

Review Article

A review of advances on natural dye sensitized solar cells (NDSSCs)

Abstract.

Currently, the situation of the economy is drastically affecting the growth and development of some growing nations with regard to the energy sector. Most developing countries still depend majorly on fossil fuels. Considering the environmental nuisance arising from the dangerous emissions from the combustion of fossil fuels and climate concerns, there is urgent need to seek other alternative energy sources to meet up with the global energy consumption demands as the human population is steadily on the increase. Energy from the sun is one of the most alternative sources that can be assessed freely as well as help in mitigating global climate change. Recent advances on dye sensitized solar cells (DSSC) using natural dyes is a welcome advancement for replacing high cost ruthenium dye. The application of natural dye for DSSC is due to their abundance in nature, low cost, simple and safe extraction from various natural resources without requiring complex synthetic procedures. Dye enhances the performance of a DSSC by providing the source of photo excited electrons. Recently, there has been research on areas that supports the exploration of different photoactive natural dyes. In this paper, we reviewed some natural dyes, energy conversion efficiencies of NDSSCs, methods of dye extraction, characterization and various fabrication techniques for improved DSSC performance from various researched articles. It was observed that there was variations in the recorded DSSCs performances and this can be attributed to steps employed by the researchers in the methods of dye extraction and DSSC fabrication.

Keywords: Dye extraction, Fabrication, Synthesis, Characterization, Efficiency.

1. INTRODUCTION

Most of the energy consumption in the world are based on fossil fuel which is non-renewable and also affects the environment negatively [1]–[3]. Industrialization, continuous increase in population and global energy consumption have led to a great demand for renewable resources. Researchers are motivated world-wide to search for more affordable,

alternative and clean methods of energy production to meet with the global energy consumption demands. Solar energy remains the most favoured renewable energy source throughout the globe due to its free abundance in nature and enormous potential for meeting the global energy consumption demands [4]. Solar energy is converted into electrical energy using solar cells through photovoltaic systems. For decades, thin film and silicon-based solar cells are been utilized for solar energy applications due to their high efficiency and stability, notwithstanding that they possess some critical drawbacks. Following the pioneering research led by Gratzel and O'Regan in 1991 [5], intensive work is ongoing for the development of more scalable and low cost solar cells. There have been recent advancements in production of modified solar cells using low cost and abundant materials with simple fabrication techniques. This advancements is being regarded as generations of solar cells which has extended to fourth generation presently. Among the generations, dye sensitized solar cell (DSSC) is a promising PV device with beneficial features. DSSC employs the concept of artificial photosynthesis in attempting to replicate the ability of plants to turn sunlight into useful energy [6]. In DSSC, chlorophyll is replaced by a light absorbing dye, the molecules of which are excited to a higher energetic state at irradiation. This energy is collected by a structure of electrolyte and catalysts, much like the surrounding structure of a leaf in photosynthesis. Unlike other types of solar cells, the dye solar cell (DSC) utilizes dye for molecular light harvesting to enhance the absorption spectra in the visible light region. It is a known fact that the energy gap size of the applied semiconductors determines the absorption frequency of light in solar cells. Ability to match the band gap of the dye with that of semiconducting oxides significantly improves the performance of the solar cell. The absorption spectra of DSSCs are determined by the combination of the nano crystalline porous semiconductor and the dye [7]. The history of dye sensitized solar cell (DSSC) dated back to 1972 when photons were converted to electric current for the first time by charge injection of excited molecules of dye into a wide band gap semiconductor with a chlorophyll sensitized zinc oxide serving as electrode. A lot of fundamental research was done on zinc oxide single crystals, but the efficiency of these devices was poor. In 1991, O'Regan and Gratzel developed a new photovoltaic cell working on the principle of plant photosynthesis [5]. Currently, natural dyes is been researched based on their abundance in nature, low cost, simple preparation methods, low toxicity as well as their ease of production [8]. The increasing interest in natural dyes is also attributed to their harmless complete biodegradation. Natural dye contains plant pigments such as flavonoids, chlorophyll, carotenoids, tannins and betalains some of which restricts the transfer of electrons from dye molecules to the conduction band of the semiconducting oxide thereby affecting the performance of a DSC. Every part of the plant can be extracted and used as a natural dye [9]. In this paper, a review of the energy conversion efficiencies of some natural dyes in DSSC fabrication and various improvements made so far are reported, methods of dye extraction, characterization and various fabrication techniques for improved PV performance are presented.

1.1. Components of DSSC

A DSSC consists of two transparent conductive oxide (TCO) coated glass substrates, semiconducting oxide, a dye sensitizer, an electrolyte and a catalyst. The TCO provides a substrate for the deposition of the semiconductor and catalyst, acting also as current collectors. Fluorine tin oxide (FTO) and indium tin oxide (ITO) are frequently used as the conductive substrate. The components of a DSSC is shown in figure 1.

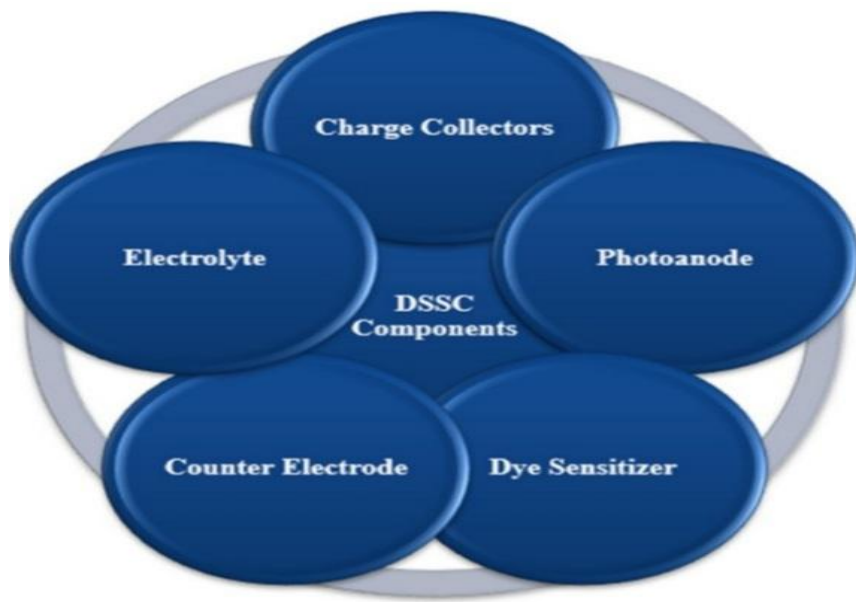


Figure 1. A typical DSSC components [10].

The working principle of DSSC is illustrated with figure 2, where S^+ , S^* , and S represents sensitizer in the excited, oxidized and ground states respectively. At irradiation, the electrons at the highest occupied molecular orbital (HOMO) of the dye becomes excited (S^*), moves to the lowest unoccupied molecular orbital (LUMO) of the dye through photoelectric effect and are injected into the conduction band of the semiconducting oxide thereby oxidizing the dye (S^+). The electrons are diffused through the mesoporous semiconducting oxide to an external circuit connected to a load. The counter electrode transports the electrons to the electrolyte, the electrolyte then donates electrons to the dye restoring it to the initial state (S). The cycle is completed as the electrolyte restores its initial state by accepting electrons from the external circuit. This continuous forward movement of electrons produces electricity. While the forward charge transfer is in process, backward charge transfer process also takes place and this reduces the efficiency of the cell drastically.

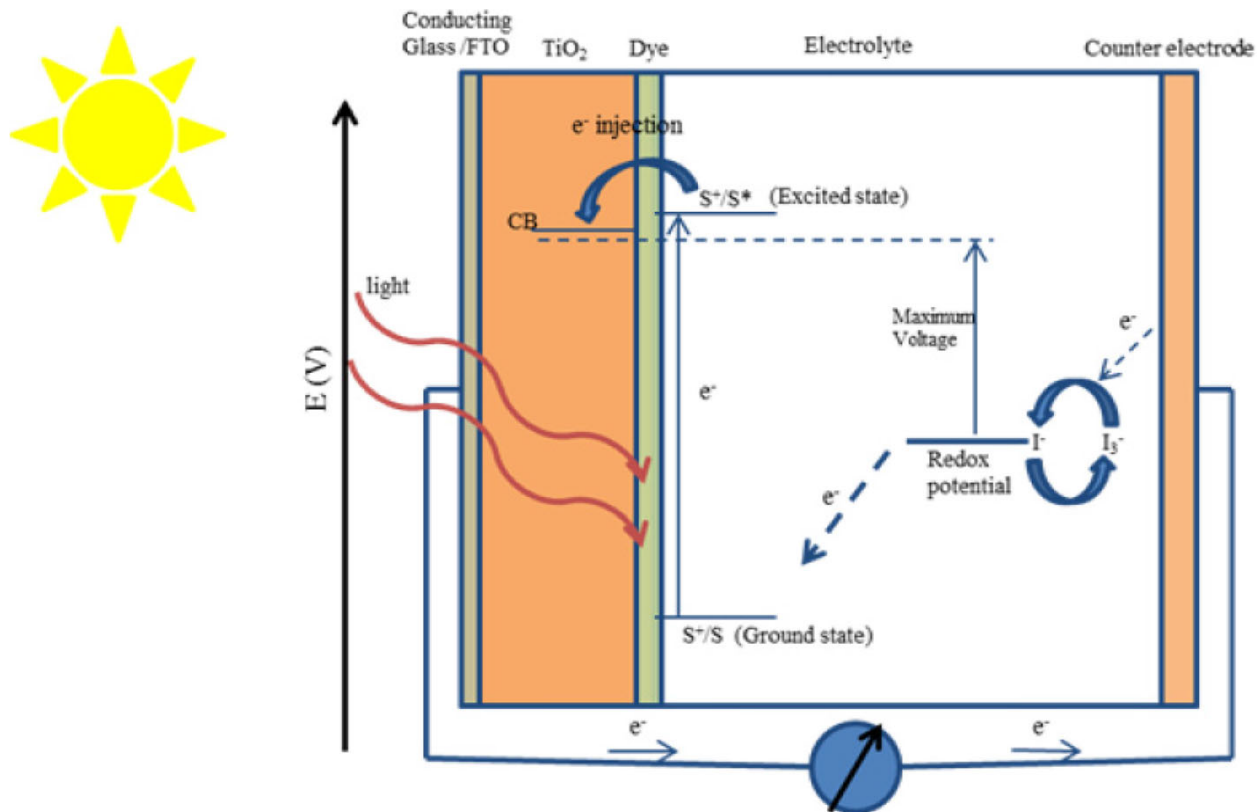


Figure 2. Schematic drawing of a DSSC showing the principles of operation [11].

1.1.1. The photoanode: This is the semiconducting oxide responsible for transporting electrons from the dye to the external circuit to produce an electric current. Titanium dioxide (TiO_2), zinc oxide (ZnO) and stannic oxide (SnO_2) are commonly used as the semiconducting oxide materials. Some recent modifications of the photo anode has been reported for enhanced performance of the cell. Offiah et al., fabricated a DSSC with a polyvinyl alcohol (PVA)- capped zinc oxide and ZnO photoanodes, the deposition of the ZnO was performed using zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and hexamethylenetetramine (HMTA) as the main precursors. Zinc acetate ($\text{Zn}(\text{CH}_2\text{COOH})_2 \cdot 2\text{H}_2\text{O}$) and ethanol were used to prepare the seed solution prior to the hydrothermal synthesis. 0.1 M ethanolic sol gel was prepared and stirred for 1 hour at room temperature. Spin coating machine adjusted to 2000 rev/min was used to coat substrates with the seed layers which served as nucleation centres on the surface of the substrate to induce the growth of the ZnO nano rods. For the nanocrystalline ZnO photo anode by hydrothermal method, 0.02 M solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.2 M HMT were mixed and stirred continuously for 2 hours at room temperature. The capping solution was prepared by dissolving 9.0 g of PVA in 450 ml of water and vigorously stirred without heating until a clear homogenous solution is formed. 20 ml of this solution was added to the zinc acetate and HMT solution, annealed at 450°C for 60 minutes before fabrication. The result showed overall power conversion efficiency of 1.2% against 0.7 % of DSSC fabricated with ZnO photo electrode [12]. Krishnapriya et al., investigated the effect of cobalt doping on the photoanode of a DSSC and recorded a power conversion efficiency of 6.86 % [13]. Research by Bartkowiak et al. recorded an improved conversion efficiency of 8.63% with a zirconium doped photoanode [14].

1.1.2. The photosensitizer: Advanced method of achieving better photovoltaic performances is by employing light harvesters (dye). The dye is chemically bonded to the surface of the semiconducting oxide material. On irradiation, the dye absorbs light and transfer electrons to the conduction band of the semiconducting oxide. Three classes of photosensitizer exists; metal complex, metal-free organic and natural sensitizers. Methods of dye application are also considered for improved PV performance. Nirmala et al., extracted natural dyes from beetroot and turmeric by immersing the photoanode inside the dye for several hours, they recorded a power conversion efficiency of 0.75% and 0.40% respectively [15]. An enhanced photoanode using rhodomyrtustomentosa (rose myrtle) dye, recorded a strong absorption in the visible light region, with power conversion efficiency of 3.53% [16]. The research by O'Regan and Gratzel on the fabrication of a DSSC with ruthenium dye recorded power conversion efficiency up to 7% [5]. The work done by [12] was also examined for the method used in sensitizing the photoanode, dye was applied by immersion of photoanode completely into the dye and allowed to stand for 24 hours, they reported a reasonable high absorbance in the visible spectrum. Considering reduction of the time consumed in traditional dye soaking method, inkjet printing of the dye molecules was introduced. Dimethylformamide was used as the solvent for easy nozzle spray and an improved efficiency of 6.4% was recorded [17]. Further improvement on the dye soaking time by employing dye application using digital printing showed improved efficiency of 7.4% [18].

1.1.3. The electrolyte: This acts as a charge transport medium to transfer positive charges towards the counter electrodes and also regenerates the dye after it injects electrons into the conduction band of the semiconducting oxide. Electrolytes for DSSC are classified into liquid, solid state and quasi-solid state electrolytes. The work of Offiah et al., was investigated to find out the effect of electrolyte on PV characteristics, the DSSC was fabricated with polyvinyl alcohol capped ZnO as photoanode and 0.1 M lithium iodide/0.05 M iodine in acetonitrile concentration of the redox mediator, they reported 1.2% efficiency [12]. Ito and Takashi fabricated a DSSC with a TiO₂ photoanode using a different concentration and combination of the redox couple, 0.2 M iodide/0.5 M N-methylbenzimidazole and 0.1 M guanidinium thiocyanate. Their result showed improved efficiency of 2.06% [19]. A cobalt based mediators was developed by selecting a suitable combination of a cobalt polypyridine complex and an organic sensitizer, the optimized DSSC yielded solar cells with conversion efficiency of 6.7% and open-circuit potentials of more than 0.9 V under 1000 W m⁻² AM1.5 illumination [20]. Hannes et al., introduced new copper complexes as redox mediators, they recorded a high voltage of 920 mV with photocurrents of 10 mA cm⁻² and 6.20% power conversion efficiency. Copper coordination complexes with a square-planar geometry show low reorganization energies and introduces smaller losses in photo voltage as recorded in their work [21]. Another report on different electrolyte achieved a V_{oc} of 1.24 V and a highly efficient and stable DSC with PCE of 13.5% under standard AM1.5 G, 100 mW cm⁻² solar radiation with copper (II/I)-based electrolyte [22].

1.1.4. The counter electrode: It assists in the regeneration of the electrolyte. A platinum (Pt) catalyst is sometimes used on the CE to accelerate the reduction reaction. Poopola et al., fabricated a DSSC using traditional platinum counter electrode, they recorded power conversion efficiency of 7.29% [23]. The works of [24] reported power conversion efficiency of 4.25% on carbon counter electrode with a ruthenium dye. When compared with the records of [25] on same carbon counter electrode but with a natural dye, efficiency was very low, 0.48%. Machida et al.,

worked with poly 3,4- ethylenedioxythiophene(PEDOT) counter electrode, their result showed lower charge transfer resistance with improved power conversion efficiency of 7.88 % [26].

2. Natural Dyes

Natural dyes are dyes derived from natural resources, they are classified as plant, animal, mineral and microbial dyes. They are also classified based on their chemical constituents; indigoid dyes, anthraquinone dyes, flavonoid dyes, carotenoid dyes, tannin-based dyes and naphthoquinone (benzoquinone) dyes. Some important plant pigments includes carotenoids, anthocyanins and betalains.

2.1. Extraction of natural dyes

All sources of natural dye contain only a small percentage of colouring pigment along with other plant and animal constituents. Therefore, different methods of dye extraction are required for optimal results, these methods includes; aqueous extraction, alkali or acid extraction, microwave and ultrasonic assisted extraction, fermentation extraction, enzymatic extraction and solvent extraction [27].

2.1.1. Aqueous extraction; this method involves breaking the dye source into smaller pieces or powdered and sieved to improve extraction efficiency. It is then soaked with water in earthen, wooden or metal vessels for a long time usually overnight to loosen the cell structure and then boiled to get the dye solution which is filtered to remove non-dye plant remnants. Generally, centrifuge are used to separate residual matter [28]. Natural dyes was extracted from bougainvillea dye, beetroot dye, eggplant dye, pollen dye and coffee dye using aqueous dye extraction method for DSSC fabrication. Absorption peaks in the range 424nm to 550nm was recorded from the work [29].

2.1.2. Alkali and acid extraction; for dyes in the form of glycosides, they can be extracted under dilute acidic or alkaline conditions. The addition of the acid or alkali facilitates the hydrolysis of glycosides resulting in better extraction. Acidified water is also used for extracting some flavone dyes to prevent oxidative degradation. Willoughby et al., reported 230nm and 290nm wavelengths on rosella dye using acid dye extraction method [30].

2.1.3. Microwave and ultrasonic assisted extraction; here, extraction efficiency is increased by the use of ultrasound or microwaves thus reducing the quantity of required solvent, time and temperature of extraction. The creation of very high temperature and pressure during extraction increases the extraction efficiency within a short time. In microwave extraction, the natural sources are treated with minimum amount of solvent in the presence of microwave energy sources. Microwave increases the rate of the processes so the extraction can be completed in a shorter time with better yield. Rabia, et al., extracted henna dye by ultrasonic and microwave assisted extraction method and observed that the method yielded more superior colour strength properties compared to other extraction techniques they had used [31].

2.1.4. Fermentation extraction; this method of extraction uses the enzymes produced by the microorganisms present in the atmosphere or those present in the natural resources to assist the extraction process. The fermentation method is similar to aqueous extraction with the exception that this method does not require high temperatures. Ito, et al., extracted monascus yellow dye from red yeast rice using fermentation method. Result revealed maximal PV characteristics [19].

2.1.5. Enzymatic extraction; plant tissues contain cellulose, starches, and pectin as binding materials, commercially available enzyme including cellulase, amylase and pectinase have been used by some researchers to loosen the surrounding material leading to the extraction of dye molecules under milder conditions. This process is beneficial in the extraction of dye from hard plant materials such as the bark, roots and the like. Lee, et al., extracted and purified squid ink using enzyme-based reaction, the cells demonstrated efficiencies of 0.72% and 0.86% respectively [32].

2.1.6. Solvent extraction; natural colouring matters depending on their nature can also be extracted by using organic solvents such as acetone, petroleum ether, chloroform, ethanol, methanol, or a mixture of solvents such as mixture of ethanol and methanol, mixture of water with alcohol. The water/alcohol extraction method is able to extract both water-soluble and water-insoluble substances from the plant resources. Acid or alkali can also be added to alcoholic solvents to facilitate hydrolysis of glycosides and release of colouring matter. Solvent extraction method was used by Ibukun, et al., for galena dye and they reported around 380nm to 800nm absorption wavelength in the visible region [33]. Extraction of dyes from Mangosteen peels by first milling and drying them for 3 – 5 days before soaking in ethanol with stirring for 12 hours at room temperature, the absorption spectra of dye solutions were characterized by using UV-Vis spectrophotometer, anthocyanin of mangosteen peels was 400 – 480 nm with power conversion efficiency of 0.042 % [31]. Kartini and Hatmanto extracted dyes from bark of tingi, tegeran and dried fruits of jalawe using aqueous and solvent extraction methods, they observed absorption peaks at 540 nm, 538 nm and 403 nm respectively [35].

3.1. Synthesis and Characterization tools

The photoanode nanostructures for DSSCs can be synthesized using various techniques, thus; sol-gel synthesis, hydrothermal synthesis, solvothermal synthesis, flame spray pyrolysis, anodization, micelle method, direct oxidation, sonochemical synthesis, microwave synthesis, and green route synthesis. Sharmila Devi et al., synthesized TiO_2 nanoparticle from TTIP precursor by sol-gel process [36], anatase phase of TiO_2 was obtained after calcination. Synthesis of TiO_2 using titanium (IV) isopropoxide (TTIP) precursor through hydrothermal process by Collazza, et al., showed pure crystalline phase of anatase for all conditions of synthesis [37]. Oshima, et al., synthesized TiO_2 with polymer gel by solvothermal method [38]. X-ray diffraction (XRD) confirmed presence of anatase TiO_2 . Synthesis of TiO_2 fine particles from titanium (IV) isopropoxide precursor by Widiyandari, et al., through flame spray pyrolysis revealed mixed phases of anatase and rutile [39]. Zakir, et al., reported phase mixture of anatase and rutile TiO_2 from titanium foil through anodization technique [40]. Suwan, et al., synthesized through Micelle microemulsion method with TTIP precursor [41]. They recorded rich anatase and half anatase/rutile phase. Synthesis of TiO_2 from titanium tri chloride precursor by Bidaye and Fernandes through direct oxidation gave a unique flower-like assembly of nanotubes [42]. Baldassari, et al., synthesized TiO_2 nanoparticle from titanium tetrachloride precursor using sonochemical process [43], result was anatase phase of TiO_2 structure. Cabello et al., synthesized using amorphous TiO_2 as precursor through microwave assisted synthesis, they reported anatase, brookite and rutile phases [44]. Amamilla and Sundaram used titanium tetrachloride precursor in TiO_2 synthesis through green route method and reported anatase phase of TiO_2 [45]

3.2. Characterization Tools

There are several techniques (characterization methods) that can be used to analyse the electronic properties of the fabricated DSSCs, they includes (a)morphological studies; electron microscopy (scanning electron microscopy, energy dispersive x-ray, transmission electron microscopy), x-ray diffraction, dye adsorption. (b)Spectroscopic studies; UV-Vis spectroscopy, x-ray photoelectron spectroscopy, Fourier transform infra-red spectroscopy. (c) Electromagnetic measurements; Hall Effect measurements, electron paramagnetic resonance analysis. (d) photo-electrochemical measurements; photovoltaic properties (short circuit current density, open circuit voltage and fill factor), electron transport, electron lifetime and electron concentration.

All natural dyes reviewed in this paper were grouped into five. Their extraction methods and photovoltaic properties were summarized in table 1-5 below

3.2.1.Natural dyes from fruits;fruits contain anthocyanin, carotenoids and some chlorophyll derivatives.Dyes from pomegranate, berry fruits, rose myrtle, grapes, terminaliacatappa, rhodonderon and other fruits have been reported from many literatures and result shows higher efficiencies than the dyes from flower petals. Two samples of pomegranate pigment extracted by squeezing out the juice and the other by solvent method of extraction showed different conversion efficiencies of 2.0 % and 0.01 % respectively. Natural pigments from cram berry, blue berry, pomegranate, rose myrtle and terminaliacatappa showed efficiencies in the range 1 % to 4%. This result can be attributed to fruits containing numerous dye pigments combined together. When they absorb light through photo-induced transformation caused by delocalization of ‘p’ electrons from carotenoid molecules, there is formation of a single chlorophyll state with a slightly higher energy which is transferred to the chlorophyll molecules where chlorophyll’s physical structure facilitates the transfer of energy from carotenoids [4].

Table 1: Dye extracts from fruit sources

Dye name	Mtd. Of Extrt.	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	IPCE (%)	λ (nm)	Ref.
Tamerillo	Solvent	0.400	0.450	0.097		19.790	330	[46]
Red dragon fruit		0.281	0.500	0.082		48.214	328	
fruit of jalawe		0.006	0.100	0.310	0.008		403	
Coffee	Solvent/ Acid						450 & below	[29]
Pomegranate	Squeezed	12.200	0.390	0.410	2.000			[47]
Blue berry		11.160	0.470	0.260	1.400			
Cram berry		6.780	0.410	0.420	1.200			
Black berry		2.720	0.420	0.380	0.400			
Grapes	Solvent	0.090	1.750	0.580	0.580		529	[48]
Black plum		0.270	1.750	0.650	0.180		533, 662	
Raspberry		1.880	1.500	0.500	0.940		534	
Chelidonium		0.345	0.490	0.370	0.062			

CorchorusOlitorius		0.550	0.540	0.400	0.120			
Rose myrtle	Solvent/	8.770	0.500	0.290	3.530		650	[16]
Begonia	Aqueous	0.630	0.531	0.720	0.240		540	[49]
Rhododendron	Solvent	1.610	0.585	0.600	0.570		540	
Coffee	Aqueous	0.850	0.559	0.690	0.330			
Tangerine peel	Solvent	0.740	0.592	0.630	0.280		446	
Terminalia Catappa		0.005	0.470	0.683	1.580			[24]
Banana peel		0.122	0.282	0.260	0.009			[9]
Mango peel		0.265	0.288	0.310	0.024			
Pomegranate		0.133	0.283	0.280	0.010			
Pineapple		0.033	0.214	0.300	0.002			

3.2.2. Dye pigments from leaves; Chlorophyll is found in virtually all photosynthetic organisms, including green plants. Chlorophyll absorbs energy from light; this energy is then used to convert carbon dioxide to carbohydrates. Chlorophyll pigments can be used as a dye sensitizer in DSSC because of its ability in absorbing photon from both visible and invisible light spectrum. This natural pigment was extracted from indigo leaf, teak leaves, bitter leaf, spinach etc. Among all natural pigments extracted from leaves, bitter leaf pigment extracted through solvent method recorded the highest conversion efficiency of 0.96%. Generally, the conversion efficiencies were poor as observed from the table, this may be attributed to dye degradation with time.

Table 2: Dye extracts from leaves of plants

Dye name	Mtd. Of Extrt.	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	IPC E (%)	λ (nm)	Ref.
Red spinach	Solvent	0.1870	0.350	0.041		17.778	242	[46]
Sorghum spp		2.8600	0.352	0.320	0.330		450-550	[50]
Leaf of indigo	Solvent /Aqueous	0.0130	0.055	0.310	0.004		718	[35]
Bitter leaf	Solvent	0.5000	0.380	0.890	0.960		400	[51]
Spinach		0.4100	0.590	0.590	0.171			[52]
Papaya leaves		0.0730	0.013			1.499		[53]
Spinach		0.0001	0.005		0.072		414 & 665	[54]
Grass jelly		0.0002	0.288		0.01		416	

					3		& 672	
Llexparaguarie nsis		0.7000	0.570	0.33 0	0.13 0			[7]
Teak		0.2900	0.460	0.79 0	0.37 0		662	[55]
Eucalyptus		0.1500	0.500	0.93 0	0.12 0		472	
Holly leaf	Aqueou s	1.1900	0.607	0.58 0		6.110		[49]

3.2.3. Natural pigments from petals; natural sources such as fruits, flowers, leaves, and bacteria exhibit different colours and contain numerous pigments that can be extracted and used in DSSC. Anthocyanin, a flavonoid pigment present in flower petals are widely used as dye for DSSC. They are a group of polyphenolic pigments that are found in plant kingdom. Anthocyanin molecules have carbonyl and hydroxyl groups which can bind to the surface of TiO₂ semiconductors. This helps in the excitation and transfer of electrons from the anthocyanin molecules to the conduction band of the photoanode. Dye pigments were extracted using different methods from various flower petals such as rose, lily, hibiscus, marigold, bougainvillea, bottle brush, blue pea, rosella, etc. Dye extract from rose using solvent and aqueous extraction method resulted in a conversion efficiencies of 0.025% and 0.38% respectively, whereas dye extract from rosella using acid water and aqueous methods gave J_{sc} of 5.0 μA/cm² and 0.203 mA/cm² respectively. The DSSC fabricated with anthocyanin from rose and terminalialalata petals extracted using aqueous process produced the highest conversion efficiency of 0.38% and 0.37% among the flower plants. Other flower pigments gave different values of photo electric properties as shown in table 3 below.

Table 3: Dye extracts from plant petals

Dye name	Mtd. Of Extrt.	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	η (%)	IPCE (%)	λ(nm)	Ref.
Boat lily	Solvent	0.7120	0.450	0.278		31.676	415	[46]
Purple hibiscus		0.4870	0.450	0.100		29.250	246	
Rosella	Acid	0.0050	0.637				230 & 290	[30]
Bougainvillea	Solvent/ Aqueous			0.595	0.250		480 & 540	[29]
Pollen							424 & 456	
Terminalia alata	Aqueous	2.2500	0.700	0.520	0.370			[56]
Rose	Solvent	0.0002	0.349		0.025		522	[54]

Blue pea		0.0002	0.318		0.033		618	
Bottle brush		0.1100	0.430	0.630	0.340		450	[55]
Marigold		0.5100	0.542	0.830	0.230		487	[49]
China loropetal		0.8400	0.518	0.630	0.270		665	
Yellow rose		0.7400	0.609	0.570	0.260		487	
Violet		1.0200	0.498	0.650	0.330		546	
Chinese rose		0.9000	0.483	0.620	0.270		516	
Rose		0.9700	0.595	0.660	0.380			
Lilly	Aqueous	0.5100	0.498	0.670	0.170			[56]
Rosella		0.2030	0.500	0.420	0.270			

3.2.4. Natural pigments from tuber plants; dye pigments extracted from beetroot, mangosteen, allium cepa, lactucasativa, perilla, petunia and others were used in DSSC fabrication as reported by many researchers. Dyes in this group have combination of chlorophyll, flavonoids, carotenoids, anthocyanins, betalains and requires different extraction techniques. For instance, beetroot which contains betalain dye was extracted simultaneously with acidified water and ethanol and the result was conversion efficiency of 0.2% whereas the beetroot extracted using only solvent produced conversion efficiency of 0.47%. Likewise, onion dyes extracted using solvent and aqueous technique showed 0.875% and 0.065% respectively. Mangosteen extract with solvent and solvent/acid extraction method resulted in 1.17% and 0.31% respectively. It should be noted that acid-acylated betacyanins are rapidly deacylated leading to degradation of betanin and destruction of complex pigments [31].

Table 4: Dye extracts from tuber plants

Dye name	Mtd. Of Extrt.	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	IPCE (%)	λ (nm)	Ref.
ASCF	Acid	0.3510	0.475	0.610	0.101			[57]
ECL		0.5240	0.418	0.470	0.106			
Thuja	Solvent	0.8100	0.490	0.380	0.150			[7]
Lactuca sativa		2.5000	0.590	0.210	0.310			
Lepidium Sativum		1.720` 0	0.500	0.510	0.575			
Allium cepa		2.6000	0.635	0.530	0.875			
Onion peels		0.2400	0.510	0.470	0.065			[50]
Yellow sweet potatoes	Aqueous	0.0003	0.515		0.057		401	[54]
Purple sweet potatoes		0.0002	0.379		0.033		532	
Perilla		1.3600	0.522	0.700	0.500		665	[49]
Petunia		0.8500	0.616	0.610	0.320		665	
Lithospermum	0.1400	0.337	0.590	0.030		520		
Knotweed	Solvent	0.6000	0.554	0.630	0.210		435	

Mangosteen pericarp		2.6900	0.689	0.630	1.170			
Beetroot				0.467	0.470		520	[29]
Red cabbage	Aqueous	0.2100	0.510	0.470	0.060			[51]
Mangosteen	Solvent/ Acid	0.4900	1.750	0.630	0.310		378	[48]
Beetroot		0.3600	1.750	0.580	0.200		478, 540	

ASCF = acanthus sennichiovenda flower; ECL = euphorbia continifolia leaf

3.2.5. Natural pigments from other dyes; Tannin-based dyes are found commonly in bark of trees, wood, leaves, buds, stems, fruits, seeds, roots, and plant galls. As plant tissues contain cellulose, starches and pectins as binding materials, enzymatic extraction process is usually employed to loosen the surrounding material leading to more efficient dye extraction. Tannin pigments extracted using solvent extraction method has conversion efficiencies of 0.38%, 0.36% and 0.002% from oak bark, bauhinia tree and tingibark respectively, whereas the dye extracted using solvent/acid method showed 0.36% from melingo skin. Generally, for carotenoid dyes, extraction must be carried out very quickly, avoiding contact with light, oxygen exposure and high temperatures in order to minimize degradation [29]. None of the authors employed nor observed such processes nor precautions and it was shown in their reports.

Table 5: Dye extracts from other sources

Dye name	Mtd. Of Extrt.	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	IPCE (%)	λ (nm)	Ref.
Fructuslycii	Solvent	0.5300	0.689	0.470	0.170		447, 425	[49]
Bauhinia tree		0.9600	0.572	0.660	0.360		665	
Jalawe		0.0064	0.100	0.310	0.008		403	[46]
Oak		1.7700	0.530	0.400	0.380			[7]
Tingibark		0.0032	0.070	0.210	0.002		540	[35]
Melingo skin	Solvent/ Acid	0.0004	0.424		0.036		475	[54]
Broccoli	Solvent	0.0002	0.561		0.069		468 & 662	
Galena							380-800	[33]

In summary, the reviewed papers portrayed different natural dye pigments used in DSSC fabrication from various researchers' with different extraction methods, majority of the researchers extracted their natural pigments using solvent extraction. Investigation output

varied from paper to paper although same dyes were used. It was observed that dye soaking method and duration varied from one researcher to another. Also, variations in solvent concentrations, repetition of dye extraction using different solvents, re-soaking of already coated FTO/TiO₂ glass in another titanium solution was observed from the various reports. Table 6 shows overall best conversion efficiencies from the recently reviewed NDSSC dyes. The natural pigment from rose myrtle showed the highest conversion efficiency of 3.35% whereas other pigments with notable efficiency ranges from 0.5-2.0% as shown in the table below.

Table 6: Summary of dye extracts with higher conversion efficiency

Dye Source	η (%)	Ref no
Rose myrtle	3.350	[16]
Pomegranate	2.000	[47]
Terminalia catappa	1.580	[24]
Blue berry	1.400	[47]
Cram berry	1.200	
Mangosteen pericarp	1.170	[49]
Bitter leaf	0.960	[51]
Raspberry	0.940	[53]
Allium cepa	0.875	
Grapes	0.580	[48]
Lepidium sativum	0.575	[7]
Rhododendron	0.570	[49]

4.1. Conclusion

Variations in investigation outputs was as a result of different steps employed by some researchers in the method of dye extraction and DSSC fabrication. The natural dye pigment extracted from rose myrtle recorded the highest conversion efficiency of 3.53%, this result may be attributed to the extraction method used by the researchers, that is, simultaneous solvent and acid extraction processes. In the extraction of anthocyanin dyes, conventional methods of pigment extraction usually employ dilute hydrochloric acid in methanol or use of ethanol and water for better result.

5. Recommendations

1. Research should be carried out using dyes extracted and stored for a longer period before fabrication to note the durability of a particular dye and how effectively it can function.
2. Dye extraction and soaking periods should be altered to investigate the effect of soaking periods on the performance of DSSC fabrication.
3. Combination of dyes (co-sensitization) for improved performances.
4. Other methods of synthesizing photoanode, should be employed for DSSC fabrication.

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