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MATERIAL SCIENCE AND NANOTECHNOLOGY

Use of natural dyes for the fabrication of dye-sensitized solar cell: a review

Cherry BHARGAVA[1] and **Pardeep Kumar SHARMA**[2*]

[1] Department of Electronics and Telecommunication Engineering, Symbiosis International (Deemed University),
Pune, Maharashtra, India-412115

[2] Stratjuris Partners, Westport, Baner, Pune, Maharashtra, India-411045

Abstract. The increasing concern for worldwide energy production is the result of global industrialization and decreasing energy resources. Despite the cost factor, solar energy continues to become more popular due to its long-term nature as a resource and growing conversion efficiency. A dye-sensitized solar cell converts visible light into electricity. The efficient use of dye as a sensitizer is the critical factor in enhancing the performance of the dye-sensitized solar cell. Natural dyes are found in abundance in leaves, flower petals, roots, and other natural resources. Due to the advantages of natural dyes such as cost-effectiveness, the simpler extraction process, and being environmentally friendly, etc., researchers are working extensively to replace synthetic dyes with natural ones. This paper highlights the various types of natural dyes and their effect on the efficiency of the dye-sensitized solar cell.

Key words: DSSC (dye-sensitized solar cell); efficiency; natural dye; performance; synthetic dye.

1. INTRODUCTION

As the global population is growing, energy resources are depleting at a similar pace. Although fossil fuels are the most abundant source of energy, by the next century, these fuel sources will have been depleted [1]. For a green and healthy environment, renewable energy resources are emphasized. Renewable resources such as solar and geothermal energy, wind power, etc. have been explored to satisfy the demand for energy. By the photosynthesis process, the sun is proven as the most efficient resource of energy for all living creatures. If approximately 1% of the earth's surface is covered with solar cells with 10% efficiency, then it will provide twice as much energy as required [2]. Solar cells are widely used in small-scale devices and power panels.

The photovoltaic effect was observed while inserting light on silver chloride during photography. The first photovoltaic cell was developed in 1839 by Becquerel using a liquid electrolyte and an electrode. Modern solar cells are very dissimilar from this first cell and use a solid-state junction between p and n-type semiconductors to convert light into electrical power. The first advanced solid-state solar cell was built by D.C. Chapman at Bell Labs in 1954. The silicon-based crystalline solar cells are fabricated by the Czochralski method. The efficiency of these cells is dependent on the temperature [3]. The second-generation solar cells such as Cadmium telluride (CdTe), Copper indium gallium selenide (CIGS) and amorphous silicon (a-Si) use solar cells as thin film and powder form. Although these cells are flexible and portable, efficiency is the critical parameter [4]. Thin-film solar cell based on a multinary compound Cu(In, Ga)Se2 has an efficiency of 20% [5].

A dye-sensitized solar cell belongs to third-generation solar cells, which have higher efficiency than a thin film-based solar cell. It was introduced by Gratzel and O'Regan in 1991. Michael Gratzel was awarded the 2010 Millennium Technology Prize for his contribution in the field of solar cells [6]. The basic structure of the dye-sensitized solar cell is made up of semiconductor coated photoanode electrode, sensitizer, electrolyte, and counter electrode [7].

Dye-sensitized solar cells are a subgroup of photoelectrochemical solar cells since they both depend on an electrolyte. They have a couple of additional features like an organic or organometallic dye sensitizer and a nanoparticulate semiconductor rather than a solid crystal semiconductor. They are a potentially significant development in solar technology, with efficiencies up to 11% reported in the literature [8]. But later, 15% solar cell efficiency as a prototype was introduced [9]. When the zinc-oxide nanorods are deposited, the quantum efficiency is enhanced [10].

While dye-sensitized solar cells do not have as high efficiency as their conventional silicon counterparts, there are already advantages for this new technology. The first and most obvious advantage is their low cost. Due to cheaper starting materials, ease of production, dye-sensitized solar cells are comparatively much less expensive to prepare in comparison with silicon crystal solar cells. Also, their overall production is less detrimental to the environment than the output of conventional silicon cells [11]. Furthermore, dye-sensitized solar cells have considerable flexibility in shape, colour, transparency, and performance also under diffuse light [12, 13]. Dye-sensitized solar cells could be incorporated into massive varieties of products, e.g. hand baggage, building assimilated photovoltaics for walls of buildings or windows [14–16].

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[*] e-mail: pardeep.sharma@stratjuris.com

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The performance of the dye-sensitized solar cell depends on the dye used in that cell. This article reviews various dyes used for the fabrication of dye-sensitized solar cells along with their efficiency.

2. WORKING OF DYE-SENSITIZED SOLAR CELL

In general, the dye-sensitized solar cells work on the pure phenomena of photoelectrochemical reaction, i.e. when sunlight or light from any source which has potential more significant than the threshold energy of the electrons in the dye, illuminates the cell, then the dye molecule within the cell disintegrates to impart an electron which moves towards the cathode and the remaining dye molecule reaches the electrolyte layer and recharges itself [17, 18]. A deficiency is created in the electrolyte, which is completed by the electron released from the anode, and thus the circuit completes, and the current moves within the circuit as shown in Fig. 1.

2.1. Steps to generate electrical energy from sunlight

The following steps convert photons (sunlight) to current (electrical energy) [19]. Figure 2 shows the pictorial view of sunlight to electrical energy conversion.

1. Photo sensitizers absorb photons that are adsorbed on the TiO_2 surface.
2. Metal Ligand Charge Transfer (MLCT) transition is responsible for the excitation of the photosensitizers from the ground state (S) to the excited state (S^*). Oxidation of the photosensitizer (S^+) takes place due to the injection of the excited electron into the conduction band of the TiO_2 photoanode.
   - Excitation process:

$$S + hv \rightarrow S^*. \tag{1}$$

   - Charge Injection:

$$S^* \rightarrow S^+ + e^-(TiO_2). \tag{2}$$

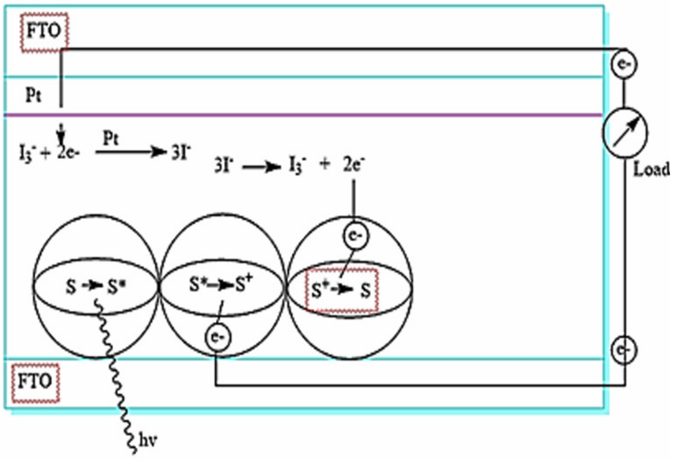

Fig. 1. Schematic representation of working of dye-sensitized solar cell [16]

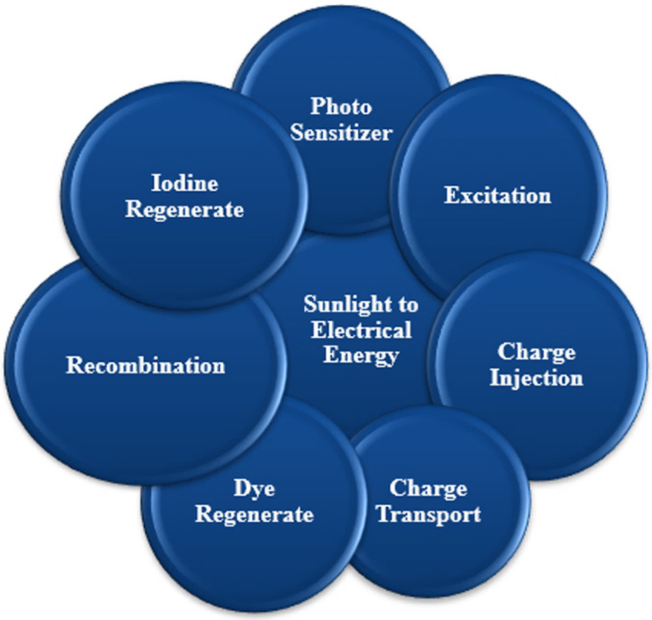

Fig. 2. Sunlight to electrical energy conversion

3. Consequently, the injected electron in the conduction band of TiO_2 diffused through TiO_2 particles toward the back-contact glass substrate and successively reached the charged electrode through the external load and wiring
   - Transportation of charge:

$$e^-(TiO_2) \rightarrow e^-(CE). \tag{3}$$

   Here, CE is the charged electrode.
4. When the electron is accepted by oxidized photosensitizer (S^+) from the I^- ion redox mediator regeneration of the ground state (S) takes place, and the I^- is oxidized to the oxidized state, I_3^- (equation 4). Nevertheless, two main (undesirable) recombination reactions decrease the overall efficiency of DSSC. The excited electron in titania can straightway recombine with the oxidized dye sensitizer or with the oxidized iodide redox couple in the electrolyte [20] (equation (5)).
   - Regeneration of dye:

$$2S^+ + 3I^- \rightarrow 2S + I_3^-. \tag{4}$$

   - Recombination:

$$S^+ + e^-(TiO_2) \rightarrow S. \tag{5}$$

5. After diffusing toward the counter electrode, the oxidized redox mediator I_3^- is reduced to I^- ions.
   - Regeneration of iodine:

$$I_3^- + 2e \rightarrow 3I^-. \tag{6}$$

Generally transfer of an electron to I_3^- can happen either at the boundary between titania and electrolyte or at areas of the anode contact (mostly TCO layer on glass) that are exposed to the electrolyte [21]. The efficiency of DSSC is governed by the following energy sections

- The excited state of the dye photosensitizer.
- The ground state of dye photosensitizer.
- The Fermi level of the titania electrode.
- The redox potential of the mediator (I^-/I_3^-) in the electrolyte [22].

The speedy retrieval of the dye sensitizer is significant for achieving longer stability in order to maintain an enduring separation of charge which is critical for the performance of the dye-sensitized solar cell.

2.2. Performance parameters for a dye-sensitized solar cell

When the light is switched on in a dye-sensitized solar cell containing the circuit system, open-circuit voltage Voc and short circuit current Isc may be obtained [23]. The ratio between maximum output power received at the output to the sunlight power is known as the overall efficiency of solar energy. The fill factor, overall conversion efficiency are the essential performance parameters of the dye-sensitized solar cell are [24]:

2.2.1. Open circuit voltage

The voltage of the cell is known as the open-circuit voltage when the cell is stated as open-circuited, and the output current is nil [25].

$$Voc = Vt \ln\left\{\left(\frac{Isc}{Io}\right)+1\right\} \tag{7}$$

2.2.2. Short circuit current (Isc)

The cell is stated as short-circuited when the output voltage is nil. The short circuit current is equivalent to the conversion of the total number of photons to hole-electron pairs [26].

$$Isc = I + Io\left\{\exp\left(\frac{V}{Vt}\right)-1\right\} \tag{8}$$

Here, Vt is the threshold voltage, and Io is the output current

2.2.3. Fill factor (FF)

It is a vital parameter for the determination of the efficiency of the cell. At a potential somewhere between an open circuit and short circuit, the maximum output power (P_{max}) can be obtained, where the cell delivers the highest power output with the voltage (V_{max}) and current (I_{max}).

$$FF = \frac{Vmax.Imax}{Voc.Isc} \tag{9}$$

2.2.4. Conversion efficiency (η)

This parameter is associated with the overall performance of the cell. It is stated as the ratio of maximum power obtained by the cell (P_{max}) to the power of the incident radiation on the illustrative area of the cell (P_{in}).

$$Efficiency = \frac{Fill\ Factor.Voc.Isc}{Incidental\ Optical\ Power} \tag{10}$$

It depends on the temperature of the cell, quality of the illumination, and the spectral distribution of the intensity, due to which, a standard measurement condition is used for the testing of solar cells [27].

3. COMPONENTS OF A DYE-SENSITIZED SOLAR CELL

The dye-sensitized solar cell consists of vital components such as conductive glass substrates, metal oxide semiconductor coating, the dye, the redox electrolyte, and the counter electrode [6]. Each component is essential for the conversion of sunlight into the current [28–30] (Fig. 3).

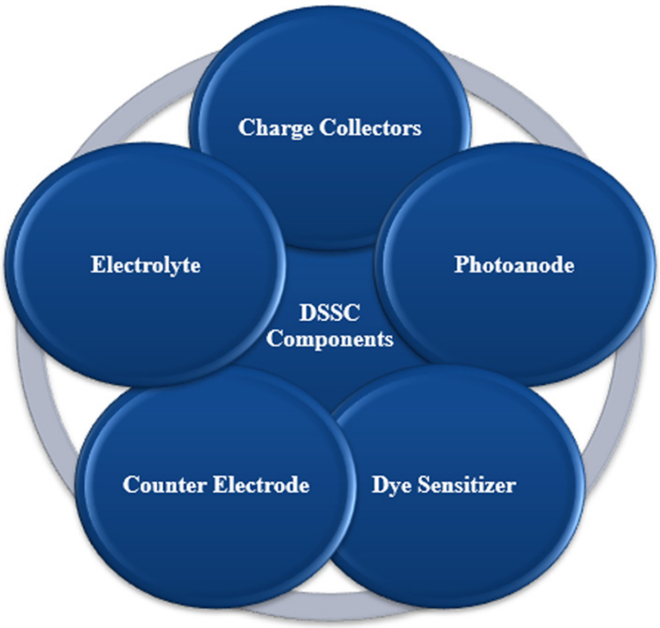

Fig. 3. Components of dye-sensitized solar cell

The conductive glass substrates used for the dye-sensitized solar cell serve as a backbone of the cell. This solid surface provides structural support for the dye-sensitized solar cell, and most importantly, it provides a complete path through which current can enter and leave the dye-sensitized solar cell when in a circuit [31]. It allows the light to pass into the cell with limited optical attenuation and also a surface to which the TiO_2 is bonded. Various types of organic or organometallic dye molecules can be used as a sensitizer for dye-sensitized solar cells, where incoming light interacts with the dye molecule, exciting an electron to a higher energy state [32]. The electrolyte in a dye-sensitized solar cell is the electron donor for the dye. It is composed of a redox couple that acts as a charge transport medium between the dye on the electrode and the counter electrode. Finally, the counter-electrode is a second TCO coated slide with catalyst deposited and heated onto the surface. It helps in the transfer of electrons into the redox electrolyte, and therefore the very little amount of catalyst is required for the cell [2]. The various components of a dye-sensitized solar cell are shown in Fig. 3.

3.1. Charge collectors

The dye-sensitized solar cells are typically assembled with two sheets of transparent conductive oxides acting as charge collectors and a substrate for the deposition of the semiconductor and catalyst [33, 34]. Transparent conducting oxides (TCO) are metal oxides coated on the soda lime (generally) glass substrate to make it electrically conductive. To reduce the energy loss, its electrical conductivity should be kept as high [35]. Generally, TCO coating is either of fluorine-doped tin oxide-FTO (SnO_2: F, FTO) or indium-doped tin oxide-ITO (In_2O_3: Sn, ITO). Nowadays, FTO coated glass is used in dye-sensitized solar cells in place of ITO coated glass due to its better thermal stability at high temperatures. The transmittance of the substrate is a deciding factor to select the TCO substrate. Recently aluminium-doped zinc oxide (AZO) has also been explored [36]. Table 1 shows the difference between various TCO coatings.

3.2. Photo anode

The photoelectrode (or photoanode) in a dye-sensitized solar cell is prepared from a skinny layer of sensitized semiconductor material (usually TiO_2, ZnO, SnO_2, etc.) with an extensive bandgap, deposited onto the TCO substrate [33]. High light-harvesting efficiency (LHE) is achieved if the semiconductor layer offers a vast surface area (high roughness) in order to get a considerable amount of sensitizer molecules adsorbed [37].

Titanium dioxide (TiO_2) is the most efficient material among the several choices of wide-bandgap semiconductors for dye-sensitized solar cell and have attracted considerable attention because of its lower cost, non-toxicity, availability in the market, biocompatibility and has excellent chemical stability [38]. The method to prepare TiO_2 nanoparticles film is very easy, and no vacuum is needed. Generally, photoelectrode thin films encompass mesoporous structured titania, obtained after sintering of a TiO_2 thin film at a temperature higher than 400°C [39]. Based on the annealing temperature, it is present in three crystalline structures, namely anatase, rutile, and brookite [40–42]. Rutile is stable while anatase and brookite are metastable.

As brookite is very difficult to synthesize, for photocatalytic activity, only rutile and anatase polymorphs are considered vital [43]. However, pure anatase displays an advanced photocatalytic activity than pure rutile [44].

3.3. Dye sensitizer

A dye is stated to be a substance which imparts colour and which has a specific affinity towards the substrate it is being applied upon. There has been a prodigious number of dyes that have been used to prepare efficient polymer solar cells [45].

3.3.1. Characteristics of dye

Some of the stringent characteristics a dye should possess for being coated on a dye-sensitized solar cell substrate are as follows:

- Since more than 50% of solar energy is emitted in the region from 400–800 nm, dyes that absorb in this region are preferred as a broad absorption spectrum helps in capturing as much of the solar radiation as possible.

Table 1

Difference between various TCO coatings

Sr. No.	Parameter	Indium-doped Tin Oxide Coated Glass	Fluorine-doped Tin Oxide Coated Glass	Aluminium-doped Zinc Oxide coated Glass
1	Temp (°C)	350°C	600°C	600°C
2	Transparency	Medium in visible light	Better to visible light	UV reflectivity is high, and transparency to visible light is better
3	Resistance	Resistance rises with temperature	Resistance is constant up to 600°C	Ideal for temperature-sensitive polymer substrates
4	Thermal stability	Lower	Excellent	Excellent
5	Conductivity	Moderate conductivity	Good conductivity	Excellent conductivity
6	Tolerance	Moderate	High	High
7	Coating	ITO coated on the passivation layer of the glass surface	On a glass surface, FTO is coated directly	Using etching, patterning of films is more facile
8	Molecular structure	Cubic structure	Tetragonal structure	Hexagonal structure
9	Reflectance in the IR zone	Lower	Higher	Higher
10	Specified Sheet resistivity	≤ 10 ohms/sq	≤ 10 ohms/sq	≤ 10 ohms/sq
11	Transmittance occurs	550 nm – $\geq 83\%$	550 nm – $\geq 85\%$	400–1000 nm = 82–83%
12	Film thickness	1800–2000 Å	1800–2000 Å	8000–8500 Å

- The extinction coefficient of the dye molecule should be high over the whole absorption spectrum. This assists in the absorption of most of the light within a monolayer of the dye because an increase of the optical density of the electrode deteriorates the photovoltage and also causes diffusion problems in the electrolyte at high current densities.
- The dye should be soluble in a particular solvent for adsorption onto the electrode and should not be absorbed by the electrolyte.
- The bonding of the dye with the substrate (affinity) should be of remarkable strength, and it should get adsorb strongly on the surface of the semiconductor to make sure that the electron is injected efficiently into its conduction band and to avoid regular leakage from the electrolyte [46].
- The electron released should have enough excitation energy when it moves through the cell to meet the electrode.
- The dye should be able to transfer the electron to the TiO_2 rapidly in order to avoid undesirable recombination to the ground state of the dye [47].
- A redox electrolyte may be used for regeneration of the dye (such a dye should be used) [45]. Also, the oxidized state of the dye must have a more positive potential than the redox couple in the electrolyte. The dye should stay stable in its oxidized form, allowing it to be reduced by an electrolyte.

3.3.2. Classification of dyes

There are broadly two general classifications of the dyes natural and synthetic (human-made). Synthetic dyes require the usage of scarce elements in their making and are challenging in treating, while natural dyes are easily processed able and can be made out of just any natural material like peels of fruits, barks of trees, leaves, fruit juices, fruit pulps, etc. Moreover, as a substitute to the noble Ru complex sensitizers, organic dyes show many advantages like easily designable molecular structures, natural synthesis, cost-effectiveness, lesser environmental issues, and higher molar extinction coefficients [48]. So, they can be considered a better substitution of synthetic, once they attain higher efficiency.

Some functional groups that are present in the dyes maintain the affinity with the electrode they have been coated on, thus enhancing the charge transfer. Natural dyes are generally used with titanium dioxide (TiO_2) (nanoparticles) coating as an electrode, as this material exists in abundance and shows higher affinity with the dyes. Associativity is a significant issue with these natural dyes, as the proper functional groups needed to enhance it is known as an anchoring group, which should make bonds with the titania via surface hydroxyl groups. The carboxylic group and its derivatives are generally part of this group. Hydroxy groups also show the tendency of binding onto TiO_2 [49]. Furthermore, sulfonate and silane have also been used. Structures of efficient sensitizers containing binding groups (phosphonic acid) were first established by Pechy *et al.* [50].

The difference between natural dyes and synthetic dyes are shown in Table 2. Due to the stability problem and colour fading issues, natural dyes are less efficient. The synthetic dyes have a maximum absorption range in the solar spectrum. Therefore, these sensitizers produce better output than natural dyes.

3.3.3. Review of various dyes for dye-sensitized solar cell

The different natural dyes that are used for the fabrication of dye-sensitized solar cells are reviewed and summarized in tabular form, as shown in Table 3. The performance of the dye-sensitized solar cell is evaluated by using various parameters such as open-circuit voltage, short circuit current, fill factor, and efficiency [51]. The plant pigmentation can be understood by maximum wavelength (λ_{max}). The comparative performance parameters of the natural dye-based dye-sensitized solar cell, with semiconductor electrode TiO_2, are shown in Table 4.

Table 2
Difference between natural dye and synthetic dye

S. No	Parameter	Natural dye	Synthetic dye
1	Fabrication Process	Simple chemical procedure	Requires multi procedures, which are costly and time-consuming
2	Availability	Natural dye is 100% available	Long term availability of man-made dyes is a problem
3	Efficiency	As the degradation of natural dye is higher, the efficiency is lower	The efficiency of synthetic dyes is higher
4	Cost	Natural dyes are cheap, as they are naturally available and require fewer chemical procedures	Synthetic dyes are costly due to their production process
5	Stability	Less stable due to the degradation process	More stable
6	Environmental effect	Environmentally friendly because of its natural occurrence	Due to its chemical nature, its effects are harmful to the environment
7	Absorption rate	400–700 nm range of the solar spectrum	up to 800nm range of the solar spectrum
8	Reproduction	Reproduction of the same shades is difficult	Easy to reproduce
9	Variety	Limited range of colours	Wide range

Table 3
Review of different dyes used and their performance as a sensitizer

S. No	Dye used	Result obtained	Reference
1	Blueberry	The photovoltaic performance is reduced due to dye aggregation and intermolecular energy transfer. The efficiency achieved is 1.13%	[53–55]
2	Dragon fruit, cabbage and grape	The voltage and current of dye-sensitized solar cells increase with light, the efficiency of dragon fruit, red cabbage, and grapes are 0.015%, 0.006%, and 0.011% respectively	[56]
3	Basella Alba Seeds	The basella alba seeds extracted dye is applied on nanocrystalline photoelectrode titanium oxide, which is further deposited on tin oxide, 48.5% film factor and 0.115% efficiency is achieved	[57]
4	Calotropis	With the dye extracted from Calotropis, better visible absorption and better temperature response at an enhanced temperature range are achieved	[58]
5	Olive leaves, red hibiscus	Numerical modelling has been studied using MATLAB. It has been shown that the photovoltaic performance of olive leaves is higher than red hibiscus flowers	[59]
6	Plant pigmentation	Efficiency is optimized (up to 50%) by using a source measure unit, due to irradiation time and dye stability	[60]
7	Blackberry	Without any polymer electrolyte, efficiency is 0.076%, the efficiency increases up to 0.242% when PAN liquid is used	[49, 54, 61–63]
8	Plant leaves dyes	The efficiency of five Chlorophyll dyes extracted are Fig (0.49%), Black Tea (0.08%), Green tea (0.03%), Henna (0.05%), Schinus terebinthifolius (0.73%)	[64]
9	Ziziphus jujuba leaves	The efficiency is 1.077%. It has been reported that the dye structure is highly connected with the TiO_2 surface	[7, 64]
10	Lemon leaves dye	The efficiency reported using lemon leaves dye is 0.036%. The efficiency is low because of poor dye absorption, which inhibits charge transfer to titanium	[65]
11	Hibiscus dye	Hibiscus enhances electron transfer, as it is ascribed to anthocyanin and adheres to TiO_2 surface. The efficiency is 1.19%	[16, 53, 61, 62, 66, 67]
12	Red Sicilian orange juice dye	For optical activity, cyanine and delphinidin are the responsible pigments. The efficiency is 1%	[49, 58]
13	Flower based dye: *Luffa cylindrica* L	The dye-sensitized solar cell exhibited open voltage of 0.52 V, short circuit current 0.44 mA cm^{-2}, fill factor of 0.60, efficiency of 0.13% and IPCE $\sim$30% (at $\lambda = 430$ nm)	[68]
14	Wild Sicilian prickly pear dye	The existence of carboxylic groups similar to that of Ru poly-pyridyl complexes offers the benefits of better interaction between the dye. The efficiency is 2.06%	[69–71]
15	Seed based dye: Eruca Sativa seeds	It has been reported that while using lithium iodide as an electrolyte, the conversion efficiency becomes double. 0.725% of efficiency is reported	[64]
16	Purple cabbage	Anthocyanins absorb long-wavelength lights and are water-soluble in nature. The 0.75% conversion efficiency is reported using purple cabbage extracted dye	[53, 72]
17	Red cabbage	This article is focused on developing dye as a precursor. The red cabbage extracted dye is used, and the efficiency reported is 2.90%	[67, 73]
18	Begonia	Anthocyanin in Begonia dye extract was stable till 150°C. The efficiency is 1.86%	[74]
19	Pomegranate	ORAC and VIS technology are used to study the anthocyanin property or pomegranate seed extracted dye. The efficiency is 1.15%	[7, 75–77]
21	Spinach leaves dye	The efficiency reported, using spinach dye, is 4%, the visible absorption range is 422–659 nm	[53, 72, 75, 78, 79]
22	Red rose petals dye	The efficiency reported with red rose dye is highest, i.e. 0.81%	[80]
23	Red turnip	The efficiency reported is 1.7%, which is 50% than the N179 base cell	[81]
24	Eggplant	Due to variable factors such as light intensity, and TiO_2 linkage, eggplant extracted dye produces different results. The efficiency reported is 0.64%	[64, 69, 71]

S. No	Dye used	Result obtained	Reference
26	Strawberry	Delphinidin-based dyes are more used than Cyanidine and pelargonidin-based dyes, due to the potential of embedding titania and transferring photons. Strawberries are rich in pelargonidin and blackberries and blueberries in cyanidin. The efficiency is 0.62%	[55, 82, 83]
27	Wormwood	The percentage efficiency of wormwood has enhanced from 0.524% to 0.9% due to the advanced application of dyes over the substrate	[72, 84]
28	Wakame	The 4.6% efficiency is reported, and dye-substrate affinity was high	[85]
29	Turmeric (Curcumin Dye)	As compared to deprotonated curcumin dye, K_2CO_3 is stabilized more and has an efficiency of 9.9%	[53, 83, 86]
30	Papaya leaf dye	The efficiency of the cell is directly related to HUMO and LUMO; the efficiency reported with papaya leaf extract is 0.28%	[87]
31	Calotropis leaves	The leaves are covered in a white powder which helps in alleviating heat by scattering incident radiation and efficiency increased to 0.214% than 0.108% for cells without powder	[88]
32	Mexican PreHispanic	The efficiency using Mexican pre-Hispanic dyes is reported as 0.24%	[89]
33	Areca catechu	The energy conversion rate is high, with an efficiency of 0.38%. The fill factor is 62.9%	[90]

Table 4

Performance parameters of natural dye-based dye-sensitized solar cell

Dye Solution	Reference	Pigment	λmax (nm)	Isc (mA)	Voc	FF	η(%)
Rhododendron	[101]	Anthocyanin	0.530	0.689	0.585	60.9	0.57
Yellow rose	[101]	Xanthophyll	487	0.600	0.554	57.1	0.270
Rosella (Hibiscus sabdariffa L.)	[102, 103]	Anthocyanin	520	1.630	0.400	0.57	0.370
Erythrina variegata	[48, 104]	Chlorophyll	451 492	0.780	0.480	0.55	–
Hibiscus surattensis	[105, 106]	Anthocyanin	545	5.450	0.390	0.54	1.140
Raspberries	[107, 108]	Betacyanin	560	0.090	0.340	61.10	0.380
Cherries	[7, 109, 110]	Betacyanin	500	0.460	0.300	38.30	0.180
Wild Sicilian prickly pear	[81]	Betalin	465	8.200	0.380	0.38	1.190
Ivy gourdfruits	[111, 112]	β – Carotene	458 480	0.240	0.640	0.49	0.990
Bitterleaf	[113, 114]	Chlorophyll	400	0.070	0.340	0.81	0.690
Spinach	[75]	Chlorophyll	437	0.470	0.550	0.51	0.130
Festuca ovina	[115]	Chlorophyll	420 660	1.180	0.540	0.69	0.460
Red cabbage	[116]	Anthocyanin	537	0.500	0.370	0.54	0.130
Pomegranate	[117]	Anthocyanin	412 665	2.050	0.560	0.52	0.590
Shiso	[101]	Chlorophyll	440 600	3.560	0.550	0.51	1.010
Botuje	[118]	Flavonoid	400	0.690	0.050	0.87	0.120
Henna	[119]	Anthocyanin	518	1.870	0.610	0.58	0.660
Ficus retusa	[120]	Chorophyll	670	10.900	0.500	0.27	1.490
Anethum graveolens	[121]	Chlorophyll	666	0.960	0.570	40.00	0.220
Madder	[122]	Anthraquinone	540	0.540	0.389	0.69	0.100

Dye Solution	Reference	Pigment	λmax (nm)	Isc (mA)	Voc	FF	η(%)
Yemenihenna	[123]	Chlorophyll	–	0.407	0.306	28.1	0.117
Sumac/Rhus	[124]	Anthocyanin	650	0.930	0.394	0.41	1.500
Tageteserecta	[125]	Xanthophyll	465	2.891	0.475	0.61	0.800
Morinda lucida	[126]	Anthocyanin	440	1.150	0.350	0.63	0.250
Gardenia yellow	[127]	Carotene	450	0.960	0.540	0.62	0.320

4. SUMMARY OF NATURAL DYES FOR DYE-SENSITIZED SOLAR CELL

As the literature depicts, many researchers are working on enhancing the efficiency of natural dyes. The conversion efficiency of the dye-sensitized solar cell is dependent on many other vital parameters [52].

It has been observed that, out of all plant pigments, anthocyanins are preferred because their absorption spectrum range is broader, i.e. gamut of red to purple [91]. Secondly, the energy absorption is enhanced in the case of chlorophyll, as it has two absorptive peaks. Another plant pigment like betalin also has a good absorption range.

The best results with natural organic dyes come from spinach with 4% efficiency [53, 72, 75, 79], red beetroot 2.71% [78, 92] and red cabbage 2.9% [93, 94]. These natural entities are rich in anthocyanin, betalains, and chlorophyll, or any such strong light sensitizers. Currently, numerous organic dyes have been used to produce output as perfect as the inorganic dyes, but the result seems to falter and would not achieve the maximum laid down by the inorganic dyes [95]. Thence, a fair amount of research work is being inputted in determining the perfect environment for the lasting and efficient functioning of the solar cells [96].

4.1. Problems associated with natural dyes

For enhancing the stability and efficiency of the dye-sensitized solar cell, many researchers are working rigorously. But still, the efficiency of natural dyes is less as compared to the human-made dyes, for dye-sensitized solar cells [66, 97–100]. Some problems with natural dyes are listed here:

- In the presence of sunlight, the dye causes instability issues in the dye-sensitized solar cells. The human-made dye such as ruthenium has less degradation in the presence of sunlight, so it shows more excellent stability.
- In dye-sensitized solar cells, there is a problem of poor absorption in the solar spectrum, especially in the red part. Due to poor absorption, a limited current is generated, which limits the output efficiency of the cell. Natural dyes are poor absorber than human-made dyes.
- If inhaled, ingested, or absorbed through the skin, natural dyes can cause harmful effects, for example, logwood has further ingredients such as haematein and hematoxylin can cause irritation or inflammation.
- Availability of raw material may depend on season or species, which can be problematic for researchers, whereas human-made dye can be produced in the laboratory throughout the year.

5. CONCLUSION

Over the past few years blackberries, blueberry, hibiscus and spinach-based dyes were frequently used. The high anthocyanin content of blackberry and blueberry and high chlorophyll concentration in spinach is a reason for their frequent usage. It should also be noted that a significant amount of research has been put into improving the efficiencies of red beetroot, red cabbage, and red turnip—this review article emphasizes natural dye and performance parameters of the dye-sensitized solar cell. The vital point for an efficient dye-sensitized solar cell is cost-effectiveness, abundance, and its environmentally friendly nature. Further research on natural dyes for increasing the stability and efficiency of dye-sensitized solar cells is encouraged. An alternative to increase stability and absorption range is hybrid dyes, which is a mixture of natural and human-made dye, such as mixing of chlorophyll dye and anthocyanin dye boosts up the efficiency. The sensitizer should have high life and high extinction coefficient, which proves sufficient binding between semiconductor and sensitizer. The hydroxyl and carboxyl groups should be present in the dye. The addition of graphene with natural dye extract may enhance the efficiency of nature dye-based dye-sensitized solar cell.

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