

Biophotovoltaics: Natural pigments in dye-sensitized solar cells



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HIGHLIGHTS

- Natural pigments are photosensitizers in dye-sensitized solar cells (DSSCs).
- Efficiency is still lower compared to synthetic pigments.
- The use of natural pigments such as carotenoids and polyphenols is cheap.
- General advantages of DSSCs are flexibility, color and transparency.
- Usage under diffuse light and therefore, indoor applications are possible.

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ABSTRACT

Dye-sensitized solar cells (DSSCs) which are also called Graetzel cells are a novel type of solar cells. Their advantages are mainly low cost production, low energy payback time, flexibility, performance also at diffuse light and multicolor options. DSSCs become more and more interesting since a huge variety of dyes including also natural dyes can be used as light harvesting elements which provide the charge carriers. A wide band gap semiconductor like TiO₂ is used for charge separation and transport. Such a DSSC contains similarities to the photosynthetic apparatus. Therefore, we summarize current available knowledge on natural dyes that have been used in DSSCs which should provide reasonable light harvesting efficiency, sustainability, low cost and easy waste management. Promising natural compounds are carotenoids, polyphenols and chlorophylls.

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1. Introduction

The idea of using the reactions of photosynthesis to convert sun light into electrical power appeared already by Melvin Calvin before 1974 [1]. The model was a photo-electrochemical cell based on a synthetic membrane where carotenoids were used as a wire inside the membrane. After absorption of a light quantum by a sensitizer molecule localized at one side of the membrane, an electron is transferred to a carotenoid and then diffuses through the

membrane to the other side where it is captured by an electron acceptor. This attractive model which was suggested for the first time to directly convert sun light into electric energy by using membranes and pigments quickly became textbook knowledge [2]. At the same time, Melvin Calvin also suggested a model for photochemical hydrogen production. Again, the model was based on the photosynthetic electron transport system [1]. Later it was directly shown that after illumination electrons are transferred from canthaxanthin, an accessory carotenoid of the photosynthetic system, to chlorophyll a, the electron collector system [3].

A similar approach has been taken in parallel in physical and chemical sciences [4]. Sun light is used to excite electrons of pigments, mainly metal complexes, into a higher energy level which are then transferred to the conduction band of a wide bandgap semiconductor. Compared to the well-known silicon devices, such dye-sensitized solar cells (DSSCs) cells are belonging to the emerging third-generation photovoltaic concept and use synthetic or natural dyes as light harvesting pigments [5,6]. They are also called Graetzel cells named after their publication in 1991 [7].

Abbreviations: DSSCs, dye-sensitized solar cells; TCO, transparent conductive oxide; ITO, indium tin oxide; FTO, fluorine doped tin oxide; FF, fill factor; Ru, ruthenium; Pt, platinum; Zn, zinc; Co, cobalt; I, iodine; Cs, caesium; Sn, tin; Ti, titanium.

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Conventional solar cells require a relatively thick and defect-free layer of expensive silicon in order to have reasonable photon capture and recombination rates. The light conversion efficiency of crystalline silicon solar cells is in the order of 25%; a DSSC currently reaches approximately 12.3% with a Zn-porphyrin and a Co-based electrolyte [8,9]. However, for DSSCs the potential to achieve production costs below 0.5 \$ per watt peak of solar electricity are reasonable [10].

Major advantages of DSSCs are the large flexibility in shape, color, transparency, and performance also under diffuse light [6,11]. DSSCs could be integrated into large varieties of products, e.g. hand bags or clothing, indoor applications, and building-integrated photovoltaics such as roll-able devices for walls of buildings or windows [12,13]. But many components of a DSSC remain to be optimized. We focus on the identification and usage of natural pigments as light harvesting elements in DSSCs. Natural pigments as photosensitizers in DSSCs have the potential to reach similar performances and stability as known from dyes based on metal complexes.

2. General composition, function and parameters of DSSCs

A DSSC is composed of two electrodes at least one of them transparent for light in the visible range [14]. In most cases glass covered with a transparent conductive oxide (TCO) material usually indium tin oxide (ITO) or fluorine doped tin oxide (FTO) is used. A basic DSSC setup is shown in Fig. 1. On the conductive surface ($\sim 15 \Omega/\square$ with a transmission of >80% from 400 to 700 nm) of the anode a nanoporous wide band gap semiconductor is deposited. Its nanocrystalline structure (nanoparticle size 20–50 nm) enhances the surface area by nearly a factor of 1000 while at the same time minimizing the optical absorption. This is usually the anatase modification of titanium(IV) oxide (TiO_2) which contains excess free electrons and is therefore an n-type semiconductor [15]. The light absorbing dye pigment is attached to the TiO_2 surface and should assemble an electrically homogeneous dipole layer [16]. Photoexcitation of the pigment from the ground state S to the excited state S^* leads to the injection of an electron into the conduction band of TiO_2 . This electron diffuses through the nanoporous TiO_2 and finally passes through the TCO layer

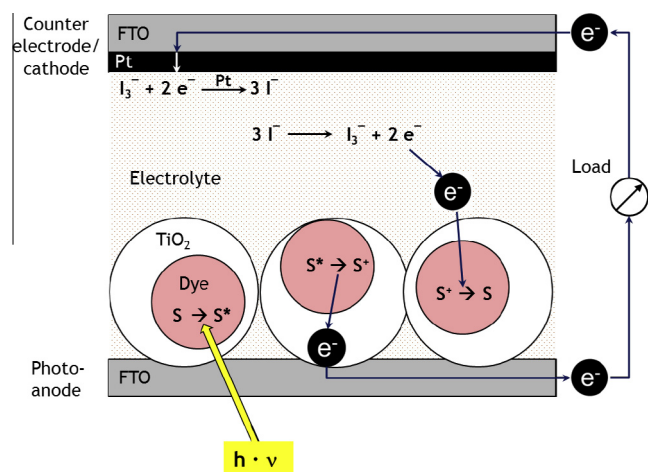


Fig. 1. Schematic setup of a DSSC. The photoanode and counter-electrode are based on fluorine-doped tin oxide (FTO) coated glass. The illumination ($h \cdot \nu$) of a DSSC with a liquid electrolyte containing I^-/I_3^- initiates a cascade of reactions which lead to an electrical current. Photons excite the dye molecule in the ground state (S) to its electronically excited state (S^*). The electronically excited dye molecule injects then an electron (e^-) into the conduction band of the semiconductor TiO_2 . The oxidized dye (S^+) is reduced by iodide (I^-). The generated tri-iodide (I_3^-) is reduced at the cathode by the catalyst platinum (Pt) to I^- which completes the cycle. The overall result is the direct conversion of light into electricity.

and the load (any electrical device). The oxidized pigment S^+ is restored by electron transfer from the electrolyte. A widely used liquid electrolyte is the iodide–triiodide (I^-/I_3^-) redox system in an organic solvent which penetrates into the nanoporous structure. I^- reduces the positively charged pigment whereby I_3^- ions are formed which diffuse to the cathode. The inner surface of the cathode contains either graphite or platinum particles as catalyst. There, I_3^- is reduced to I^- and the cycle is finished [17].

The ideal energetic pathway of an electron in a DSSC is shown in Fig. 2. The maximal obtainable voltage (ΔV) is the difference between the Fermi level of the conduction band of TiO_2 and the redox potential of the redox couple (I^-/I_3^-).

A DSSC can be characterised with an IV-diagram where the corresponding current (I) at rising voltage (V) is plotted (Fig. 3). At a bias of 0 V the short circuit current (I_{SC}) is measured and when the current reaches 0 A the open circuit voltage (V_{OC}) is defined. The maximum power output (P_{max}) generated by a DSSC is reached when the product of the current and the voltage is maximal. With the equation below, the maximum power is calculated. The corresponding factors are called current at maximal power (I_{mp}) and voltage at maximal power (V_{mp}).

$$P_{max} = I_{mp} \times V_{mp}$$

Often, the current density (J) [mA/cm^2] instead of the current (I) [mA] is stated to allow a better comparison between measurements of different solar cells. Therefore, the I_{SC} and I_{mp} become J_{SC} and J_{mp} , respectively, whereby J_{SC} and J_{mp} are independent from the photoactive area.

How efficient a solar cell can convert the power of the incident light into electricity is, beside its life time stability, in the center of interest. The solar energy to electricity conversion efficiency (η) is calculated with the following equation:

$$\eta = P_{max}/P_{in} = I_{mp} \times V_{mp}/P_{in} = I_{SC} \times V_{OC} \times FF/P_{in}$$

The incident power (P_{in}) is the irradiance illuminated on the DSSCs. P_{in} has to be measured beforehand. The efficiency is between 0% and 100%.

Besides I_{SC} , V_{OC} and η also the fill factor (FF) belongs to the four key performance parameters of a solar cell [5]. The fill factor is a value between 0 and 1 that describes the shape of the IV-curve, where a high value indicates a more preferable rectangular shape described by the following equation [6]:

$$FF = I_{mp} \times V_{mp}/I_{SC} \times V_{OC}$$

To compare different solar cell concepts and devices a standard light spectrum (AM1.5) and measurement conditions (homogeneous illumination of $100 \text{ mW}/\text{cm}^2$ at 23°C) are defined.

First experiments were performed mainly with dyes based on ruthenium (Ru) complexes e. g. N719 (di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II)) [18]. Later the use of metal-free synthetic dyes such as indoline dyes was introduced [19]. However, the overall electrochemical configuration, like composition of the electrolyte or the layer thicknesses, has to be adopted to obtain optimal efficiency of the DSSCs.

The basic principle of a DSSC with natural dyes is to exchange the above-mentioned synthetic dyes of the set-up of DSSCs with natural ones. Developing and optimizing materials for organic solar cells is generally not yet rational, but rather empirical. The reason for this is that multiple parameters have to be taken into account when new types of materials and dyes are designed for organic solar cells. The photovoltaic cell's efficiency does not only depend on the pigment's molecular structure, but also strongly on solid-state properties, such as morphology, self-assembly and aggregation of the dye molecules. In the case of DSSCs even more parameters have an influence on the efficiency such as the type

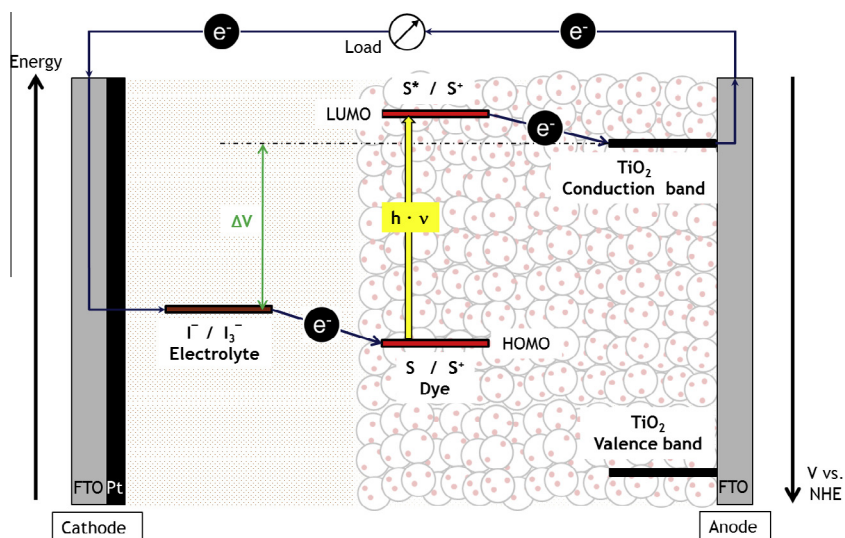


Fig. 2. Simple energy level diagram with electron transfer processes of a DSSC with liquid electrolyte. The maximal voltage (ΔV) achievable with a DSSC is defined as the difference of the redox potential of the electrolyte's redox couple (I^-/I_3^-) and the Fermi level of the semiconductor's conduction band. ΔV is equal to the open circuit voltage (V_{OC}). The gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the dye (S) influences its light absorption properties, which means the efficiency of getting electronically excited, oxidised and reduced and moreover, the spectral absorption range. However, other chemical structure characteristics of the dye and the binding between the dye and the TiO_2 also crucially influence the solar energy to electricity efficiency (η) of a DSSC. V vs. NHE means that the redox potential is relative to the redox potential of the normal hydrogen electrode (NHE).

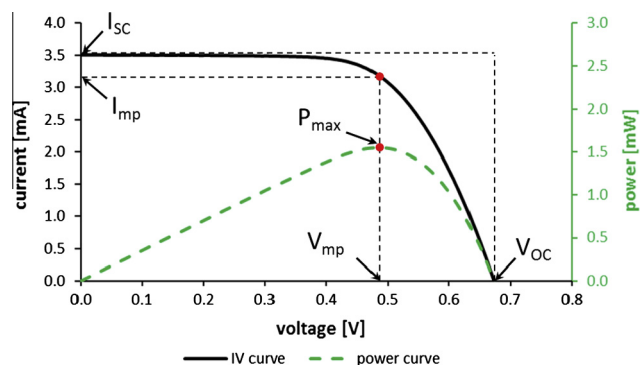


Fig. 3. Photocurrent-voltage characteristics of a DSSC. The photosensitizer was the ruthenium (Ru) complex dye N719. The liquid electrolyte contained the redox couple I^-/I_3^- . Similar curves are obtained with natural photosensitizers.

of the photoelectrode, the dye's anchoring group and the electrolyte with the respective redox couple. Hence, the optimal design of organic dyes regarding to an enhancement of the DSSCs' performance can only be derived from approximate trends. In general, the design of a photosensitizer consists of a donor-acceptor-substituted π -conjugated bridge. The acceptor part is the dye's anchoring group which is attached to the TiO_2 (Fig. 4a) [20]. Up to now mainly electrolytes known from DSSCs with synthetic dyes are used for DSSCs with natural dyes [21].

Dye-cocktails or co-sensitization could yield higher efficiencies if the absorption spectra of the different dyes do not overlap too much in order to extend the overall absorption spectrum. However, limitations could be in a lower TiO_2 surface area for a particular dye or intermolecular interactions between the different dyes which may result in lower electron injection efficiency [22].

3. Natural pigments used in DSSCs

Based on the results with Ru-complexes also a variety of metal-organic dyes such as Zn-porphyrin derivatives have been tested [23]. Prerequisites for photosensitizers to function in DSSCs are

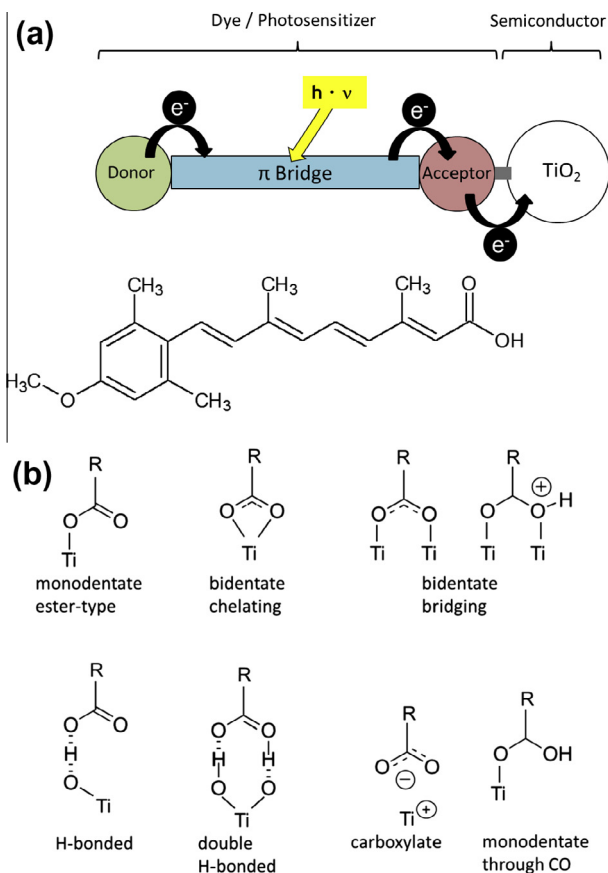


Fig. 4. (a) Donor- π -acceptor structure principle of an organic dye in DSSCs with TiO_2 photoanodes. (b) Possible binding modes of a COOH-group to TiO_2 .

the absorption in the visible or near-infrared regions of the solar spectrum and the binding to the semiconductor TiO_2 [24]. The functional group necessary to interact with the TiO_2 surface is a carboxylic or other peripheral acidic anchoring group [6,25]. The

Table 1
Natural dyes used in DSSCs.

Plant source	Structure or structural class	Photoactive area (cm ²)	J_{sc} (mA/cm ²)	V_{oc} (mV)	η /FF	Remark	Reference
Black rice	Anthocyanin	1	1.142	551	na/0.52	Fractionated extract	[38]
Erythrina Variegata	Carotenoid, Chlorophyll	1	0.776	484	na/0.55	Fractionated extract	[38]
Rosa xanthina	Anthocyanin	1	0.637	492	na/0.52	Fractionated extract	[38]
Kelp	Chlorophyll	1	0.433	441	na/0.62	Fractionated extract	[38]
Capsicum	Carotenoid	1	0.225	412	na/0.63	Fractionated extract	[38]
Begonia		0.2	0.63	537	0.24/0.72	Extract	[40]
Rhododendron		0.2	1.61	585	0.57/0.61	Extract	[40]
Perilla		0.2	1.36	522	0.5/0.70	Extract	[40]
Mangosteen pericarp		0.2	2.69	686	1.17/0.63	Extract	[40]
Mangosteen pericarp	α -Mangostin/ β -mangostin	0.2	2.55	621	0.92/0.58	Fractionated extract	[40]
Mangosteen pericarp	Rutin	0.2	2.92	611	1.12/0.63	Fractionated extract	[40]
Hibiscus sabdariffa L.	Cyanidin-3-glycosides/delphinidin-3-glycoside	–	1.63	404	0.37/0.57	Aqueous extract	[78]
Beta vulgaris rubra	Betalains	0.5	9.5	425	1.7/0.37	Aqueous extract	[79]
Rhoeo spathacea Stearn	–	–	10.9	496	1.5/0.27	Ethanol extracts, aqueous electrolyte	[80]
Bixa orellana L.	Bixin	0.5	1.1	570	0.37/0.59	Fractionated extract	[81]
Spinach	Modified chlorophyll/neoanthin	–	11.8	550	3.9/0.60	Isolated compounds	[37]
Spinach	Modified chlorophyll/violaxanthin	–	11.4	540	3.7/0.61	Isolated compounds	[37]
Spinach	Modified chlorophyll/lutein	–	12.5	540	4.0/0.59	Isolated compounds	[37,37]
n.a.	Modified chlorophyll/ β -carotene	–	13.7	530	4.2/0.58	Isolated compounds	[37]
Chaste tree fruit	–	–	1.06 ^x	390	na/0.48	Extract	[82]
Mulberry	–	–	0.86 ^x	422	na/0.43	Extract	[82]
Cabbage-palm fruit	–	–	0.37 ^x	442	na/0.61	Extract	[82]
Calafate fruit	Delphinidin	–	0.96	520	na/0.56	Aqueous extract	[83]
Jaboticaba skin	Peonidin	–	2.6	660	na/0.62	Ethanol extract	[83]
Gardenia fruit	Crocin/ crocin	1.0	2.84 0.45	430 580	0.56/0.46 0.16/0.60	Isolated compounds	[84]
Red Sicilian orange "Moro"	Cyanin	0.5–1.0	3.84	340	0.66/0.50	Fruit juice	[85]
Eggplant skin	Nasunin	0.5–1.0	3.40	350	0.48/0.40	Ethanol extract	[85]
Prickly pear	Betaxanthin	1.0	8.8	389	2.06/0.60	Acidified juice	[16]
Tradescantia Zebrina	Anthocyanin	–	0.63	350	0.23/0.55	Ethanol extract	[86]
Kapok	Anthocyanin/carotenoid	–	0.87	360	0.3/0.49	Ethanol extract	[86]
Pitaya	Not reported	–	0.5	330	0.17/0.52	Ethanol extract	[86]
Canarium odontophyllum	Anthocyanin	–	2.45	385	0.59/0.62	Ethanol extract	[87]
Ixora sp.	Anthocyanin	–	6.26	351	0.96/0.44	Ethanol extract	[87]
C. odontophyllum + Ixora sp.	Anthocyanin	–	6.26	384	1.13/0.47	Mixed ethanol extract	[87]
C. odontophyllum + Ixora sp.	Anthocyanin	–	9.80	343	1.55/0.46	Ethanol extracts in consecutive layers	[87]
Rhododendron sp.	Anthocyanin	0.27	0.85	544	0.33/0.72	Ethanol extract	[88]

n.a. = not applicable x = current not normalized to cell area.

TiO₂ binding moiety of large π -aromatic molecules is very often a carboxylic group [26].

There are several possible chemical functional groups that are able to bind the dye to the TiO₂. The best anchoring groups for metal oxides are phosphonic acids followed by carboxylic acids and their derivatives, such as acid chlorides, amides, esters or carboxylate salts [25]. The carboxylic group is the most frequently used anchoring group.

In order to form bonds, the dye's binding groups react with surface hydroxyl groups of the metal oxide. In the case of phosphonic acids or carboxylic acids, a reversible binding with high equilibrium binding constants is established between the photosensitizer and TiO₂. In basic conditions (usually pH \geq 9) the dyes are easily desorbed again. There are several binding modes between the TiO₂ and a dye molecule with at least one carboxylic group (COOH) (Fig. 4b) [25,27,28]. Which mode of chemisorption between TiO₂ and COOH is prevalent depends on the dye's structure, its anchoring groups, the pH, and the metal oxide's preparation [25].

The interaction of TiO₂ with cyanin, an anthocyanidine, is via the hydroxyl-ketone tautomer of cyanin [24]. The main issues which have to be taken into account are an appropriate anchoring of the molecules while allowing a fast and energetically optimized charge transfer. The π electrons of the carboxylic group should be in resonance with the π electrons of the polyene backbone in order

to be able to shift the electrons through the anchoring group into the conduction band of the semiconductor. The color of dyes also depends on such delocalized π electrons.

Over 80 metal-free organic dyes that can be prepared by cheaper methods have been described [20]. The highest η was 9.5% with a novel indoline dye [29]. A special method for the modification of the TiO₂ layer with the metal-free organic dye D102 has recently been reported to result in a significant increase of η [30].

Natural dyes as photosensitizers for DSSCs are very attractive because they are of low cost, abundant in supply, and sustainable. An early proof that carotenoids can function as photosensitizers in DSSCs was with 8'-apo- β -caroten-8'-oic acid bound to TiO₂. A photocurrent stable for 1 h under continuous radiation was measured and an ordered monolayer structure of the TiO₂-bound carotenoid has been suggested [31]. Since then, carotenoids have already been successfully used in DSSCs [32–34]. The highest η with single carotenoids was 2.6% [35]. The optimal length of carotenoids consists of seven conjugated π bonds [36]. By using carotenoids in combination with chlorophyll derivatives η can be increased to up to 4.2% [37]. This increase is probably due to similarities to photosynthesis.

Several extracts have been discovered as efficient photosensitizers. The effect of a black rice extract has been attributed to an anthocyanin with an o-hydroxyquinon moiety [38]. A different

Table 2
Chemical structures of natural dye classes.

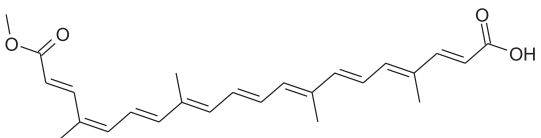
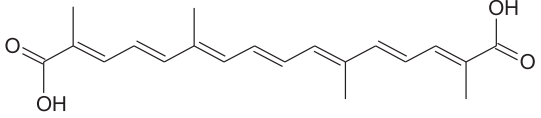
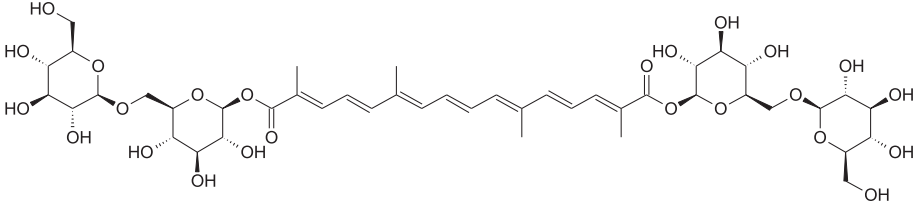
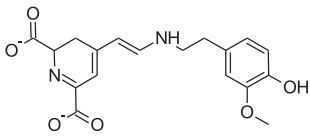
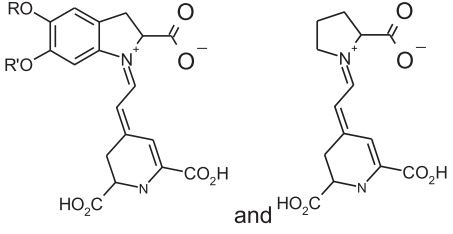
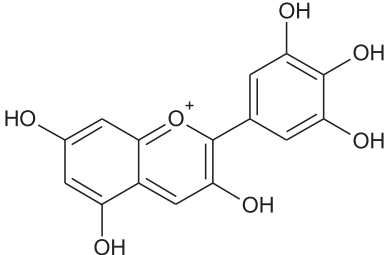
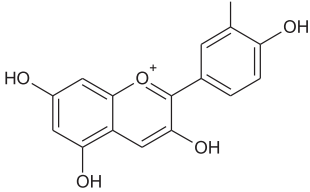
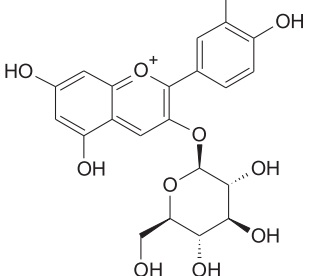
Name	Chemical structure
Bixin	
Crocetin	
Crocin	
Betaxanthin	
Betalains	 , R and R' = H or R = β -D-glucose
Delphinidin (an anthocyanidin)	
Cyanidin (an anthocyanidin)	
Cyanin (an anthocyanin)	

Table 2 (continued)

Name	Chemical structure
Nasunin (an anthocyanin)	
Peonidin (an anthocyanidin)	
α-Mangostin	
β-mangostin	
Chlorophyll a	
Rutin (a flavonol glycoside)	

(continued on next page)

Table 2 (continued)

Name	Chemical structure
Methyl-3-carboxy-3-devinylpyropheophorbide (a modified chlorophyll)	
Neoxanthin	
Violaxanthin	
Lutein	
β -Carotene	

study showed that amongst 20 plant extracts a mangosteen pericarp extract showed the highest efficiency η of 1.17%. The active component has been described as rutin [39]. An overall comparison identified an extract of *Rhoeo spathacea* with an efficiency η of 1.49% as attractive source amongst others [40]. The glycosides of anthocyanidins, the anthocyanins, seem to be more efficient than the anthocyanidins. An explanation could be the better solubility in H_2O . Nevertheless, the interaction of cyanidin with TiO_2 particles for the use in DSSCs was suggested already in 2007 [41].

The natural dyes used so far in DSSCs are summarized in Table 1. Data are often obtained under different conditions and device setups by different authors and therefore, they are in some cases difficult to compare directly. The photosensitizers belong to different chemical classes, which contain mainly carotenoids, betalains, flavonoids, or chlorophylls (Table 2). A high η of 2.06% was obtained with an extract of Sicilian prickly pear [21]. Promising natural carotenoids are crocetin or bixin.

Stability of natural photosensitizers in DSSCs is debated. To protect natural photosensitizers from degradation DSSCs are assembled under an inert atmosphere [42]. The stability of anthocyanins and betalains when protected from direct sunlight is more than one year [21]. An alternative approach to this issue of depleting dyes is mimicking nature: an annual exchange of dyes

might be the solution. However, the development of concepts and solutions for an easy-to-handle exchange of the dye in such devices is still required.

For Zinc oxide (ZnO) as semiconductor it has been shown by a computational Discrete Fourier Transform study that the carotenoid retinoic acid would be most efficient compared to other natural carotenoids, e.g. crocetin and bixin [43]. But ZnO has mainly been describes as interlayers in bulk heterojunction solar cells [44].

4. Improvements of future DSSCs

The most efficient dyes are synthetic and therefore, still petroleum based. Some of them even require limited heavy metals as active centers what makes the recycling more difficult. Carotenoids, chlorophylls, anthocyanins or other natural dyes as photosensitizers are sustainable and are available in large amounts. However, efficient and fast extraction methods for purification are necessary.

The pigments of DSSCs degrade when exposed to ultraviolet radiation in combination with oxygen. A UV protection foil consisting of UV filters or UV absorbing luminescent chromophores (which emit at longer wavelengths) can be applied on the outside of the anode. Inside the DSSCs antioxidants could be added to protect the pigments from oxidation.

Foliage trees replace their leaves every year. Therefore, in foliage trees the stability of the photo conversion system is less than one year. Silicon-based solar cells are guaranteed to last for 25 years. This time might not be easily reached by solar cells with natural pigments for light harvesting. Possible solutions would be to replenish the pigments every year. This is only feasible when it is cheap and easy to handle. Another possibility would be lowest price foil solar cells that can be removed from the wall or roof as a whole.

The currently most efficient Graetzel cells are still slightly less efficient in comparison to standard silicon-based solar cells. But as a result of the light absorption mechanism of the pigments, DSSCs work even in low-light conditions. Therefore, DSSCs are able to work under cloudy skies and indirect sunlight, whereas inorganic semiconductor-based photovoltaic cells would suffer a cut-off at some lower limit of illumination. Since the cut-off of DSSCs is so low, they are even proposed for indoor use, collecting energy for small devices from the light inside buildings [45].

The major disadvantage of the conventional DSSC design is the use of the liquid electrolyte, which requires an appropriate encapsulation against leakage and contamination. Furthermore, at high temperatures, stability problems have to be addressed. High temperatures cause the liquid to expand what stresses the sealing of the DSSCs. Another major drawback of the electrolyte solution are volatile organic solvents requiring again a careful sealing. This, along with the fact that the solvents permeate plastics, has not allowed a large-scale outdoor application yet.

Antireflective (AR) coating exists for conventional photovoltaics. However, the processes have to be adjusted to flexible DSSCs since sintering is done at temperatures too high for polymers and the AR coatings are not flexible yet. To apply AR coatings on DSSCs, conductive polymers with higher melting temperatures, e.g. based on graphene [46], are already in use [47].

UV filters may be used since carotenoids and other (natural) dyes are sensitive to UV-light. Tetraethylorthosilicate has been described to decrease UV degradation of *Beta vulgaris* pigments in DSSCs [48].

Several different improvements and modifications of the TiO₂ semiconductor have been described. It has been claimed that TiO₂ with a dispersion of nanosized copper (Cu) that is embedded in an inert carbon shell could increase the efficiency η compared to pure TiO₂ by at least 23% [49]. An increase of the TiO₂ surface area with well-aligned hierarchical TiO₂ tubular macro-channel arrays, obtained by hydrothermal synthesis, resulted in an improvement of η of approximately 0.8% [50]. Furthermore, an increase of the particle size of TiO₂ in the light scattering layer leads to an enhancement of η of approximately 5% [51]. Bamboo-type TiO₂ nanotubes improved η due to higher dye loading by a factor of 1.4 [52]. The addition of carbon black to the dye alizarin yellow and TiO₂ enhanced the conductive band of nano-TiO₂ and thereby increased the short-circuit current [53]. TiO₂ submicro-rings could help in synthesizing TiO₂ directly onto TCO [54]. Infrared rapid thermal annealing reduced the sintering of TiO₂ from hours to minutes [55].

An increase of η with the Ru based dye N719 was obtained when copper phthalocyanine constituted an additional shell to the TiO₂-dye complex. Due to cascade charge transfer this increase was 41.08% [56].

Pt, the catalyst used for the counter electrode, has a limited natural availability and high costs. Therefore, DSSCs with a more efficient Pt cathode have been prepared by homogeneous deposition employing ethylene glycol with a promising improvement of η [57]. In a different approach, Pt coated cathodes were replaced by hierarchical micro/nano-structured cobalt sulphide spindles with η very close to that of the DSSCs with Pt containing electrodes

[58]. Another promising approach to replace the Pt coated electrode with a similar η are porous carbon plates as a conductive substrate with vertically oriented ordered mesoporous carbon films as the catalytic layer [59].

The I^-/I_3^- redox system has been replaced with a more efficient system based on cobalt complexes [10,60]. With this electrolyte an efficiency η of 12.3% was reached which is the highest η of a DSSC obtained so far [61,62]. Another suggestion for the replacement of the I^-/I_3^- electrolyte is a new heteroleptic copper(I) complex with a phosphonic acid anchoring ligand [63].

A further goal is to make both electrodes photoactive. Such cell types are called double junction hybrid DSSCs. All natural pigments described here inject electrons into *n*-type semiconductors like TiO₂ at the photoanode after light absorption. Recently, positive (*p*-)type semiconductors like nickel(II) oxide (NiO) or copper(I) thiocyanate (CuSCN) that transport positive holes have been reported [6,20]. Pigments working with such *p*-type semiconductors must be able to take electrons from the *p*-type semiconductor upon excitation with light. The electron is then transferred to the electrolyte which is currently again the I^-/I_3^- redox system. Prerequisites of such dyes working with *p*-type semiconductors are that the highest occupied molecular orbital (HOMO) of the dye must be below the valence band of the *p*-type semiconductor and that the lowest unoccupied molecular orbital (LUMO) must be higher than that of the redox potential of the electrolyte. The photosensitizer at the anode attached to an *n*-type semiconductor, e.g. carotenoids, absorbs light in the blue range of the spectrum and a photosensitizer attached to a *p*-type semiconductor at the cathode should absorb red light and transmit positive holes into the semiconductor [6]. In such a way the utilizable light spectrum is considerably broadened what should increase η significantly.

Using a solid state electrolyte system improves the stability of a DSSC and facilitates its fabrication. But η of solid state devices is lower compared to η of DSSCs with a liquid electrolyte [23]. However, solid-state mesoscopic perovskite-sensitized solar cells yielding a η of over 15% have been described recently [64–66]. Another promising new type of an all-solid-state, inorganic DSSC that consisted of the *p*-type direct bandgap semiconductor CsSnI₃ and *n*-type nano-porous TiO₂ with the dye N719 showed an η of 10.2% [67,68].

A successful attempt to maximize the surface area and thereby to increase the efficiency η of DSSCs was the arrangement of single DSSCs like needles around a branch of a pine tree to capture sun light from all directions [69]. The anode was composed of a spiral Ti wire (without TCO) coated with TiO₂ to which the Ru dye N719 was attached. The anode was wrapped around a cathode which consisted of either a straight Pt or Ti wire coated with a Pt film. The whole composition was placed inside a glass tube filled with I^-/I_3^- redox couple electrolyte. Several such 3D-DSSCs were arranged in series-parallel connections to simulate a pine tree. Efficiencies η were above 3%.

A future big advantage for the usage of natural pigments for DSSCs is the possibility of recombinant expression and therefore, large scale production of such dyes. The genes coding for the enzymes which are involved in the synthesis of the pigments can be expressed in microorganisms, either in the wild-type form or with mutations that lead to a modified product [70–74].

Single-walled carbon nanotubes show high electron mobility but cannot be used as such in DSSCs. Therefore, modified single-walled carbon nanotubes are required. An M13 phage that expresses a pVIII major coat protein with a peptide insert binding to single-walled carbon nanotubes-TiO₂ nanocrystals has been selected from a phage library [75]. Such nanocomposites were used as photoanodes in DSSCs which may increase stability of large modules. The efficiency η with the Ru-complex dye N719 was 10.6%.

To come closer to natural photosynthesis, a major part of photosystem I of a thermophilic cyanobacterium has been used as photosensitizer [76]. The efficiency η was 0.08% which leaves significant optimization challenges. A future goal is the coupling of the DSSC's charge separation mechanism to oxidative phosphorylation and to split H₂O into molecular H₂ and O₂ for energy storage [4]. This would also involve photosystem II or a similar complex where oxidation of H₂O occurs [77].

5. Cost estimations of photosensitizers

The price of the dye can be calculated according to the following equation [21]:

$$P_{\text{total}} = \Gamma \times M_{\text{dye}} \times P_{\text{mass}} / I_{\text{AM1.5}} \times \eta$$

P_{total} is the price per Watt peak (€ W^{-1}), Γ is surface coverage of the dye (mol cm^{-2}), M_{dye} is the molecular mass of the dye (g mol^{-1}), P_{mass} is the price per mass (€ g^{-1}), $I_{\text{AM1.5}}$ is the sun light intensity of AM 1.5 (W m^{-2}) and η is the efficiency as already described. The price P_{total} for ruthenium based compounds has been calculated to approximately 0.8 € W^{-1} [21]. Therefore the costs of the dye for a DSSC based panel of 3 kWp will be in the range of 2400 € [21]. It has been estimated that the dyes contribute to 10–15% to the total costs of a DSSC.

P_{total} for organic dyes has been claimed to be in a similar range than those for ruthenium based dyes [21]. This is mainly due to costly synthesis. However, stability has not been included in the formula.

The costs for natural dyes are currently very difficult to estimate. They mainly depend on the availability of the source and the extraction method. One needs to concentrate on cheap sources or even waste streams of the food industry, e.g. skins of pressed grapes. Then, it still has to be experimentally clarified how much purification of a plant extract is needed. Since complexes of different molecules or combination of dyes may work more efficiently, crude extraction may be sufficient which would dramatically decrease the costs for natural dyes. In addition, there is no chemical by-product waste management. Furthermore, natural dyes are usually non-toxic and fully biodegradable. To increase η of DSSCs with natural dyes, intensive basic research is growing from physics to biology. Taking all these arguments into consideration, natural dyes are expected to be significantly cheaper than synthetic dyes used in DSSCs. As discussed, only stability is an uncertain parameter, but could probably be improved by adding stabilizers like antioxidants, e.g. vitamin C or E (unpublished).

6. Conclusions

Natural pigments can be used as photosensitizers in DSSCs. However, the efficiency η is still by a factor of 3–4 lower than with synthetic dyes. But natural pigments are normally non-poisonous, can be disposed easily, and should be cheaper and more environmentally friendly than synthetic metal complexes. Therefore, natural dyes as light harvesting elements in DSSCs can contribute to a sustainable solution for the future energy production. Nature supplies a huge variety of putative structures for photosensitizers and combinations may enhance stability, efficiencies, and sustainability.

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