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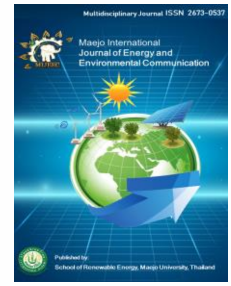

ARTICLE

Natural dye (chlorophyll, anthocyanin, carotenoid, flavonoid) photosensitizer for dye-sensitized solar cell: A review

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A B S T R A C T

For many years, dye-sensitized sunlight cells (DSSC), which are feasible and have significant potential to harvest and convert light into renewable energy, have been the subject of serious research. DSSC is a great alternative for low-cost solar panels due to its simplicity in fabrication and acceptable efficiency. While synthetic dyes can produce higher efficiency, their production costs and complexity in synthesizing toxic chemicals that are harmful to the environment, people, and the environment present another problem. Therefore, several studies have focused on natural dyes extracted from plants (chlorophyll-anthocyanin, flavonoid and carotenoid) because of their advantages such as high absorption, low cost, no toxicity, eco-friendly and easy extraction. This review also highlights the development of dye-sensitized sun cells by using natural dyes as photosensitizers.

1. Introduction

Electricity is an essential element of human life. It is a key factor in modern technology, economic development, and quality of life (Krishnamoorthy et al., 2021). Most electricity from Thailand comes from natural fuels like oil, natural gas and coal. These fuels must go through combustion before being converted into electrical energy (Nguyen et al., 2020). Pollution from combustion, including wastewater and other wastes, can also take the form of gases, dust, and smoke. This harms the ecosystem and contributes to the greenhouse effect, among other things (Sophanodorn et al., 2020). Nonrenewable energy is to blame for a number of environmental issues, including pollution, acid rain, layer loss, and temperature change. Nonrenewable resources such as fossil fuels cannot be replenished quickly after they are used to supply our ever-increasing energy demands (Ramaraj et al., 2015). Renewable energy sources such as sunlight, wind and tides can withstand nonrenewables like fossil fuels. Photovoltaic systems (solar cells) convert sunlight into electricity. It plays a major role among all renewable resources (Bhuyar et al., 2021). This energy can be used routinely in buildings and vehicles that are exposed to the sun for long periods of time. Economical with less industrial waste. Fossil fuels are a leading cause of climate change (Ramaraj & Unpaprom, 2019). The rate at which greenhouse gases are rising rapidly is 49 gigatons per year (GT CO2eq/year in 2010). In 2010, 78% of total global emissions came from dioxide gas emissions, mainly from industrial processes and fossil fuels. Concentrations of greenhouse gases in the atmosphere could climb from the current level of 430 ppm if current activities are not mitigated CO2eq by 2011 to 1300ppm by 2100. This may lead to a 4.8°C rise in global

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surface temperatures in extreme cases (Lau and Soroush 2019). This led to the development of renewable energy sources to address environmental issues. The sun is the most sustainable source of energy (Unpaprom et al., 2021). Cleaner, carbon-free energy that can keep up with future demand is one of its main advantages. The world has realized pollution's negative effects on the environment (Manmai et al., 2019). As the global population's energy demand increases in response to economic, industrial, technological, and social developments, adequate energy supply is becoming a priority as many countries are focusing on renewable energy sources (Manmai et al., 2020). To replace natural fuel sources to reduce the environmental and human health impact.

Converting to renewable energy is a way to reduce our dependence on fossil fuels. Renewable energy can also be defined as the energy used to replace fuel (Wannapokin et al., 2017). There are two main types of energy nonrenewable and renewable energy. One is coal, natural gas, nuclear, and the other is an energy source that can be used again (Unpaprom et al., 2015). Renewable energy includes solar, wind, biomass, hydrogen, and other clean energy. The sun is the source of solar energy. It is a form of renewable energy that is utilized and then naturally emerges. It is safe and clean energy (Vu et al., 2018). Use It can be converted to electric power using a solar cell Energy device. Solar energy is clean and does not pollute the surrounding environment (Mejica et al., 2021). It was completely silent at work. Without Noisy, wear-free. Easy to use, requires very little maintenance. Most countries, especially those that are near the Equator, have it. It is almost like having an electricity source. There are two main ways to utilize solar energy: producing electricity or using solar power to heat.

The environment Solar energy plays an increasing role in developing alternative energy sources for human life. The best way to convert Solar energy is through photovoltaics (Khammee et al., 2021). However, this can be very costly because of the high cost involved in the production. Solar cells are made of silicon elements. These have already undergone purification and are prepared to be rolled out. The manufacturing process may suffer as a result of this. Thus, solar cells were invented. When considering the source of solar energy, it is very attractive because it is clean and sustainable. in bringing solar energy to use Most solar energy is cheap. converted into electrical energy using a device called Solar cells, which are mostly made from silicon, have disadvantages of being expensive and fragile during the manufacturing process. for solar cells that photosensitive dye so called "”ye-sensitized solar cells (DSSCs)" (O'Regan & Gratzal, 1991) as an alternative to solar cells.

Photovoltaic technology is gaining popularity as it has the potential to generate green energy. Its abundant resource base can meet the world's energy needs (Mejica et al., 2020). However, solar energy is easy to extract using photovoltaic (PV) technology and inexpensive (Kabir et al., 2019). The photovoltaic system has seen tremendous development over the years. It evolved from its first generation to the current generation in which the dye-sensitized, or DSSC, cell is now. Although the solar cell is still in the experimental stage and under development, recent research results have significantly improved its performance (Roy, 2020). Researchers are attracted to the DSSC's low cost, low light absorption, easy fabrication and environmental friendliness. However, DSSC is less efficient than other PV cells. Increasing the cells' productivity with the help of light is crucial. The enhancement of dye photosensitizer plays a vital role in improving the performance of DSSC. Synthetic dyes are commonly used (Kumara et al., 2017). Although synthetic dyes are more efficient, they pose a problem because of their production cost, complexity, and use of toxic chemicals. These chemicals can cause harm to the environment and people. Natural dyes are colors made from natural raw materials, such as plants, animals, and minerals. Natural dyes can be made from raw materials such as leaves, trees and parts of animals. Can give color according to your needs and use different production methods. One of the most common products is fabric dye. This is a source for raw materials. Local knowledge and resources can be used to their best use. The researcher sees solar cells becoming more efficient from flowers and leaves. Exploration of natural dyes from plants has been the subject of many studies (Kumara et al., 2017). This is due to their advantages such as high absorption coefficients and low cost, non-toxic, environmentally friendly, and simple extraction method. This review paper also discusses the development of dye-sensitized photovoltaic cells using natural dye as a photosensitizer. It also summarizes the performance of DSSC based upon natural dye from different research papers.

2. Dye-sensitized solar cells (DSSC)

2.1 Dye-sensitized solar cells: a brief history

O'Regan and Gratzel (1991) described a photovoltaic cell that could convert light into electricity using low- to medium-purity materials. This cell was created through cheap cost processes. The device was described as having a thickness of 10 mm. It was made from a thin film of TiO_2 nanoparticles, which are optically transparent and coated with dye to act as the photosensitizer. Under simulated sunlight, the experiment achieved an overall energy conversion efficiency of 7.1 to 7.9%, and 12% under daylight. It was also found that the current density of approximately 12 mA/cm^2 is significant. This allows for a high level of stability which can sustain at most 5 million cycles without degradation.

2.2 Dye-sensitized solar cell components

Because of its practical properties, DDSSC has been the subject of intensive research for solar light conversion. This photoelectrochemical device converts light into electricity (Iftikhar et al., 2019; O'Regan and Gratzel 1991). It works in a similar way to chlorophyll in plants. It harvests sunlight and converts it into energy, such as TiO_2. A DSSC is a multilayered device. Each layer undergoes systematic examination to determine its individuality and interaction with other layers. The dye-sensitized photovoltaic cell (Fig. 1) is made up of four components: photoelectrode, dye, redox electrode and counter electrode (cathode) (Amadi et al., 2015).

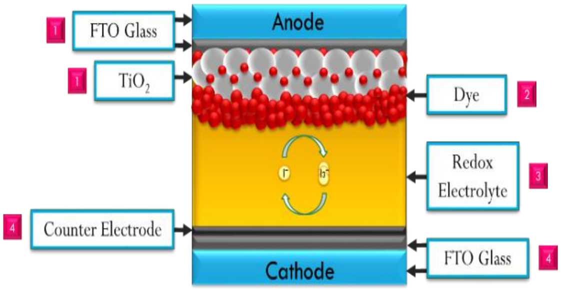

Figure 1 Structure of Dye-sensitized solar cell

2.3 Mechanism of Dye-sensitized solar cells

As the landmark publication of O'Regan & Gratzel in the early 1990s about DSSC, the system was repeatedly described as artificial photosynthesis. A single layer of dye molecules, also known as sensitizers, can absorb incident light and transform it into charge carriers with either a positive or negative charge, similar to the way chlorophyll in plants does. The DSSC is home to a variety of chemical reactions. Equations 1 through 7 show the sequence of chemical reactions. The Redox reaction (also known as the Reduction and Oxidation reactions) plays an important role in the overall process. It allows the electron to continue its life cycle within the device.

Dye excitation

$$S\ (\text{on } TiO_2) + h\nu \rightarrow S^*\ (\text{on } TiO_2) \qquad (1)$$

Electron injection

$$S^*(\text{on } TiO_2) \rightarrow S^+\ (\text{on } TiO_2) + e^-\ (\text{on } TiO_2) \qquad (2)$$

Dye regeneration/ Mediator oxidation

$$2S^+\ (\text{on } TiO_2) + 3I^- \rightarrow 2S\ (\text{on } TiO_2) + I^- \qquad (3)$$

Mediator regeneration

$$I^-_3 + 2e^-\ (Pt) \rightarrow 3I^- \qquad (4)$$

Dye recombination

$$S^+\ (\text{on } TiO_2) + e^-(\text{on } TiO_2) \rightarrow S\ (\text{on } TiO_2) \qquad (5)$$

$$I^-_3 + 2e^-\ (\text{on } TiO_2) \rightarrow 3I^- \qquad (6)$$

Recombination due to Oxidation

$$S^*\ (\text{on } TiO_2) \rightarrow S\ (\text{on } TiO_2) \qquad (7)$$

The following steps make up the entire process of a dye-sensitized solar cell, as shown in Figure 2 (Narayan & Raturi, 2011):

1. The dye becomes excited when exposed to light. The dye is electronically excited when the light passes through the transparent photoanode.
2. The photon bestows sufficient energy upon the electrons, allowing them to break free of the molecule. The energy provided by the photon is sufficient for the electron to break free of the molecule. In this manner, the excited dye molecules can quickly inject electrons into the TiO_2 layer, which can also function as a semiconductor. This process takes only a few seconds.
3. Injection of an excited electron. The electrons travel through the TiO_2 film via diffusion, before reaching the anode.
4. Electricity is produced by the movement of electrons within the device.
5. Regeneration of electrolyte through accepting electrons from counter electrode and returning it to its reduced state.
6. The electrons that are accepted by the reduced state of a redox mediator and which then becomes oxidized in the process of dye regeneration lead to the dye being able to regenerate itself.

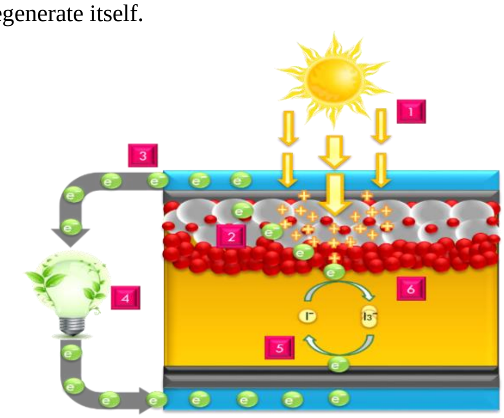

Figure 2 The organizational framework of the DSSC

3. Natural Photosensitizer

The dye used as a sensitizer is the main factor that determines the performance of dye-senitized solar cells. Because of their low cost, ease of access, availability of raw materials, and lack of threat to the environment, natural dyes are an attractive alternative to costly and rare organic sensitizers. Sensitizers can be made from various components of plants, such as bark, leaves, and flower petals. These pigments' properties and other parameters have resulted in different performance. This brief review discusses the operation, components, and emergence of dye-sensitized solar cell components. It also includes the research done over the years on natural dye-based dye sensitized sun cells. The color of the leaves, fruit, and flowers of plants vary from red to purple (Khammee et al., 2021).

There are many natural dyes that can be extracted using a simple process. Many researches have shown that it is possible to get useful DSC photosensitizers from natural products. However, the effectiveness of natural dye sensitizers has not been proven satisfactory. This paper examines the interactions between natural dyes extracted from black rice, capsicum and erythrina variegata flowers, rosaxanthina and kelp. The best photosensitizing effect was seen in extracts from natural fruits, leaves, and flowers. It was determined that black rice extract had the highest results. Natural dye is promising because of its simplicity, availability, and low cost (Mejica et al., 2021).

The role of the dye in solar energy to electricity conversion is well-known. Numerous studies have been done that focused on organic metal complexes as well as organic dyes' molecular engine. Because of their versatility, these natural pigments can be used in many fields. The advantages of using natural dyes to sensitize dye-sensitized cells (DSSCs), include low cost extraction, easy availability, and eco-friendly (Mejica et al., 2020). DSSCs have been a mainstay of renewable energy and a cost-effective alternative to nonrenewable energy since the 90's. These natural dyes are attractive because of their high absorption coefficients, abundant resources, simple preparation, and environmental friendliness. The significance of the cost-effective synthesis of natural dye-based DSSC stems from the fact that it does not call for the use of expensive ingredients or noble metals like Ru (Shalini et al., 2015).

These plant pigments have an electrical structure that interacts directly with sunlight, and as a result, they change the wavelengths of light that are transmitted and reflected by the various plant sections. This is how plant pigments are created. Each pigment is classified according to its maximum absorbance (l_{max}) as well as the color that humans can see. Natural dyes are classified as anthocyanins, flavonoids, carotenoid and chlorophyll. These dyes are easier to extract from plants than synthetic ones (Yusuf, 2018). The most common varieties of pigments found in plant hues, such as those found in fruits and flowers, are outlined in Table 1 below (Delgado Vargas et al., 2000).

Table 1 Pigment types commonly found in flowers and fruits

Name	Pigment type	Examples
Cream	Flavonols and flavones	Most cream flowers
Pink to red	Anthocyanin and/or cyanidin Pelargonidin and/or cyanidin Betacyanin	Tomato, Lisianthus flowers, apple fruit, Tulipa flowers, Bougainvillea
Orange	Anthocyanin & aurone mix, Anthocyanin & chalcone mix Betacyanin Carotenoid, Pelargonidin alone	Marigold flowers, Pelargonium Snapdragon, Carnation flowers, Purslane flowers
Yellow	Carotenoid, Aurone, Chalcone, Flavonol, Betaxanthin	Almost exclusively yellow flowers and fruit, flowers of Antirrhinum majus, Dianthus, Cotton, and Portulaca, as well as Portulaca flowers
Green	Chlorophyll, Delphinidin, Cyanidin	All of the flowers and fruit being green, the majority of the flowers and fruit being blue, and morning glory flowers
Purple	Carotenoid, Cyanidin &/or delphinidin, Cyanidin &/or Delphinidin	Fruits of the pepper plant, eggplant, and cymbidium orchids
Black	Delphinidin	Few black flowers, e.g. Viola (pansy)

Therefore, DSSC technology works by mimicking the process of photosynthesis. Instead, it replaces chlorophyll with pigments that absorb light energy. This allows the incoming light to excite molecules to a higher-energy state. The structure of the electrolyte collects this energy. And catalyst similar to the structure of leaves in photosynthesis (Khammee et al., 2021). While DSSC technology has long been recognized as a low-cost method of generating electricity, security issues hinder the commercial application. The old system was a liquid type that used iodine and a bio-solvent to produce electricity (Mejica et al., 2021). Therefore, developing a DSSC containing an all-solid material electrolyte like the currently commercial DSSC series eliminates the inherent safety issues in liquid-based systems. It also provides higher energy production rates under weak light sources, such as warehouses. This is because the bio pigments used work best with the wavelengths of indoor light sources.

3.1 Chlorophyll

The pigment known as chlorophyll, which is created naturally during the process of photosynthesis, is responsible for giving plants their characteristic green color (Ramaraj et al., 2013). Chlorophyll is divisible into its two basic subtypes, chlorophyll-a and chlorophyll-b, which can be further subdivided (Tipnee et al., 2015). Because of their capacity to take in blue and red light, this pigment and its derivatives have the potential to act as photosensitizers in DSSC. It was discovered that the chlorophyll pigment known as methyl trans-32-carboxy-pyropheophorbide, which is generated from chlorophyll-a, is the one that has the maximum efficiency. [Citation needed] When contrasted with the absorption spectra of chlorophyll-a, the spectrum of chlorophyll-b exhibits a blue tint in addition to a Doppler shift (Fig. 3) (Shalini et al., 2016).

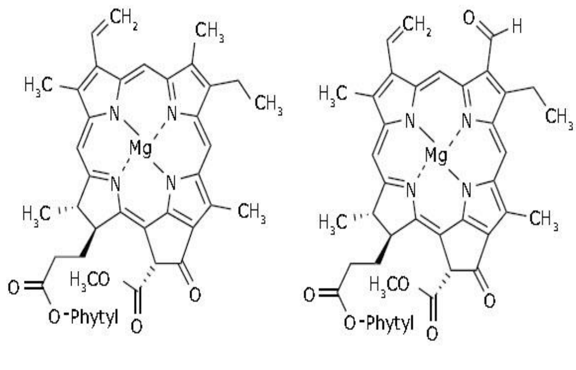

Figure 3 Chlorophyll chemical structure

3.2 Anthocyanin

When it comes to plant pigments, anthocyanins are second only to chlorophyll in terms of importance (Shalini et al., 2015). According to Delgado–Vargas (2000), anthocyanins are the pigments that give fruits and plants their vibrant hues, such as blue, red, and purple. These colors are present on the surface of the fruit and plant. In addition to this, they have light absorbances in the range of wavelengths that goes from 522-555 nm (Kumara et al., 2017). The conditions in which these pigments are found determine their appearance. When exposed to an acidic environment, the pigment anthocyanin is red, but when it is discovered in alkaline conditions, it is blue. An overall representation of the molecular structure of anthocyanin can be seen in Figure 4. In spite of the fact that they belong to the flavonoids, the oxygen atoms in the C-ring of the fundamental flavonoid structures have a positive charge in these molecules. The stability of anthocyanin is influenced by a variety of parameters, including pH, light, temperature, and structure. Additionally, anthocyanin can be found in the skin of grapes and in red cabbage and other naturally colored foods. Table 2 representing naturally occurring anthocyanidins.

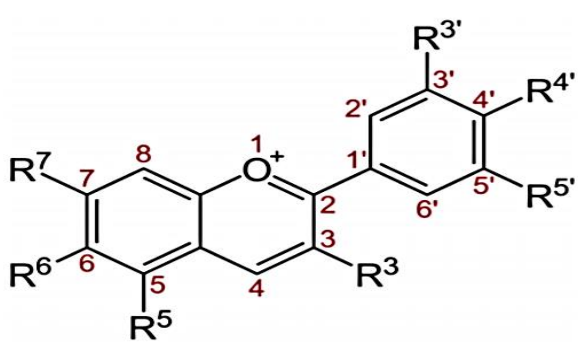

Figure 4 Anthocyanin's fundamental structure (Khoo et al., 2017).

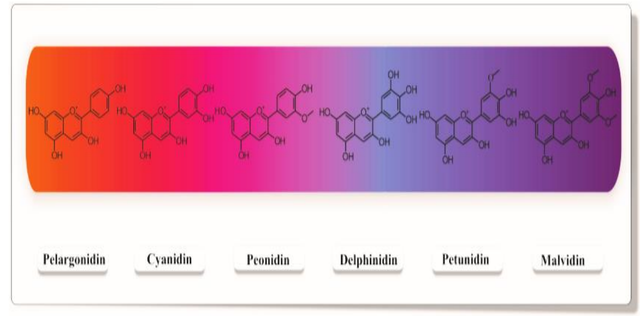

Figure 5 Visible color spectrum of common anthocyanidins (Sladonja et al., 2018)

Table 2 Naturally occurring anthocyanidins

Name	Color produced
Pelargonidin	Orange, salmon
Cyanidin	Magenta and Crimson
Peonidin	Magenta
Delphinidin	Purple, mauve and blue
Petunidin	Purple
Malvidin	Purple
Apigeninidin	Orange
Aurantinidin	Orange
6-Hydroxycyanidin	Red
Luteolinidin	Orange
Triacetidin	Red

There are also carbonyl or hydroxyl groups connected to the surface of anthocyanin molecules that are bound to the TiO_2 semiconductor. Both electron excitation and electron transfer from the anthocyanin molecule to the conduction band are aided by this (Shalini et al., 2015).

3.3 Flavonoids

Those flavonoids with a C6-C3-C6 carbon structure are the ones that have the widest distribution and the highest level of physiological activity. One of the categories of flavonoids is called flavone. It is made up of a g-ring that connects two benzene rings together (Khammee et al., 2020). The fundamental chemical structure of typical flavonoids is depicted in Figure 6. This pigment's charge transfer changes from HOMO, which stands for "highest-occupied molecule orbital," to LUMO, which stands for "lowest unoccupied molecular orbital," and as a result, less energy is required. The result is a wide optical phenomenon in the visible region. Flavonoid molecules can be easily absorbed into semiconductor bands such as TiO_2. This is accomplished by Ti (IV) dispersing an OH counter ion, which then mixes with the proton that is being injected by the flavonoid (Khammee et al., 2020).

Although flavonoids have a similar structure, only some of them can absorb visible light.

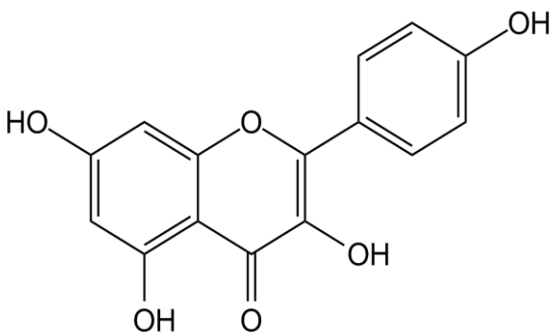

Figure 6 Basic structure of flavonoids

Shalini et al. said that the amount of flavonoids in nature is limited. This is because it depends on their chemical makeup and how much flavan-3-ol is changed into flavonols and anthocyanins.

3.4 Carotenoids

Carotenoids are a group of over 600 isoprenoids that give many red, yellow, and orange fruits and flowers their unique colors (Tipnee et al., 2015). The backbone of these organic molecules is a C40 olidene, which is often cyclized to make an ionone ring at the end. Because of this structure, carotenoids can take in short-wave visible light. Many fruits, flowers, and tiny living things have these pigments. These pigments are responsible for the creation of yellow, red and orange colors. They can also play an important part in protecting photosynthesis. There are two main types of carotenoids: xanthophylls, which are carotenoids that contain oxygen, and carotenes, which are hydrocarbons with no oxygen.

4. Criteria for natural dye photosensitizer

For a dye to be considered best one for DSSC, a dye must meet a number of important requirements, such as:

1. To strongly bind to TiO_2, you can either create a carboxylic group or a hydroxyl band. You can also inject electrons into the TiO_2 conduction spectrum.
2. Those with a high molar absorption coefficient can soak up solar radiation from the near-IR all the way through the visible spectrum.
3. To be a good dye for DSSC applications, a dye needs to meet several important requirements, such as:
4. It has a higher energy level for the lowest molecular orbital that is not filled (LUMO) than TiO_2. This is so that TiO_2 can be charged effectively while also having.
5. A level of energy for the highest occupied molecular orbital (HOMO) that is low enough compared to the redox pair to allow the oxidized color to be regenerated quickly.

5. Performance parameter for DSSC

Kumara et al. (2017) said that four photovoltaic parameters are used to measure how well DSSCs work: (a) open-circuit voltage (V_{oc}), (b) short circuit current density (J_{sc}), (c) fill factor (ff), and (d) energy conversion efficiency (ECE)/(η). These values are often determined using the current density-voltage (J-V) curve, as shown in Fig. 7.

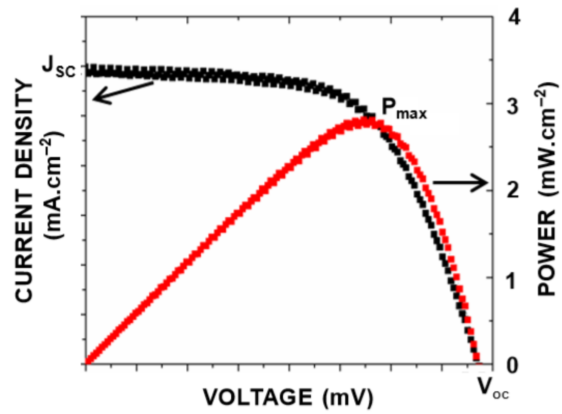

Figure 7 Example of how the current density and voltage of DSSC work

5.1 Open-circuit voltage (V_{oc})

The open-circuit voltage, also known as V_{oc}, is determined by the electrical potential difference between the solar cell's electrodes that are exposed to light and in an open-circuit condition. Moreover, it is the maximum

$$V_{oc} = \frac{E_{CB}}{e} + \frac{k_B T}{e} \cdot \ln\left(\frac{n}{N_{CB}}\right) - \frac{E_{redox}}{e} \quad (8)$$

Where e is the elementary charge of the electrons, n is the number of the electrons in the conduction band, k_B is the Boltzmann constant, T is the absolute temperature, N_{CB} is the density of accessible states at the conduction band, and E_{redox} is the redox potential of the redox mediator (electrolyte) (Kumara et al., 2017; Yao et al., 2015).

Hence, the maximum V_{oc} of a DSSC corresponds to the difference between the energy level (E_{CB}) of the photoelectrode's Fermi level that is exposed to light and the redox potential (E_{redox}) of the electrolyte. The Fermi level is used to describe the upper collection of electron energy levels at absolute temperature. In the process of dye recombination Eq. (5) and Eq. (6), the value of actual V_{oc} becomes lower than the theoretical value (Kumara et al., 2017; Yao et al., 2015).

5.2 Short circuit current density (J_{sc})

The photocurrent measured in milliamperes per square centimeter (mA/cm^2) is denoted by the value J_{sc}, which is computed for a DSSC when it is exposed to irradiation in a short circuit. The Jsc is determined by the interaction that takes place between the dye sensitizer and the TiO_2 particle, as well as the absorption coefficient of the dye sensitizer. Therefore, a high Jsc is associated with the following characteristics: 1) intense light-absorption capabilities of dyes over a wide range of sunlight; 2) high electron-injection efficiencies from photo-excited dyes to the

CB of TiO_2; and 3) efficient reduction of the oxidized dye by I^-. All of these characteristics can be found in high concentrations in dyes that have high Jsc values.

5.3 Fill factor

The fill factor, also known as FF, is a parameter used to determine the overall quality of the solar cell. It is figured out by contrasting the maximum power that the cell can produce, which is denoted by the notation P_{MAX}, with the theoretical power that can be calculated using the open-circuit voltage and the short-circuit current.

The FF is typically calculated as:

$$FF = \frac{J_m \times V_m}{J_{sc} \times V_{oc}} \quad (9)$$

The fill factor (FF) is a measurement of the maximum power production from a solar cell. It reflects the amount of electrical and electrochemical losses that occur while the cell is in operation, where J_m and V_m are the maximum current and voltage, respectively. In order to achieve a greater fill factor, it is necessary to improve the shunt resistance and decrease the series resistance. This will result in a reduction in the overvoltage that is required for diffusion and charge transfer (Dawoud, 2016).

5.4 Power conversion efficiency

When comparing the performance of different solar cells, the evaluation of efficiency is the most relevant and significant performance characteristic to look at. The ratio of the solar cell's highest electrical energy output to the solar radiance energy input is used to determine the power conversion efficiency of the cell. The maximum amount of power that a solar cell is capable of producing is equal to the product of the maximum amount of current, which is measured in J_m, and the maximum amount of voltage, which is measured in V_m.

$$P_{\max} = J_m \times V_m \quad (10)$$

Power conversion efficiency under sunlight irradiation (e.g., AM 1.5) can be obtained using:

$$n = \frac{P_{max}}{P_{in}} = \frac{(J_m \times V_m)}{P_{in}} = \frac{(J_{sc} \times V_{oc} \times FF)}{P_{in}} \quad (11)$$

Where P_{in} is the power per unit area of the incident light with a standard value of 100 mW/cm^2 under AM 1.5 solar light, besides the solar cell performance itself, it depends on the incident light spectrum and intensity as well as operating temperature (Dawoud, 2016; Rho et al., 2015).

5.5 (IPCE) Incident-photon-to-electron conversion efficiency

The efficiency (n) of DSSC, as shown in Eq. 11, measures the overall conversion of light incident on it to electrical power but does not calculate for the amount of light absorbed by the dye. The incident photon to current conversion efficiency (IPCE) is an important parameter that measures the absorbed light's percentage getting converted to current. It is defined as the number of electrons flowing through an external circuit under short circuit condition per incident photon and is given by Eq. 12 (Jena et al., 2012):

$$PCE = 1240(V * nm) \times \frac{J_{sc}(\lambda)[A/cm^2]}{\lambda[nm] \times P_{in}(\lambda)[W/cm^2]} \quad (12)$$

6. Fabrication cost

The relation between the cost of a DSSC photoanode and the properties of materials used to fabricate it can be derived by considering the Lambert–Beer expression of the absorbance (A)

$$A = \varepsilon * c * d \quad (13)$$

where c (mol cm^{-3}) is the dye concentration in the TiO_2 layer and d (cm) the TiO_2 layer thickness.

By using the equation of Calogero et al., 2015, we can derive the cost per Watt-peak P_{tot}^{Dye} of the dye:

$$P_{tot}^{Dye} = \left(\frac{A * M_{Dye} * P_{mass}^{Dye}}{\varepsilon * I_{AM1.5} * \eta} \right) \quad (14)$$

where M_{Dye} (g mol^{-1}) is the molecular mass of the dye, P_{mass}^{Dye} (Baht per g) the price per mass of the dye, and $I_{AM1.5}$ (W m^{-2}) the light power density.

Eq. 14 defines the cost of the dye. However, when a different dye is used, ε it varies, and consequently, a different thickness of TiO_2 is needed to achieve the same absorbance. Values of several parameters used for cost estimation are displayed in Table 3. This will affect the total cost of the cell, being the TiO_2 cost not negligible. By using an approach similar to that described above for the dye, we can express the cost of the TiO_2 per W_p as:

$$P_{tot}^{TiO_2} = \left(\frac{A * \rho_{TiO_2} * P_{tot}^{TiO_2}}{R * \varepsilon * c * I_{AM1.5} * \eta} \right) \quad (15)$$

Where $R = \left(\frac{thickness\ of\ sintered\ TiO_2\ layer}{thickness\ of\ deposited\ TiO_2\ paste} \right)$

(typically, R = 0.1–0.15), $P_{mass}^{TiO_2}$ the price per mass of TiO_2 paste and ρ_{TiO_2} (g cm^{-3}) is the density of TiO_2 paste.

The total cost of the photo-anode P_{tot}^{PhA} (excluding the cost of the glass) is:

$$P_{tot}^{PhA} = \frac{A * M_{Dye} * P_{mass}^{Dye}}{\varepsilon * I_{AM1.5} * \eta} + \frac{A * \rho_{TiO_2} * P_{mass}^{TiO_2}}{R * \varepsilon * c * I_{AM1.5} * \eta}$$

$$= \frac{A}{\varepsilon * I_{AM1.5} * \eta}\left[M_{Dye} * P_{mass}^{Dye} + \frac{\rho_{TiO_2} * P_{mass}^{TiO_2}}{R * c}\right] \quad (16)$$

Table 3 Values of several parameters used for cost estimation (Calogero et al., 2015)

Parameters	Value
TiO_2 paste density (g cm^{-3})	0.82
R	0.15
Price of TiO_2 paste (Euro per kg)	2500
Price of two TCO (Euro per m^2)	16
Price of solvent-based electrolyte paste (Euro per 1)	1250
Price of Pt-catalyst (Euro per m^2)	0.8
Light power density (W m^{-2})	1000
Absorbance (A)	1.5

7. Current status

Researches have focused on the use of natural dyes as photosensitizers for dye-sensitized cells. The number of studies on natural dyes has been rising over the last few years, according to reports. The data from the ISI Web of Knowledge (Fig. 8 shows that the number of publications has increased over time. It is a sign that DSSC based upon natural dyes has seen many improvements. These solar cells are currently gaining more attention. This field is full of challenges that aim to improve the quality and performance.

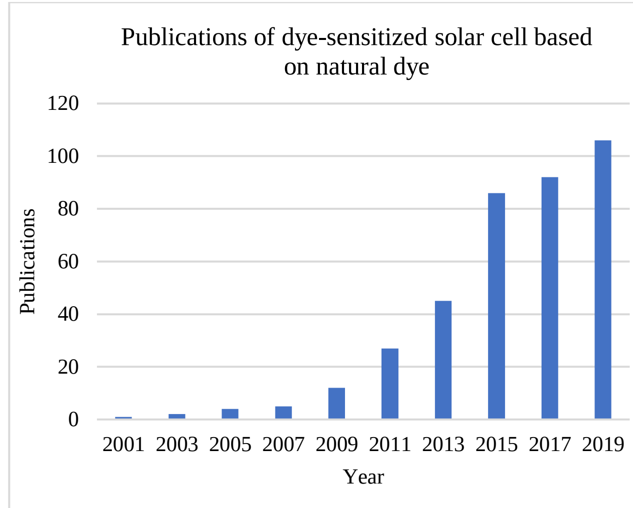

Figure 8 The number of published publications related to DSSC per year from literature search using the keywords 'dye-sensitized solar cell' & 'natural dye' (data source ISI Web of Knowledge).

There are many data available on the performance of DSSC when combined with natural dye. Anthocyanin and chlorophyll are the most commonly used pigments. Each pigment has the ability to absorb light and give electrons to the sun (Khammee et al., 2021). They can also be extracted efficiently using organic solvents such as ethanol or methanol (Mejica et al., 2021). Anthocyanin pigments are the most versatile of all the pigment types (chlorophyll-anthocyanin, flavonoid, and carotenoid). They can absorb light and provide electrons to the solar cell (Mejica et al., 2020).

However, DSSC's life cycle, stability, durability, and longevity can be improved by exploring more plants and improving the photoanode and counter electrode and electrolyte fabrication. Solar should be sealed properly to ensure a longer life span. The table 4 contains some research results from different journals on the dye-sensitize photochemical parameters using chlorophyll and anthocyanin pigments from leaves, seeds and flowers, fruits and vegetables, and tree barks.

Table 4 Photoelectric performance of DSSC integrated with natural dye from various plants

Dye	λ_{max} (nm)	J_{sc} (mA/cm^2)	V_{OC} (V)	FF	η (%)	Reference
CHLOROPHYLLS						
Spinach	-	0.33	0.639	0.337	0.0713	Ahliha et al., 2017
Kelp	-	0.433	0.441	0.52	-	Hao et al., 2006
Bahraini henna	-	0.368	0.426	24.6	0.128	Jasim, 2012
Undaria pinnatifida	665	0.8	0.36	0.69	0.178	Calogero et al., 2014
Walnuts	510	0.73	0.304	0.39	0.0104	El-Agez et al., 2012
Anethum graveolens	666	0.96	0.57	40.0	0.22	Taya et al., 2013
China Loropetal	665	0.84	0.518	62.6	0.27	
Perilla	665	1.36	0.522	69.9	0.50	
Chinese rose	516	0.90	0.483	61.9	0.21	
Erythrina variegata	451	0.78	0.48	0.55	-	Hao et al., 2006
ANTHOCYANIN						
Begonia	540	0.63	0.537	72.2	0.24	Huizhi et al., 2011

Rhododendron	540	1.61	0.585	60.9	0.57	
Violet	546	1.02	0.498	64.5	0.33	
Black rice	-	0.126	0.580	0.272	0.0198	Ahliha et al., 2017
Hibiscus rosa-sinensis	534	4.04	0.40	0.63	1.02	
Bauhinia tree	665	0.95	0.572	66.0	0.36	
Dragon fruit	535	0.20	0.22	0.30	0.22	
Red onion	532	0.51	0.44	0.48	0.14	
Redcabbage	537	0.50	0.37	0.54	0.13	
Sesbania grandiflora	544	4.40	0.41	0.57	1.02	
CAROTENOIDS						
Gardenia yellow	450	0.96	0.54	0.62	0.32	Park et al., 2013
Turmeric	525	0.288	0.529	0.48	0.03	
Tomato	-	0.51	0.14	0.37	0.03	Supriyanto et al., 2018
Orange fruit	-	0.37	0.06	0.58	0.02	
Carrot	-	0.36	0.04	0.64	0.009	
Achiote	474	1.1	0.57	0.59	0.37	Gómez -Ortiz et al., 2010
FLAVONOIDS						
Cosmos sulphureus	505,590	1.041	0.447	0.61	0.54	Narayan & Raturi, 2011
Punica granatum peel	400	3.341	0.716	0.776	1.86	

3. Conclusion

This article discusses natural photosensitizers with different natural dyes and DSSC performance were reviewed. Solar-to-electric is popular. Natural dyes are widespread. Non-toxic and easy to extract. The DSSC's performance isn't as good as the first generation, but its unique and practical qualities make it attractive to reduce reliance on non-renewable fuels to combat global warming. Young DSSCs can innovate and develop. Injecting electrons into TiO_2 is different from "promoting" electrons in cells. Low-energy electrons can recombine with silicon holes, releasing photons or other energy. Rarely, atoms' electrons can join photoexcited holes. DSSC implants electrons into TiO_2. Dye recycles electrons. The dye absorbs electrons faster. TiO_2 and electrolyte recombination is problematic in optimized devices. Platinum-coated electrolytes quickly transfer electrons. Differential dynamics make DSSC low-light capable. Weather doesn't affect DSSCs. Conventional designs cut out under low illumination when charge carrier mobility and recombination are issues. Indoors. Light energy is converted to portable power. DSSCs are more efficient than other thin-film technologies at high temperatures. Rising temperature "mechanically" shifts semiconductor electrons to the conduction band. Traditional silicon cells need shielding. They're usually stored in a metal-lined glass box. Cellular heating reduces efficiency. Fronts of DSSCs are conductive. This accelerates heat dissipation and cools interiors.

4. Future research perspectives

Natural dyes are taking over due to the high cost, complexity, and potentially harmful effects of synthetic dyes for DSSC. Natural dyes are more affordable, easier to obtain, cheaper, and safer than synthetic dyes. They can also work under low light conditions. Studies on various natural pigments have revealed the differences in their ability to harvest light and convert it into electricity. This will improve the performance of the DSSC, its stability, durability, and life cycle.

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