

Review

Toward Eco-Friendly Dye-Sensitized Solar Cells (DSSCs): Natural Dyes and Aqueous Electrolytes

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Abstract: Due to their low cost, facile fabrication, and high-power conversion efficiency (PCE), dye-sensitized solar cells (DSSCs) have attracted much attention. Ruthenium (Ru) complex dyes and organic solvent-based electrolytes are typically used in high-efficiency DSSCs. However, Ru dyes are expensive and require a complex synthesis process. Organic solvents are toxic, environmentally hazardous, and explosive, and can cause leakage problems due to their low surface tension. This review summarizes and discusses previous works to replace them with natural dyes and water-based electrolytes to fabricate low-cost, safe, biocompatible, and environmentally friendly DSSCs. Although the performance of “eco-friendly DSSCs” remains less than 1%, continuous efforts to improve the PCE can accelerate the development of more practical devices, such as designing novel redox couples and photosensitizers, interfacial engineering of photoanodes and electrolytes, and biomimetic approaches inspired by natural systems.

Keywords: dye sensitized solar cells (DSSCs); natural dye; aqueous electrolyte; eco-friendly DSSCs



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1. Introduction

Since the late 19th century, renewable energy resources, such as solar, hydropower, geothermal, biomass, and biofuel energy, have attracted much attention to substitute fossil fuel, the main cause of global warming [1]. Solar energy is a limitless energy source without the emission of CO₂, which accounts for a large portion of greenhouse gas. Solar energy can be converted into other types of energy by photovoltaic or photothermal mechanisms [2–4]. A solar cell utilizes solar energy by converting sunlight into electricity based on the photovoltaic mechanism. While a silicon solar cell is the representative one, other types of cells, such as organic solar cells, thin-film solar cells, dye-sensitized solar cells (DSSCs), and perovskite solar cells, have also been studied as economical alternatives [5–7]. DSSCs are one of the third-generation photovoltaic devices suggested as an alternative to conventional Si-based solar cells. DSSCs have various advantages, such as a low cost and robust fabrication process, reasonable power conversion efficiency (PCE), and semitransparency [8,9]. The color of the photoanode can be varied using different dyes adsorbed on it. Additionally, DSSCs operate efficiently even under low-light intensity, enabling them to be used indoors.

DSSCs are composed of a transparent electrode, a photoanode, a dye sensitizer, an electrolyte, and a counter electrode. In 1991, Brian O’Regan and Michael Grätzel reported DSSCs with a high PCE of 7.12%, based on a transparent nanoporous film of titanium dioxide (TiO₂) and ruthenium (Ru) complex dye [10]. Since then, researchers have developed novel dyes, electrolytes, photoanodes, and counter electrodes, to further improve the efficiency of DSSCs. Recently, a high PCE of 14.34% was attained by Kakiage et al. via the

co-sensitization of alkoxysilyl-anchor dye (ADEKA-1) and a carboxy-anchor organic dye (LEG4) using various co-adsorbents with a $(\text{Co}(\text{phen})_3)^{2+/3+}$ (phen = 1,10-phenanthroline) redox electrolyte [11]. Concerning tandem-type cells, Eom et al. reported a high PCE value of 14.64% in a tandem cell structure, where alkylated thieno(3,2-*b*)indole-based organic dye (SGT-137) and Zn(II)-porphyrin dye (SGT-021) with a $(\text{Co}(\text{bpy})_3)^{2+/3+}$ redox electrolyte were used [12]. For high-efficiency DSSCs, Ru-complexes and organic solvents are mainly used as dyes and electrolyte solvents, respectively. However, Ru-complex dyes are expensive and synthesized via complicated synthesis processes [13,14]. Ru compounds are treated as moderately toxic, environmentally hazardous, and carcinogenic. Moreover, organic solvents are generally toxic and explosive and cause environmental problems [15–17]. Ironically, DSSCs that mimic photosynthesis in natural leaves to produce energy are made of materials that could be harmful to nature. Because of these problems, researchers are making efforts to increase efficiency and develop more environmentally friendly DSSCs.

Herein, we review various efforts to fabricate DSSCs based on eco-friendly components, such as natural photosensitizers and water-based electrolytes. First, the harmful effect of typical high-efficient DSSCs on the environment is discussed. Next, we discuss recent research to employ natural dyes derived from nature and aqueous electrolytes in DSSCs. Finally, the example studies of DSSCs fully based on environmentally benign dyes and electrolytes are discussed.

2. Problems or Harmful Effects

For high-efficiency DSSCs, Ru-complex dyes and organic solvent-based electrolytes are typically used. However, due to some issues in terms of possible human toxicity, potential environmental impact, production cost, stability, and safety, they are unfavorable and may need to be replaced with other materials.

For high-efficiency DSSCs, electrolytes with low viscosity, high dielectric constant, good solubility, and high chemical stability are required [18–20]. Various solvents have been used for DSSCs. Table 1 presents the melting point, boiling point, vapor pressure (*P*), and viscosity (*η*) of organic solvents popularly used. Nitrile-based solvents, such as acetonitrile (ACN) and 3-methoxypropionitrile (MPN), are considered the most preferred solvents for electrolytes. Ethylene carbonate (EC), propylene carbonate (PC), γ -butyrolactone (GBL), and N-methyl-2-pyrrolidone (NMP) are also used due to their low vapor pressure and volatility. However, such organic solvents are not the best choice in terms of safety [19]. ACN can be metabolized to produce hydrogen cyanide, which is the source of the observed toxic effects in microsomes, especially in the liver [21,22]. EC is converted into ethylene glycol, which is toxic alcohol, causing metabolic acidosis during ingestion [23,24]. GBL is the precursor of γ -hydroxybutyrate (GHB), which can affect the central nervous system [25,26]. Additionally, some organic solvents have low viscosity, resulting in easy electrolyte leakage and high flammability. Regarding health issues, a high volatility at room temperature causes absorption into the human body due to the high exposure possibility to the solvents. Thus, the solvents are unsuitable given the fabrication of DSSCs that are safe for humans and the environment.

Table 1. Melting point, boiling point, vapor pressure, and viscosity of organic solvents popularly used. All parameter values at 25 °C unless otherwise indicated.

Organic Solvent	Melting Point (°C)	Boiling Point (°C)	Vapor Pressure (Torr, at 25 °C)	Viscosity (cP, at 25 °C)
Acetonitrile (ACN)	−45	81.6	88.8	0.334
3-methoxypropionitrile (MPN)	−62.9	164	1.72 (30 °C)	2.5
Valeronitrile	−96	139	2.794	0.78 (19 °C)
3-methyl-2-oxazolidinone (NMO)	15	88	0.00877	2.5
Ethylene carbonate (EC)	36	238	0.0098	90
Propylene carbonate (PC)	−49	241	0.058	2.5
γ -butyrolactone (GBL)	−44	204	0.45 (20 °C)	1.7
N-methyl-2-pyrrolidone (NMP)	−24	203	0.342	1.65

In DSSCs, the dye sensitizer plays a crucial role in absorbing light and converting it into electricity. For high PCE, having a wide range of absorption wavelengths in visible light is important. Ru-complex dyes absorb a wide range of absorption wavelength from 300 nm to 600 nm in visible light, resulting in high-efficiency DSSCs with the maximum efficiency of 11.18% [27,28]. The Ru-complex dyes, such as N719, N3, and black dye, are the most widely used due to their long-excited lifetime, wide absorption wavelength, and highly efficient metal-to-ligand charge transfer, despite their low molar extinction coefficients [29–33]. However, Ru-complex dyes are expensive, need sophisticated and complex syntheses processes [13,14], and cause environmental problems, which could be problems to be used in cost-effective and eco-friendly DSSCs. Although Ru is nontoxic, its compounds, such as ruthenium oxide (RuO_4), are highly toxic and volatile [34–36]. Materials that undergo dye synthesis processes are also harmful to health and cause environmental pollution. For example, ammonium thiocyanate and hydrochloric acid are harmful to health, have high causticity, and generate chlorine [37]. Recently, metal-free organic dyes were developed to replace Ru-based dyes, but organic dyes could be toxic and carcinogenic and produce hazardous pollutants during their synthesis [38,39]. All in all, the typical components in DSSCs, organic solvents, and Ru-based complex dyes may need to be replaced to realize low cost, biocompatible, and environmentally benign devices. Water and natural dyes derived from plants could be excellent alternatives.

3. Natural Dyes Extracted from Nature

Natural photosensitizers are extracted from parts of plants, such as leaves, fruits, and flowers. The dyes contain anthocyanin, chlorophyll, carotenoid, and betalain. The molecular structures of the natural dyes are shown in Figure 1. Anthocyanins are generally obtained from petals of flowers and fruits and absorb 450–580 nm wavelength of visible light with a maximum peak at the 520 nm region [40–43]. Anthocyanins contain carbonyl ($-\text{CO}-$) and hydroxyl ($-\text{OH}$) groups. The functional groups enable the molecules to be stably bound to the surface of TiO_2 , which facilitates electron injection from anthocyanin molecules to the conduction band of TiO_2 [44–47]. Chlorophyll, a key molecule in photosynthesis, is a green pigment commonly found in green leaves and plants. Chlorophyll absorbs 400–450 and 640–680 nm wavelength of visible light and has a maximum peak at 430 nm [48,49]. Carotenoids are yellow, orange, and red pigments obtained from colored vegetables, plants, and algae. Betalains are yellow and red pigments obtained from petals of flowers, fruits, leaves, and roots of plants. The process of extracting natural dye is simple and possibly environmentally friendly. Therefore, many studies have been actively performed to adopt the natural dyes as a photosensitizer of DSSCs to realize eco-friendly DSSCs.

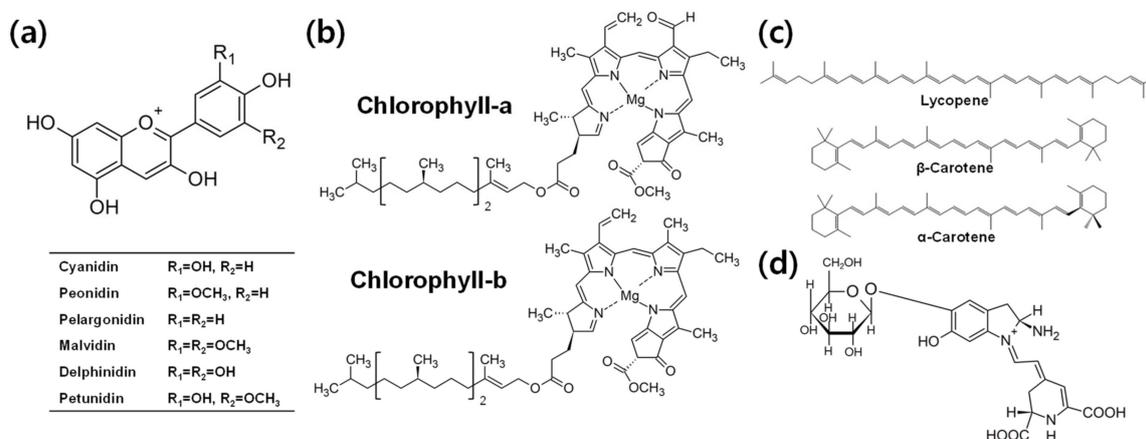


Figure 1. Chemical structures of (a) anthocyanins, (b) chlorophylls, (c) carotenoids, and (d) betalain, reprinted with permission from [50]. Copyright 2019 Springer Nature.

Table 2 summarizes the previous works on DSSCs based on natural dyes, including the types and sources of naturally derived dyes, materials for photoanodes, electrolytes, and cathodes, and their PCE. Compared to those based on organic or metal-based dyes, DSSCs based on natural dyes exhibited low PCE (mostly < 1%). One of the main reasons is that natural dyes absorb a narrow range of light, which inhibits the increase in PCE, whereas organic and rare metal-based dyes have a broad absorption spectrum of visible light [27,28].

Table 2. Types and sources of natural dyes, photoanodes, electrolytes, and cathodes used for the natural dye based-DSSCs and their corresponding photovoltaic performance.

Natural Dye	Dye Sources	Photoanode	Electrolyte	Cathode	PCE (%)	Ref.
Chlorophyll	Spinach	TiO ₂ treated with TiCl ₄	I ⁻ /I ₃ ⁻ in EG	Carbon	0.56	[51]
	Spinach	TiO ₂	I ⁻ /I ₃ ⁻ in EG	Graphite	0.398	[52]
	Spinach	ZnO	I ⁻ /I ₃ ⁻	Carbon	0.1312	[49]
	Spinach	TiO ₂	I ⁻ /I ₃ ⁻	Graphite	0.49	[53]
	Spinach	TiO ₂	I ⁻ /I ₃ ⁻ in ACN	Pt	0.29	[54]
	Spinach	TiO ₂	I ⁻ /I ₃ ⁻	Pt	0.1712	[55]
	Neem	ZnO	I ⁻ /I ₃ ⁻ in EG/ACN	Stainless foil	0.13	[56]
	Wormwood	TiO ₂	I ⁻ /I ₃ ⁻ in ACN	Pt	0.538	[29]
	Ipomoea	TiO ₂	I ⁻ /I ₃ ⁻	Pt	0.278	[57]
	Lemon leaves	TiO ₂	I ⁻ /I ₃ ⁻ in ACN	Pt	0.04	[41]
	Papaya leaves	TiO ₂	I ⁻ /I ₃ ⁻ in ACN	Pt	0.07	[58]
	Bermuda grass	TiO ₂	I ⁻ /I ₃ ⁻ in t-BuOH/ACN	Pt	0.113	[59]
	Papaya peels	ZnO	I ⁻ /I ₃ ⁻	FTO	0.017	[60]
	Pandan leaves	TiO ₂	NaI in PVDF-HFP	Pt	0.51	[61]
	Pterocarpus Indicus Willd	TiO ₂	I ⁻ /I ₃ ⁻ in EG	Carbon	0.0232	[62]
	Anthocyanin	Melinjo skin	TiO ₂	I ⁻ /I ₃ ⁻	Pt	0.036
Purple cabbage		ZnO	I ⁻ /I ₃ ⁻	Carbon	0.102	[64]
Purple cabbage		ZnO	I ⁻ /I ₃ ⁻	Carbon	0.1015	[49]
Siahkooti peel		TiO ₂	I ⁻ /I ₃ ⁻ in ACN	Pt	0.32	[45]
Raspberries		TiO ₂	I ⁻ /I ₃ ⁻ in ACN	Pt	1.5	[41]
Mangosteen peel		TiO ₂ treated with TiCl ₄	T ₂ /T ⁻ in ACN	Mangosteen peel carbon (MPC)	2.63	[65]
Dragon fruit		TiO ₂	I ⁻ /I ₃ ⁻	Pt	0.22	[66]
Cumini		TiO ₂	I ⁻ /I ₃ ⁻ in PEO:PEG	Pt	0.07	[67]
Pomegranate		TiO ₂	I ⁻ /I ₃ ⁻ :PEG in ACN	Pt	0.028	[68]
Red cabbage		TiO ₂	I ⁻ /I ₃ ⁻ in PEG	Carbon	0.024	[40]
Fistula flower		TiO ₂	I ⁻ /I ₃ ⁻ in ACN	Pt	0.21	[69]
Rhododendron flower (red)		TiO ₂	I ⁻ /I ₃ ⁻	Pt	0.33	[70]
Canarium odontophyllum		TiO ₂	I ⁻ /I ₃ ⁻ in EG/ACN	Pt	0.96	[42]
Areca catechu		TiO ₂	I ⁻ /I ₃ ⁻	Pt	0.38	[71]
Pomegranate		TiO ₂ -WO ₃	I ⁻ /I ₃ ⁻ in chitosan	Pt	1.8	[72]
Mangosteen peel		TiO ₂	I ⁻ /I ₃ ⁻	Pt	0.199	[73]
Black rice		TiO ₂	NaI in PVDF-HFP	Pt	0.56	[61]
Rosella		TiO ₂	I ⁻ /I ₃ ⁻ in EG	Pt	0.37	[43]
Onion peel		TiO ₂	I ⁻ /I ₃ ⁻	Pt	0.0647	[55]
Acanthus sennii chiovenda flower		TiO ₂	I ⁻ /I ₃ ⁻ in gel electrolyte	PEDOT	0.15	[74]
Consolida jadis		TiO ₂	I ⁻ /I ₃ ⁻ in ACN/VN	Steel mesh	0.6	[75]
Petals of Ixora coccinea		TiO ₂	I ⁻ /I ₃ ⁻ in ACN/EC	Pt	0.76	[76]
Blueberry		TiO ₂	I ⁻ /I ₃ ⁻	Pt	0.69	[77]

Table 2. Cont.

Natural Dye	Dye Sources	Photoanode	Electrolyte	Cathode	PCE (%)	Ref.
Betalain	Cactus	TiO ₂	I ⁻ /I ₃ ⁻ in t-BuOH/ACN	Pt	0.674	[59]
	Yellow sweet potato	TiO ₂	I ⁻ /I ₃ ⁻	Pt	0.057	[63]
	Beetroot	TiO ₂ treated with TiCl ₄	I ⁻ /I ₃ ⁻ in EG	Carbon	0.49	[51]
	Beetroot	ZnO	I ⁻ /I ₃ ⁻	Carbon	0.179	[64]
	Beetroot	TiO ₂	I ⁻ /I ₃ ⁻ in ACN/EC	Graphite	1.3	[78]
	Turmeric stem	ZnO	I ⁻ /I ₃ ⁻	Carbon	0.3045	[79]
	Turmeric	TiO ₂	I ⁻ /I ₃ ⁻ in EG	Carbon	0.33	[80]
	Bougainvillea spectabilis	TiO ₂	I ⁻ /I ₃ ⁻ in ACN/EC	Pt	0.21	[76]
Lawson	Lawsonia inermis	TiO ₂	I ⁻ /I ₃ ⁻	Pt	1.47	[81]
	Henna leaves	TiO ₂	I ⁻ /I ₃ ⁻ in ACN	Graphite	1.08	[78]
Carotenoid	Orange peel	TiO ₂	I ⁻ /I ₃ ⁻ :PEG in ACN	Pt	0.005	[68]
Curcumin	Turmeric root	TiO ₂	I ⁻ /I ₃ ⁻ in EG	Carbon	0.11	[82]
Indigo	Indigofera tinctoria	TiO ₂ treated with TiCl ₄	I ⁻ /I ₃ ⁻ in MPN	Pt	0.114	[14]

The condition of natural dyes and concentration of dye extract solutions are affected by the extraction temperature, pH, and the types of solvents. For example, high temperatures can thermally degrade dyes, whereas low temperatures can limit the solubility of dyes in extracting solvents [43]. Moreover, dyes have different solubilities depending on the types of solvents because the molecules of natural dyes have different polarities [71,83,84]. Figure 2a shows the absorbance of anthocyanin extracted from *Areca catechu* according to different extracting solvents [71]. Wongcharee et al. investigated the effect of the types of extracting solvents on the efficiency of the resulting DSSCs [43]. It has been reported that although anthocyanin is more soluble in ethanol than water, the photocatalytic decomposition by TiO₂ occurred in the presence of ethanol, decreasing the efficiency after being exposed to sunlight for some time. It has been concluded that ethanol is unsuitable as an anthocyanin-extracting solvent. Thus, the appropriate choice of extracting solvents is important in the dye extraction process.

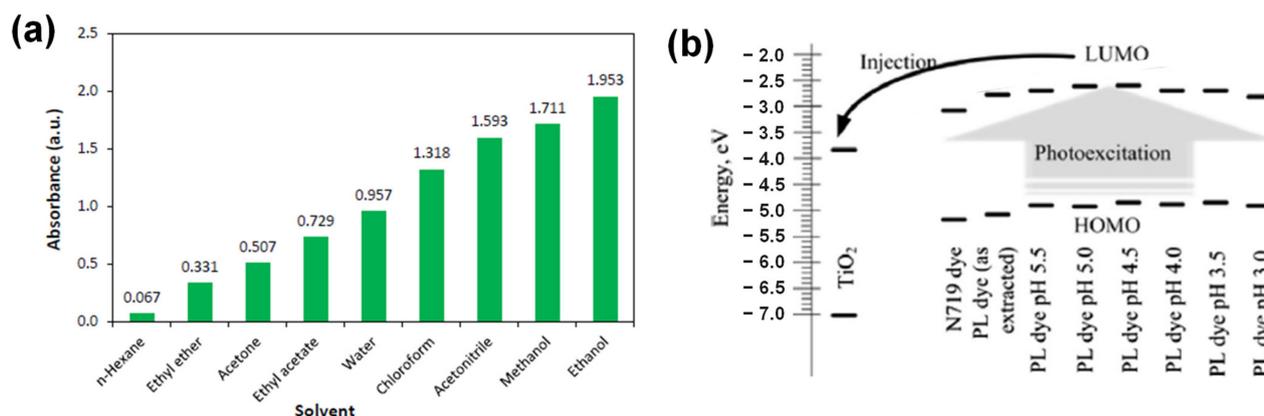


Figure 2. (a) Absorbance of the anthocyanin extracted from *Areca catechu* depending on the types of extracting solvents. Wavelength region of adsorption is from 400 to 800 nm. Reprinted with permission from [71]. Copyright 2020 Elsevier. (b) HOMO and LUMO levels of the chlorophyll extracted from PLs depending on the pH of the extracting solvent. Reprinted with permission from [58]. Copyright 2015 Elsevier.

The pH adjustment of extracting solvents and the addition of acid can affect the properties of dyes, such as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels, absorption spectra, polarity, and stability. The addition

of acid changes the HOMO and LUMO levels of dyes, which is closely related to the V_{OC} value. Suyitno et al. investigated the HOMO and LUMO levels of chlorophyll extracted from papaya leaves (PLs) depending on the pH of the extracting solvent (Figure 2b) [58]. After the pH changed to 3.5 by acidification, the bandgap lowered from 2.30 to 2.16 eV, and the PCE was improved four times from 0.07% to 0.28%. Acidification also increases the polarity of the extracting solvents, such as ethanol or methanol, which could enhance the dye separation from source materials, thereby increasing the concentration of the dye extract solution and absorption value, which assists in higher harvesting from sunlight [43,57,85]. However, high-pH conditions can decompose natural dyes, thereby degrading the PCE of DSSCs. Therefore, it is important to carefully optimize the acid or alkali treatment conditions depending on the types of natural dyes.

The mixture of multiple natural dyes can absorb a wider range of wavelength of light (Figure 3a). For a high photocurrent, the LUMO and HOMO levels should also be above the conduction and valence bands of the photoanode materials, respectively, thereby increasing the injection of photoelectrons and reducing recombination loss [79,86]. A mixture of multiple dyes can facilitate the photoelectron injection and increase the electron lifetime due to the intermediate energy level of electrons in adjacent dye molecules (Figure 3b) [59,87]. Consequently, it has been reported that the PCE of DSSCs can be improved by employing a dye cocktail (Table 3). The most frequently used natural dye is anthocyanin because its carbonyl and hydroxyl groups form a stable bonding to the photoanode surface. The combination of dyes, the optimal mixing ratios of the dyes, and the resulting photovoltaic performances of the DSSCs are presented in Table 3. The optimal ratio may differ depending on the types of natural dyes and electrolytes. Kumar et al. fabricated a co-sensitized solar cell with a high PCE of 1.139% (Figure 3c) by mixing chlorophyll and anthocyanin in a ratio of 1:1 [59]. In their study, the dyes were extracted from cactus and bermudagrass, respectively. The dye-mixing ratio is important to obtain a maximum PCE. For example, Bashar et al. reported that when betalain and chlorophyll were mixed in an optimized mixing ratio of 4:1, a maximum PCE of 0.99% was obtained. By combining anthocyanin and chlorophyll, a maximum PCE of 1.29% was obtained in the ratio of 1:1 [29]. Instead of employing a simple mixture of multiple dyes, Kumara et al. performed the sequential adsorption of natural dyes for the layered co-sensitization (Figure 3d) [42]. The PCE of DSSCs prepared by the layered co-sensitization was 1.55%, which exceeded that of DSSCs with homogenous adsorption of the dyes (1.13%).

Table 3. Combination and ratio of natural dyes and the photovoltaic parameters.

Combination of Natural Dye	Ratio	V_{OC} (V)	J_{SC} (mA/cm ²)	FF	PCE (%)	Ref.
Anthocyanin + Chlorophyll	1:1	0.532	1.45	0.67	0.5175	[49]
Anthocyanin + Chlorophyll	2:1	0.675	2.55	0.67	1.15	[29]
Anthocyanin + Chlorophyll	1:1	0.66	3.16	0.62	1.29	[61]
Anthocyanin + Chlorophyll	1:1	0.47	2.63	0.58	0.72	[61]
Anthocyanin + Betalain	1:1	0.56	1.12	0.6	0.3824	[64]
Anthocyanin + Anthocyanin	1:1	0.38	6.26	0.47	1.13	[42]
Betalain + Chlorophyll	1:1	0.495	4.97	0.46	1.139	[59]
Betalain + Chlorophyll	4:1	0.386	4.74	0.54	0.99	[51]
Anthocyanin + Betalain + Chlorophyll	1:1:1	0.53	1.65	0.68	0.602	[79]

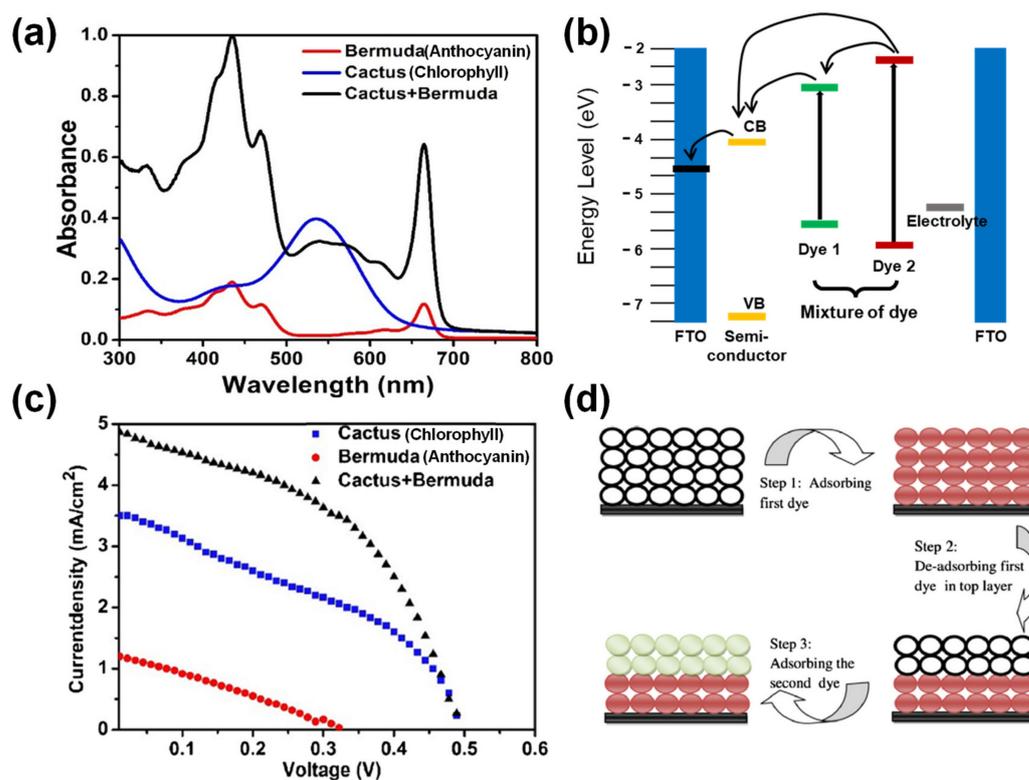


Figure 3. (a) UV-vis absorption spectra of the natural dyes from bermudagrass (anthocyanin) and cactus (chlorophyll), and their mixture. Reprinted with permission from [59]. Copyright 2016 Elsevier. (b) Energy band schematic of a DSSC containing mixed natural dyes. (c) *J-V* curve of DSSCs sensitized by chlorophyll, anthocyanin, and their mixture. Reprinted with permission from [59]. Copyright 2016 Elsevier. (d) Fabrication process of a layered co-sensitized solar cell. Reprinted with permission from [42]. Copyright 2013 Elsevier.

4. Aqueous Electrolyte

4.1. Aqueous Electrolyte

To develop eco-friendly DSSCs, efforts to replace organic electrolytes with aqueous electrolytes have progressed for several years (Table 4). In 2010, Law et al. replaced MPN with water when preparing an electrolyte (comprising 2.0 M 1-propyl-3-methylimidazolium iodide (PMII), 0.05 M iodine, 0.1 M guanidinium thiocyanate (GuSCN), and 0.5 M 4-tert-butylpyridine (TBP)). When the MPN was completely displaced by water, the PCE decreased from 5.5% to 2.4% (Figure 4a) [88]. Similarly, Vaghasiya et al. fabricated DSSCs based on aqueous electrolytes containing organic ionic liquid. The effect of water content on the PCE was investigated, showing that the PCE reduced from 5.61% (0% water) to 3.46% (100% of water) [89].

Although ionic liquids, such as PMII, 1-butyl-3-methylimidazolium iodide (BMII), and 1-ethyl-3-methylimidazolium iodide (EMII), are typically used in organic electrolytes of DSSCs, they are not completely soluble in water, and surfactants are needed to avoid phase separation in the electrolyte. Instead of using ionic liquids, water-soluble salts, such as KI, NaI, and LiI, are employed in water-based electrolytes. Bella et al. investigated the effect of the iodide/triiodide concentration in the electrolyte and the types of counter-ions, resulting in the KI salt-based electrolyte exceeding the NaI-based one in performance, attaining a PCE value of 0.8% (D131 dye, $V_{OC} = 0.488$ V, $J_{SC} = 2.70$ mA/cm², and FF = 0.62) [90]. The desorption of the dye molecules from the photoanode surface in aqueous electrolytes can also decrease the performance of the DSSCs based on aqueous electrolytes than common DSSCs based on organic electrolytes. Co-absorbents, such as chenodeoxycholic acid (CDCA), which co-grafts with the dye onto the photoanode surface, prevent detachment

and aggregation of the dye in water and reduce the charge recombination, resulting in improvement in PCE and stability of DSSCs based on an aqueous electrolyte [91–95]. With a CDCA-to-dye molar ratio of 18:1, a PCE value of 1.25% (D131 dye, $V_{OC} = 0.59$ V, $J_{SC} = 3.86$ mA/cm², and FF = 0.55) was reached using an aqueous electrolyte containing 0.5 M NaI and 10 mM I₂ [92].

To minimize the dye desorption in the presence of water and prevent evaporation or leakage of electrolytes, quasi-solid gel electrolytes were introduced by gelation of aqueous electrolytes. Gel electrolytes for DSSCs have been researched for decades for better device stability; however, several components in the electrolytes are still petroleum-derived, harmful, corrosive, or expensive [96]. For more eco-friendly DSSCs, aqueous and bio-derived gels based on xanthan gum (XG) [95,97,98], cellulose [96], and agarose [99] have been developed recently. XG is a water-soluble polysaccharide and a well-known stabilizing agent widely used in the food and cosmetic industries. Additionally, because XG is thixotropic, meaning that its viscosity decreases when an external force is applied, the gel electrolyte based on XG can penetrate the mesoporous TiO₂ electrode [100,101]. Park et al. developed half aqueous XG-based gel electrolyte with PMII and MPN solvent for DSSCs. The resulting device reached a PCE value of 4.40% even after 288 h, indicating that the XG-based electrolyte enhanced the long-term stability [101]. Galliano et al. prepared 100% aqueous XG-based electrolyte containing NaI salt, based on which the resulting DSSC device showed only a slightly lower PCE value of 1.93% than that based on a liquid-state electrolyte (2.28%) due to lower diffusion coefficient and UV-vis absorption. Moreover, it exhibited impressive stability after more than 1500 h of the aging test (Figure 4b) [97]. Further study to enhance the PCE was conducted using a cobalt-based redox couple, leading to an overall PCE of 4.47% and stability for five days [98]. The aqueous gel electrolyte based on carboxymethylcellulose (CMC) was prepared and used for DSSCs, which showed a PCE value of 0.72% in optimum CMC concentration (5.5 wt.%), without any additives and surface treatment of the photoanode, such as UVO or TiCl₄ [96]. In the study conducted by Haro et al., a bioderived gel electrolyte was developed using lignin, a lignocellulose material, which is the most available material on earth for biofuels. The resulting DSSCs with the lignin-based electrolyte exhibited a PCE value of 1.54% with $V_{OC} = 0.63$ V, $J_{SC} = 3.62$ mA/cm², and FF = 0.67 [102].

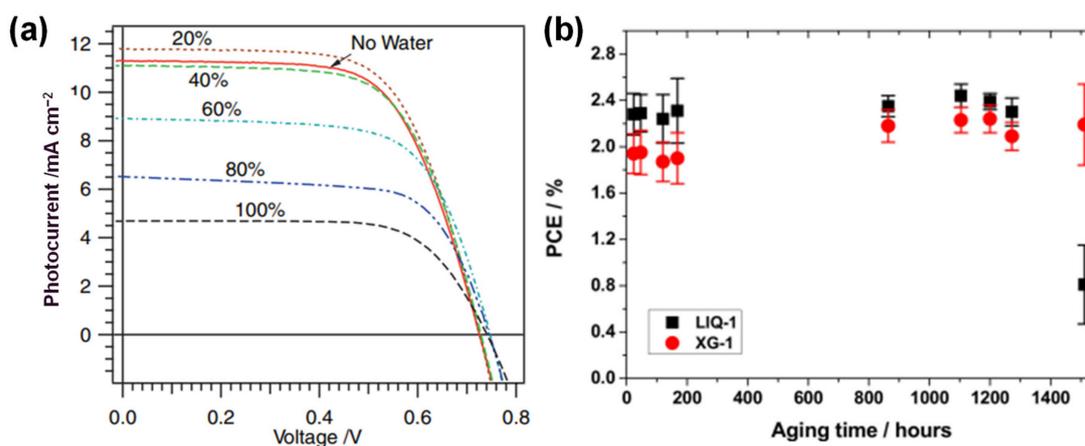


Figure 4. (a) *J*-*V* curves of the aqueous electrolyte-based DSSCs according to the content of water in the electrolyte based on the water–MPN mixture. Reprinted with permission from [88]. Copyright 2010 Wiley. (b) Stability in photovoltaic performance of DSSCs based on aqueous electrolytes (black squares) and hydrogel electrolytes (red circles). Reprinted with permission from [97]. Copyright 2020 MDPI.

Table 4. Photovoltaic performance of DSSCs with aqueous electrolytes.

Dye	Electrolyte	Content of Water (%)	Photoanode	Cathode	PCE (%)	Ref.
LEG4	0.15 M TEMPO, 0.05 M TEMPOBF ₄ , LiClO ₄ , 0.2 M NMBI in H ₂ O	100	TiO ₂	Pt	4.14	[103]
D131	5.5 M KI, 0.05 M I ₂ in H ₂ O	100	TiO ₂	Pt	0.73	[90]
BH2	2 M NaI, 0.02 M I ₂ , 0.5 M GuSCN in an aqueous solution saturated CDCA	100	TiO ₂	NiO	0.056	[91]
CdS QD	0.5 M Na ₂ S, 2 M S, 0.2 M KCl in MeOH:H ₂ O	30	TiO ₂	Pt	1.15	[104]
N719/Z907	2 M NaI, 0.02 M I ₂ , 0.5 M GuSCN in H ₂ O	100	TiO ₂	Pt	0.68	[105]
	2 M NaI, 0.02 M I ₂ , 0.5 M GuSCN, and 1 g natural rubber in H ₂ O				0.46	
JK-259	2 M PMMI, 0.05 M I ₂ , 0.1 M GuSCN, 0.5 M TBP, 1% Triton X-100 in H ₂ O	100	TiO ₂	Pt	1.16	[106]
JK-262					2.1	
N719	2 M NaI, 0.2 M I ₂ , 0.1 M GuSCN in H ₂ O	100	TiO ₂	Pt	2.51	[107]
	2 M NaI, 0.2 M I ₂ , 0.1 M GuSCN, and 0.2 wt.% FC-134 in H ₂ O				3.69	
T169	T-/DS in the presence of H ₂ O ₂	100	TiO ₂	PEDOT	4.5	[108]
D205	1 M TEMPOL in an aqueous 1 M NaBF ₄ solution	100	TiO ₂	Nafion	2.1	[109]
D131	0.5 M TEMPOL in an aqueous 0.5 M NaCl solution in the presence of 0.1 M H ₂ O ₂	100	TiO ₂	Pt	1.3	[110]
TG6	2 M PMMI, 0.05 M I ₂ , 0.1 M GuSCN, 0.5 M TBP in MPN:H ₂ O	0	TiO ₂	Pt	5.5	[88]
		60			4.5	
		100			2.4	
D131	0.5 M NaI, 25 mM I ₂ in H ₂ O	100	TiO ₂	Pt	0.2	[94]
D205					0.1	
D149					0.14	
V35	2 M KI, 0.01 M I ₂ in an aqueous solution saturated CDCA	100	TiO ₂	PEDOT	3.01	[111]
SK3	2 M LiI, 0.02 M I ₂ , 1 M GuSCN in H ₂ O	100	TiO ₂	Pt	1.27	[112]
N719	1 M LiI, 0.02 M I ₂ in H ₂ O	100	TiO ₂	Pt	0.1	[113]
	1 M LiI, 0.02 M I ₂ , Rice starch in H ₂ O				0.35	
D131	5 M NaI, 0.03 M I ₂ in an aqueous solution saturated CDCA	100	TiO ₂	Pt	2.44	[97]
	5 M NaI, 0.03 M I ₂ , 5 wt.% of XG in an aqueous solution saturated CDCA				2.23	
MK2	0.21 M Co(bpy) ₃ Cl ₂ , 0.07 M Co(bpy) ₃ Cl ₃ , 1.5 wt.% of XG in H ₂ O	100	TiO ₂	Pt	4.47	[98]
D131	5.5 M KI, 0.05 M I ₂ , 5.5 wt.% CMC in H ₂ O	100	TiO ₂	Pt	0.72	[96]
	4.5 M NaI, 0.05 M I ₂ , 5.5 wt.% CMC in H ₂ O				0.61	
N3	0.5 M KI, 0.025 M I ₂ in H ₂ O	100	TiO ₂	Pt	0.6	[114,115]
N719					0.5	
N3					1.3	
N719	0.5 M KI, 0.025 M I ₂ in 35% aqueous ethanol solution	65			1.1	
D131	5 M NaI, 0.01 M I ₂ in an aqueous solution saturated CDCA	100	TiO ₂	Pt	2.37	[116]
N3	0.5 M LiI, 0.025 M I ₂ in H ₂ O	100	SnO ₂ /TiO ₂	Pt	0.66	[117]

4.2. Efforts to Improve Performance

The relatively poor performance of DSSCs using aqueous electrolytes compared to organic electrolytes can be attributed to various causes: (1) less wettability of the photoanode surface [104,107,108,112]; (2) desorption of the dye from the surface of the semiconductor [89,118–120]; (3) reduction in the diffusion coefficient [89,104,107,108,112]; (4) recombination derived from a higher concentration of free iodine [91,121]; and (5) negative shift of the conduction band [122–124]. To overcome these problems, endeavors to improve performances, such as adding surfactants, developing novel redox couples and hydrophobic sensitizers, and chemical and morphological modification of the photoanode surface have been performed. In this chapter, we will discuss the efforts to improve aqueous DSSCs.

4.2.1. Development of Novel Redox Couples and Photosensitizers

To overcome the low V_{OC} and J_{SC} values of aqueous DSSCs, novel redox couples and sensitizers were developed to have fast kinetics and a high positive redox potential, which is related to high V_{OC} . The radical of 4-hydroxy-2,2,6,6-tetramethylpiperidinoxyl (4-hydroxy-TEMPO or TEMPOL (Figure 5a)), which has 0.7 V of redox potential in water, was developed and was added to an aqueous electrolyte in DSSCs with a D131 dye [109,110], resulting in a PCE value of 1.3% ($V_{OC} = 0.81$ V, $J_{SC} = 3.1$ mA/cm², and FF = 0.56) [110]. Additionally, Kato et al. immobilized TEMPOL on the Nafion layer coated on a counter electrode to enhance the reduction peak current and achieved a PCE value of 2.1% with 1.0 M TEMPOL/TEMPOL⁺ and D205 dye ($V_{OC} = 0.69$ V, $J_{SC} = 4.5$ mA/cm², and FF = 0.64) [109]. The high V_{OC} compared to that of the previously reported aqueous systems was due to the high positive redox potential of the TEMPOL/TEMPOL⁺ redox couple [103]. J_{SC} remained constant or only slightly higher than without TEMPOL/TEMPOL⁺, which was attributed to the recombination between TEMPOL⁺ and the use of the highly hydrophobic dyes [108,125,126]. Fayad et al. introduced a new water-soluble redox couple based on a thiolate/disulfide (T⁻/DS) in an aqueous electrolyte and new zwitterionic dye (T169) to improve poor wetting, showing excellent performance with $V_{OC} = 0.55$ V, $J_{SC} = 13.30$ mA/cm², FF = 0.62, and PCE = 4.50% [108].

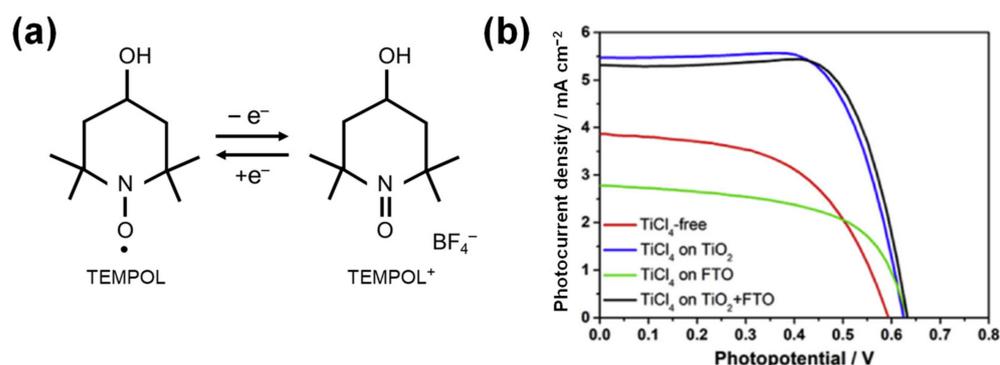


Figure 5. (a) Redox reaction of the TEMPOL/TEMPOL⁺. (b) *J*-*V* curves of the DSSCs based on aqueous electrolytes containing 5 M NaI and 0.01 M I₂, with or without TiCl₄ treatment on photoanodes. Reprinted with permission from [116]. Copyright 2019 Elsevier.

4.2.2. Interface Engineering of Photoanodes and Aqueous Electrolytes

Surfactants are widely used to impede phase separations in aqueous electrolytes, including organic ionic liquids [88,127], and improve incomplete wettability between hydrophobic semiconductor photoanode and aqueous electrolytes by reducing the interfacial tension [106,128]. For a 100% aqueous electrolyte, Zhang et al. applied ionic surfactants (AOT and FK-1 as anionic surfactants and CTAB and FC-134 as cationic surfactants) to 100% water-electrolyte incorporating NaI and I₂. Both the anionic and cationic surfactants could improve the PCE from 2.51% (without surfactant) to 2.98% (with 0.1 wt.% of AOT)

and 3.96% (with 0.2 wt.% of FC-134) due to the better wettability of the aqueous electrolyte and dye-coated TiO₂ layer [107]. However, since the surfactants could decrease the DSSC performance by imposing a diffusion limitation of the redox couple, caution should be taken to use the appropriate redox couple and surfactants [103].

Chemical and morphological modification of photoanode surfaces could also enhance the performance of DSSCs. Miyasaka et al. treated a TiO₂ photoanode with ozone and UV light to increase its hydrophilicity and absorbed dye on the TiO₂ surface in the presence of tert-butylpyridine (TBP) to reinforce the dye–TiO₂ binding. The PCE was enhanced from 0.6% to 1.1% with an aqueous electrolyte (0.5 M KI and 25 mM I₂ in water) [114,115]. Furthermore, an increase in the active surface area is a method for improving the photocurrent and, therefore, the PCE of DSSCs. TiCl₄ treatment on TiO₂ surface forms a rough nanolayer of TiO₂, causing the surface area augmentation and increasing the light-harvesting efficiency and adsorption of dye [129,130]. The TiCl₄ treatment on the TiO₂ surface also inhibited the charge recombination between the electrons and the oxidized redox couple through the barrier effect [116,131,132]. In fact, in research activities on various types of solar cells, including DSSCs, TiCl₄ treatment has been actively utilized to increase efficiency. Bella et al. used the TiCl₄ treatment, which improved the PCE of DSSCs based on an aqueous electrolyte comprising NaI and I₂ from 1.25% to 2.37% (Figure 5b) [116]. The TiCl₄ liquid deposition process could damage the semiconductor film, resulting in flaking off from the fluorine-doped tin oxide (FTO) after a long treatment time (>4 h). Therefore, Pham et al. introduced a shorter (<1 h) and more effective nanoTiO₂-layer-coating method on SnO₂ film using a (NH₄)₂TiF₆ solution. With this approach, the PCE increased ten times, from 0.067% (no treatment) to 0.66% ((NH₄)₂TiF₆ treatment), which was higher compared to the 0.204% improvement using the TiCl₄ solution treatment [117]. S. Castro et al. employed anchoring molecules, trioctylmethyl ammonium dodecanedioate (DTMA) containing carboxyl groups and alkyl chains, to the TiO₂ layer before the dye adsorption step. The molecules are anchored onto the TiO₂ layer by acting as selective physical barriers that hinder the triiodide molecules from contacting the TiO₂ layer [133].

5. Efforts to Obtain Fully Eco-Friendly DSSCs

In previous chapters, we discussed the studies where artificially synthesized dyes and organic solvent-based electrolytes were individually replaced with eco-friendly materials of natural dyes and water-based electrolytes, respectively. Here, studies to realize fully “green” DSSCs by simultaneously using both natural dyes and aqueous electrolytes are introduced (Figure 6a).

Gu et al. attained a PCE value of 0.01% using natural dye from purple cabbage and an aqueous electrolyte, including 0.5 M KI and 50 mM I₂ [134]. Kim et al. improved the PCE of DSSCs based on chlorophyll and 100% aqueous electrolyte with KI/I₂ via O₂ plasma treatment. The treatment enhanced the hydrophilicity of the TiO₂ photoanode surface, thereby increasing the PCE from 0.023% ($V_{OC} = 0.46$ V, $J_{SC} = 0.089$ mA/cm², and FF = 0.56) to 0.033% ($V_{OC} = 0.46$ V, $J_{SC} = 0.14$ mA/cm², and FF = 0.52) [118]. Furthermore, Hon et al. used a 35% aqueous ethanol electrolyte, including 0.1 M Ce(NO₃)₃/0.05 Ce(NO₃)₄ and Au nanoparticles, which can create a Schottky barrier between the Au nanoparticles and the TiO₂ electrode to enhance the photocurrent. They achieved a PCE value of 1.49% [135].

Other examples of approaches for more eco-friendly and low-cost DSSCs, besides using natural dyes and aqueous electrolytes, are to use a CoS-deposited carbon fabric [136] and graphite electrode [134] as a counter electrode or develop the eco-friendly synthesis process of TiO₂ using *Terminalia arjuna* bark extract. As an intriguing approach for eco-friendly DSSCs, Koo et al. reported a biomimetic, regenerable DSSC with microfluidic hydrogels inspired by the vein of a leaf (Figure 6b), which showed a PCE value of 0.21%, with $V_{OC} = 0.63$ V, $J_{SC} = 0.59$ mA/cm², and FF = 0.57. In microfluidic DSSCs with organic eosin Y dye, the dyes and aqueous electrolytes could be repeatedly infused and supplied to the device through the microfluidic hydrogel network, thereby continuously regenerating the DSSCs [99].

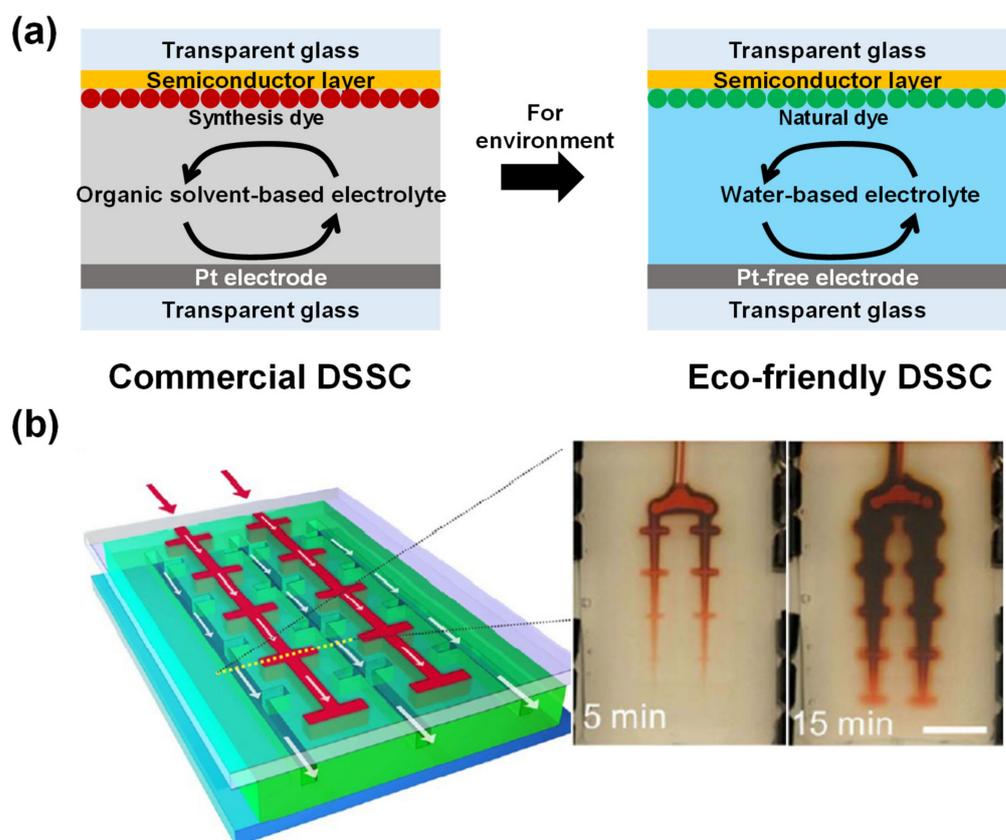


Figure 6. (a) Scheme of general DSSCs containing a synthesized dye and organic electrolyte and eco-friendly DSSCs containing a natural dye and aqueous electrolyte. (b) DSSC assembled with an aqueous gel electrolyte mimicking a leaf vein. Reprinted with permission from [99]. Copyright 2013 Elsevier.

6. Conclusions and Future Outlooks

Due to low cost, facile fabrication, and high conversion efficiency, DSSCs have attracted much attention as new renewable energy devices. To replace the expensive and toxic materials in typical DSSCs with less harmful ones, efforts using natural dyes and aqueous electrolytes have been made. The DSSCs based on natural dyes and aqueous electrolytes, however, showed a lower efficiency than conventional DSSCs due to poor wettability, desorption of dye, low-diffusion coefficient of ions, recombination of photoanodes, and negative shift of the conduction band. Various efforts, such as the combination of the dyes, addition of the surfactants, and treatment of the photoanode, have improved the performance of aqueous DSSCs. Today, a few studies on fully eco-friendly DSSCs have been reported, even though the efficiency is still very low. Attaining long-term stability of the eco-friendly DSSCs is another key task. Fortunately, it has been reported that an aqueous electrolyte could be more durable than an organic solvent-based electrolyte, possibly due to the low volatility, high surface tension, high specific heat, and high boiling point of water [19,90]. Research on fully eco-friendly DSSCs with enhanced efficiency and stability should be conducted to develop more practical energy devices with the minimum environmental footprint.

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