)		PEO:KI/I ₂	0.546	/	/	0.194	[77]
8	<i>Brassica rapa</i>	Chlorophyll	Nano-composite ZnO/TiO ₂ (1:3)		PEO:KI/I ₂	0.500	/	/	0.210	[77]
9	<i>Bassiasco paria</i>	Chlorophyll	TiO ₂	FTO glass	I ⁻ /I ₃ ⁻	0.58	0.42	0.76	0.18	[29]
10	<i>Curcuma longa</i>	Curcumin	TiO ₂ NP / TiNT	FTO glass	I ⁻ /I ₃ ⁻	620	4.59	7.99	0.22	[45]
11	<i>Rubia tinctorum</i>	Anthraquinone	TiO ₂	FTO glass	I ⁻ /I ₃ ⁻	330	0.03	0.36	0.05	[27]

^avolume ratio; ^bdoublelayer photoanode with 0.71 wt.% graphene oxide

3. CONCLUSION

This review outlines various materials used in manufacturing DSSCs including semiconductor nanoparticles, types of electrolytes and types of counter electrodes. A special emphasis is placed on the selection of light-harvesting pigments as the DSSC part responsible for achieving high photovoltaic performances. Effects of the chemical structure of the pigment, particularly the anchoring groups, on the photovoltaic performance are also discussed together with the mechanism of their chemisorption onto the semiconductor.

In addition to beneficial environmental effects, the favourable physico-chemical properties together with affordability and sustainability make natural pigments promising candidates for advancing the DSSC technology. On the other hand, low efficiency and low stability still prevent their application at a larger scale. Regardless of the class they belong to, natural pigments do not achieve efficiencies greater than 3 %, either used alone or in a mixture. Hence, their future application, which would provide photovoltaic performance similar to that achieved by applying synthetic dyes, requires a concerted effort in terms of various optimizations of all DSSC components.

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Potencijal odabranih biljnih pigmenata za korišćenje u solarnim ćelijama aktiviranim bojom: trenutni status

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(Osvežimo naše znanje)

Izvod

Treća generacija solarnih ćelija, u koje spadaju i solarne ćelije aktivirane bojom, privukla je veliku pažnju istraživača tokom poslednjih decenija, prevashodno zbog svoje netoksičnosti i ekonomičnosti. U ovom radu sumirano je dosadašnje istraživanje biljnih pigmenata sa mogućnošću primene kao fotosenzitizatora u solarnim ćelijama, pri čemu je fokus stavljen na njihovo izolovanje, prečišćavanje i faktore koji utiču na njihova fizičko-hemijska svojstva. Istraživanja o solarnim ćelijama uglavnom su usmerena ka flavonoidima, antocijaninima, karotenoidima, betalanim i hlorofilu, kao ekološki najprihvatljivijim prirodnim fotosenzitivnim jedinjenjima. Pored toga, podaci o solarnoj efikasnosti, do kojih se došlo primenom različitih tipova poluprovodnika i elektrolita, takođe su prikazani u ovom radu. Osnovni cilj ovog rada je da se istaknu mogućnosti upotrebe prirodnih fotosenzitivnih pigmenata u izradi solarnih ćelija i da se stavi akcenat na one kandidate čijom će se primenom u solarnim ćelijama postići najbolje performanse.

Ključne reči: Fotonaponske ćelije; flavonoidi; antocijanini; karotenoidi; betalaini; hlorofil

