

Review Article

How components of Dye-sensitized solar cells contribute to efficient solar energy capture

ABSTRACT

Herein, we reviewed the main components of dye-sensitized solar cells (DSSCs) which are an emerging cheap and environmentally benign alternative for solar energy capture and conversion to electricity. The role of individual parts such as the semiconductor electrode, counter electrode, photosensitizer, electrolyte, and substrate and their contribution to the overall efficiency (η) of DSSCs is discussed. In addition, parameters such as short circuit current, open circuit voltage, and fill factor used to quantify the efficiency of DSSCs are addressed. The highest solar-to-electric energy conversion efficiency of 13 % has been achieved using titanium dioxide as a semiconductor electrode, a triiodide system as an electrolyte, and platinum counter electrodes. Semiconductors made of such as glass, carbon, conductive polymers and other metal oxides have lower efficiencies (< 8 %). In addition, synthetic photosensitizers especially ruthenium complexes have higher efficiencies (10-11 %) compared to natural dyes among which the highest efficiency (4.6 %) achieved using chlorophyll. The performance of natural dyes based on efficiency of the DSSC is generally in the order: chlorophyll > anthocyanins > carotenoids highly attributed to their structure which not dictates electron release and recombination but also attachment to other components. The DSSC performance is not fixed but rather tunable by variations in the components to achieve desired structural and electronic properties such as firm anchorage between the photosensitizer and the semiconductors, the reduction of the energy band gap by incorporation of other metal salts to extend the absorption range and use of additives that prevent electron recombination with the photosensitizer or any hindrances in the electrolyte redox reactions.

Keywords: synthetic dyes, photosensitizers, efficiency, photoanodes, counter electrodes

1. INTRODUCTION

Energy is crucial to the survival of mankind and sustainability of ecosystems by facilitation of key processes ranging from manufacturing to transportation. Green and renewable energy sources are cheap and environmentally benign alternatives to the commonly used coal and petroleum which are not only non-renewable but also contribute to global warming and the release of pollutants with detrimental effects on the environment and living organisms [1]. With the current trend in alternative renewable energy sources, it is

estimated to account for 27 % of the total energy consumed by 2030 [2]. Renewable energy sources include hydroelectric power, wind, geothermal, and solar energy. Solar energy is key among the renewable energy source because it is non-toxic, quiet and require less sophisticated equipment to generate compared to all other forms of energy [3-5]. The energy from the sun amounts to 3.8×10^6 Joules per year or 4.4×10^{16} watts making a potential source of energy [6].

Photovoltaics (PV) have been employed for decades to harness solar energy. The PV technology is generally classified into first, second, and third generations. The first-generation PV is made of silicon-based materials comprising either polycrystalline or monocrystalline or silicon which is abundant and cheap giving solar-to-electricity conversion between 12-16 % [7]. The second-generation solar cells also called thin film solar cells use amorphous silicon [8]. It has the advantage of reduced power loss due to low temperature coefficient [9]. They also contain other non-crystalline additives such as cadmium telluride (CDTe), copper indium gallium diselenide (CIGS) making the PV light and flexible, however, they have relatively low efficiencies [10] compared to the first generation solar cells. The CDTe solar cells have a module efficiency of 10.9 % and laboratory efficiency of 16.7 % however they are toxic and have low light tolerance [9]. On the other hand the CIGS have efficiencies of 13.5 % in the module and 19.9 % in laboratory with high durability, low cost and their band gap is tunable to achieve tandem cells [11, 12].

The third generation employs quantum dots (QDs) [13, 14], dye-sensitized solar cells (DSSCs) [5, 15], and perovskite solar cells (PSC) [16]. The cells are designed to create an electrical potential difference that push electrons to external circuits [17]. The use of DSSCs has found wide application since its fabrication by O'Regan and Grätzel in 1991 due to low production and design costs [18] and the ability to achieve ≈ 10 % efficiency compared to silicon solar cells [19].

The DSSCs comprise five major components which include the electrolyte [20], visible light adsorber dye [21], counter electrode [22], transparent conductive oxide substrate [23],

and semiconductor [24]. The semiconductor supports the dye by anchorage and also facilitates electron transfer. It is made up of nanostructures which include the nanowires, nanotubes, nano horns, nanotubes, nano cones and nano sheets which are attached to the transparent conductive oxide [25]. The electrolyte acts as charge carriers as it collects electrons from the cathode and transports them back to the dye for restoration [15]. The photosensitizer which can be a synthetic or natural dye release electrons when struck by photons which enters semiconductor with a small band gap allowing electron transfer to the transparent conductive oxide that moves electrons to the load [26]. The counter electrode connected to load then transfer electrons to the electrolyte that acts as the mediator regenerating the oxidized dye and thus completing the circuit [27]. A simplified mode of operation of a DSSC is summarized in Figure 1. It is worth noting that the efficiency DSSCs is greatly determined by the ability to regenerate the photosensitizer [28].

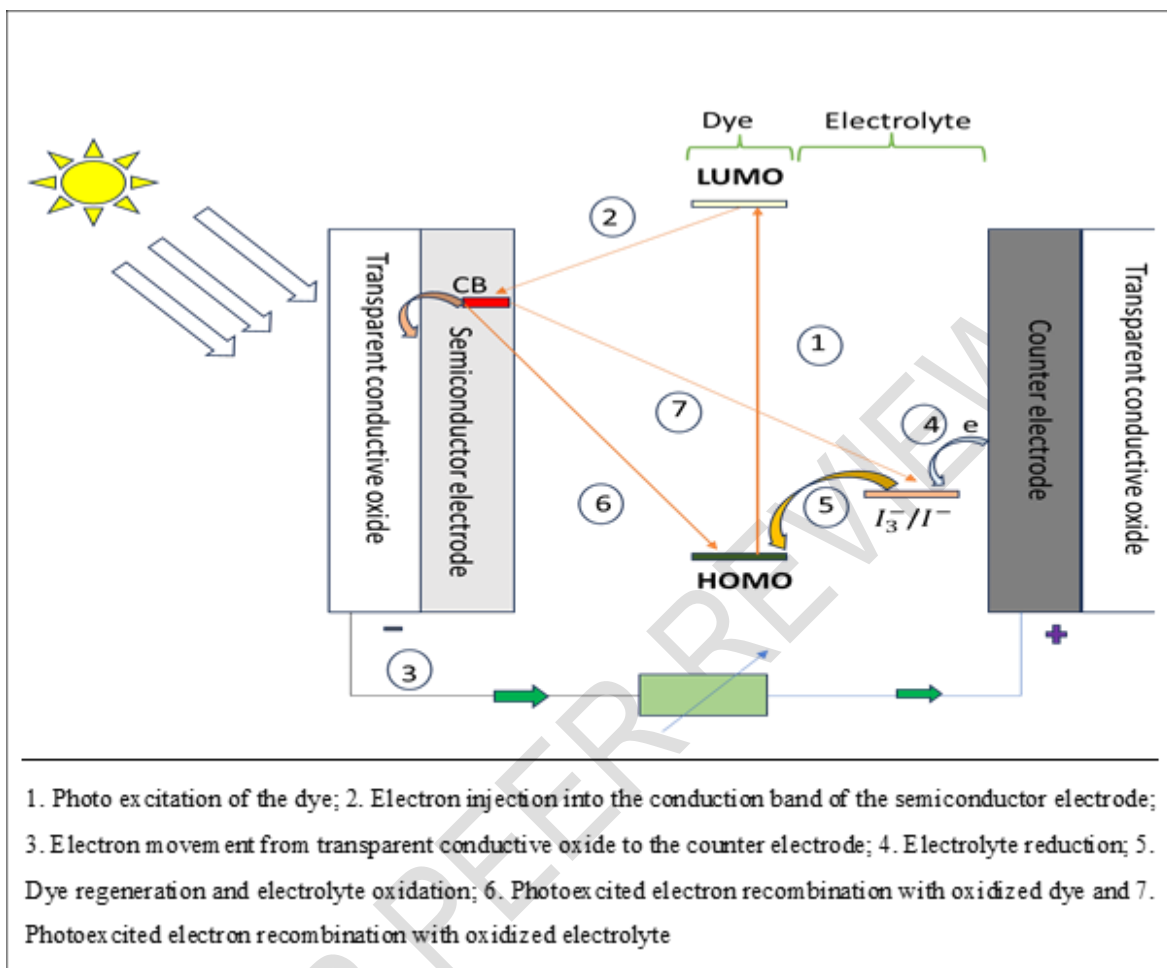


Fig 1. Structure and operation of a dye-sensitized solar cell.

Factors that influence the performance dye-sensitized solar cells

Different characterization techniques are used to assess the performance of DSSCs and to monitor the different stages such as photon absorption and electron excitation, charge transfer, and photosensitizer regeneration [9, 29, 30]. Four common photochemical parameters used include short circuit current density (J_{sc}), open circuit voltage (V_{oc}), Fill Factor (FF), and conversion efficiency (η) [31]. The parameters are determined from a photocurrent density-voltage plot (J-V) curve at 1.5 standard global air mass (AM) (Figure 2) [32].

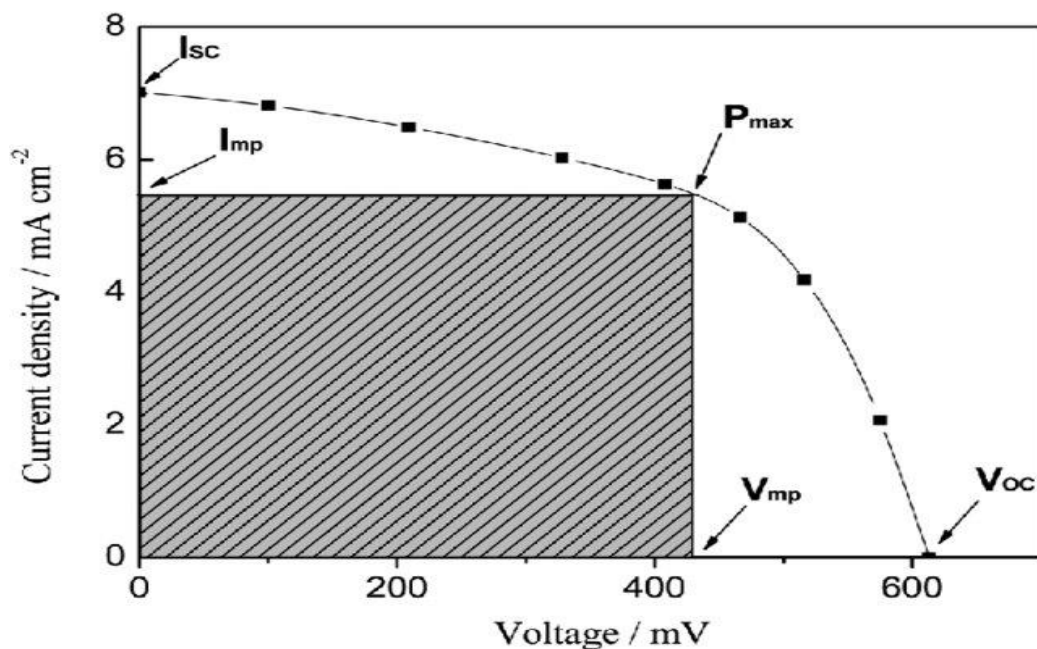


Fig 2. J-V characteristic curve of the DSSC performance [33].

The J_{sc} is estimated at zero potential difference and relatively low circuit irradiation [34] and it depends on the semiconductor-dye bond strength, ability of electron migration to the CB and ease of reducing the electrolyte. On the other hand, the V_{oc} is the potential difference when the current flowing through the circuit is zero [34]. It depends on the difference between the redox potential of the electrolyte and the conduction band Fermi level (E_{CB}) of the semiconductor electrode [34]. Further, the fill factor (FF) is the ratio of the experimental maximum power and the theoretical maximum power [32] which depends on the effects of resistance during ion transport and the resistance of the counter electrode. It should be noted that all components play role in solar capture and the efficiency is determined from the ratio of the maximum power output to the energy of incident photons of light [35]. The electrocatalytic activity and electrolytic conductivity that influence the DSSC performance depend on the counter electrode [36, 37] which have been fabricated using several techniques such as electrochemical deposition, chemical reduction, thermal decomposition, in situ polymerization, hydrothermal reaction and sputter deposition. The later technique is the commonly used because of high purity, uniformity, good adhesion, repeatability but also high

melting point materials can be sputtered [38]. It has been observed that platinum electrodes give a relatively high efficiency [39] but have drawbacks such as high toxicity, less abundance, expensive and non-inertness reacting with redox mediators which corrodes the electrode observed from the formation of platinum iodide which hinders its application [40, 41]. Alternative electrodes made of conductive polymers, carbonaceous material, and carbides, nitrides, sulphides, and oxides of other metals have been used in DSSCs to replace platinum (Table 1).

Table 1. Counter electrode materials used in DSSCs.

| Counter electrodes | Jsc (mA/cm ²) | Voc (V) | FF | η % | Reference |
|----------------------------------|---------------------------|---------|------|-------|-----------|
| Platinum | 12.00 | 0.69 | 0.76 | 13.00 | [19] |
| TiN nanotube | 15.78 | 0.76 | 0.64 | 7.73 | [42] |
| Glassy carbon | 16.50 | 0.71 | 0.65 | 7.56 | [43] |
| Polyoyrrole | 11.00 | 0.79 | 0.64 | 7.77 | [44] |
| NiCO ₂ S ₄ | 14.11 | 0.72 | 0.60 | 6.10 | [45] |
| W ₁₈ O ₄₉ | 17.14 | 0.70 | 0.66 | 7.94 | [46] |

The efficiency of the counter electrode is determined by a rise in the fill factor (FF) which is influenced by the series resistance (SR) and charge transfer resistance (CTR) [47-49]. A reduction in the CTR increases SR which signifies a high electron movement from the counter electrode to the electrolyte enhancing reduction and thus electron continuity leading to high solar-to-electric energy conversion efficiency [48-50]. Brian O'Regan and Michael Grätzel [19] designed a DSSC with a platinum counter electrode which gave an efficiency of 12 % attributed to the morphology and the exposure of the surface facets [22]. Li et al [51] designed a counter electrode using titanium nitride nanoparticles with relatively close efficiency of 7.73 % attributed to interfacial active sites [52].

The solar conversion efficiency also depends on the electrolyte which should have a very fast charge carrier transfer rate from the semiconductor to the counter electrode to rapidly regenerate the oxidized dye [45, 53-55]. Three types of electrolytes have been used in DSSCs;

solid-state, liquid, and quasi-solid electrolytes. A liquid electrolyte containing the redox couple of iodide/triiodide [56] and copper complex ($\text{Cu}^{+2/+1}$) has been widely with efficiencies $>27\%$ [57]. However, the low redox couple-potential of iodide/triiodide causes a decrease in the V_{oc} and thus energy loss [58]. The iodide/triiodide has an electrode potential of 0.35 V in comparison with the standard hydrogen electrode however the slow electron recombination as a result of low reduction kinetics of either I_2 or I_3^- is major drawback affecting the performance of DSSCs [59]. In addition, under low iodine concentration the electrolyte conductivity is low whereas high concentrations promote recombination reactions at semiconductor interface that decrease the efficiency [60]. Nevertheless, the recombination of the electrolyte with electrons can be reduced by additives such as methyl benzimidazole [61], 4-*tert*-butylpyridine [62] and guanidiumthiocyanate [63] which improve on the DSSC efficiency and stability. The alternative quasi-solid [64] and solid-state electrolytes [65] without electrolyte loss generally give less efficient DSSCs (Table 2).

Table 2. Type of electrolytes applied in DSSCs

| Electrolyte | Jsc (mA/cm ²) | Voc (V) | FF | η (%) | Reference |
|-------------|---------------------------|---------|------|------------|-----------|
| Solid state | 15.1 | 0.64 | 0.72 | 6.95 | [65] |
| Liquid | 19.99 | 0.69 | 0.72 | 9.96 | [56] |
| Quasi solid | 15.53 | 0.77 | 0.77 | 8.25 | [64] |

Another key component determining the efficiency of a DSSC is the photoanode whose properties should match with those of other parts especially the dye molecule and the transparent conductive substrate to achieve high efficiency [66, 67]. In addition, it must have a high surface area to readily transfer the electron to the substrate, high resistance to corrosion by the electrolyte, and have excellent surface properties to firmly adsorb the photosensitizer dye [68, 69]. Titanium(IV) oxide (TiO_2) is the commonly used photoanode in DSSCs because of its, low toxicity and abundance, with sizes ranging from 15-30 nm and varying thickness (10-15 μm) making it a suitable material [70]. It exists in three crystalline forms; rutile, brookite, and anatase but the latter has found great application because of its high refractive index ($n=$

2.5), and band gap (3.2 eV) which enables fast movement of electrons [67, 71, 72] compared to ZnO, Zn₂SnO₄ and SnO₂. The band gaps of selected semi-conductors are summarized in Figure 3. Research works have also reported use metal oxides such as WO₃ [73], SrTiO₃ [74], ZnO [75], Zn₂SnO₄ [76], and Nb₂O₅ [77] in DSSCs as shown in Figure 4 [78, 79].

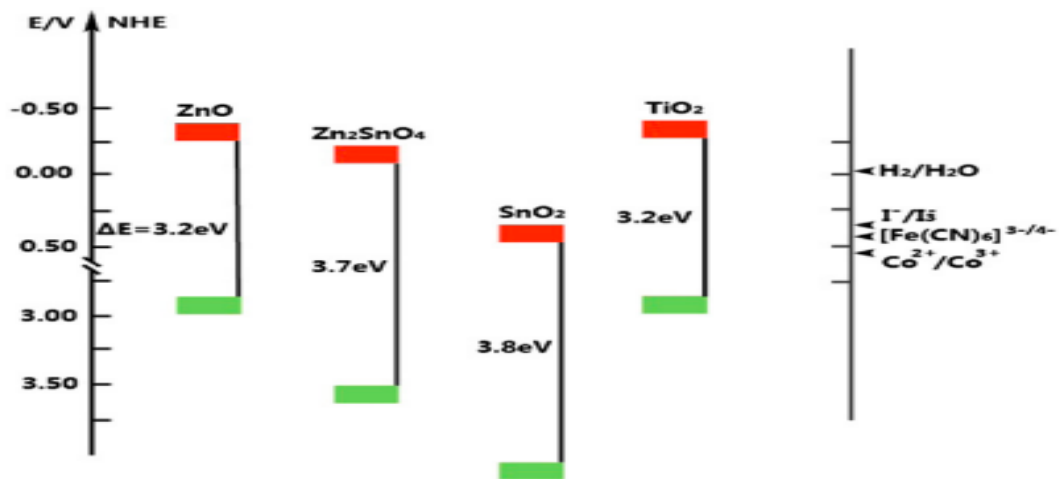


Fig 3. Band gaps of selected semiconductors with reference hydrogen.

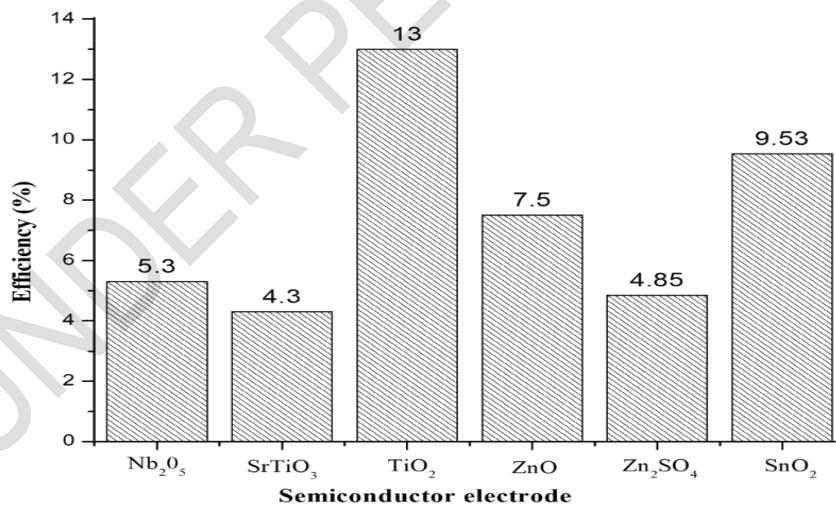


Fig 4. Comparison of the highest-performing semiconductor electrodes.

Photoanodes are fabricated using a number of techniques which include hydrothermal, spin coating, spray pyrolysis, chemical vapour deposition and sol gel are

employed in synthesis [80]. These techniques give a variety of nanostructures such as the nanowires, nanorods, nanoparticles, nanosheets and nanotubes [81]. It is worth mentioning that the structures highly depend on pH and temperature used during fabrication. Barbé et al [82] designed a method used to prepare TiO₂ nanoparticles by hydrolysis of a titanium precursor such as titanium (IV) alkoxide with excess water catalyzed by an acid or base followed by hydrothermal growth and crystallization. Under acidic conditions, transmission electron microscopy revealed that the nanoparticles mainly consisting of anatase phase had 101 surfaces. Under basic condition, Hore et al. reported semiconductors with mesoporous layers which resulted into low recombination rates, high Voc with weak dye-semiconductor bonds [83].

Mathew et al [84] fabricated a DSSC containing TiO₂ achieving a conversion efficiency of 13% which is the highest compared to other semiconductor electrodes. The low efficiency compared to silicon solar cells was attributed to slow electron mobility in addition to light absorption only in the UV region [28]. Nevertheless enhancement of DSSC performance has been achieved by metal doping using aluminium (Al) [85], lanthanum (La) [86], niobium (Nb) [87], tungsten (W) [88], nickel (Ni) [89], and the used of non-metal additives such as carbon (C) [90], fluorine (F) [91], nitrogen (N) [92] and sulphur (S) [93] to modify the energy band gap. The transparent conductive oxides have found great application in DSSCs and they include fluorine-doped tin oxide (FTO) and indium-doped tin oxide (ITO) both of which are transparent and have a wide band gap [94]. The oxides have high optical activity in the visible and near infrared regions [95]. However, FTO has a slight edge in that it more transparent allowing photons to strike the dye with ease and also has a higher thermal capacity, better electrical conductivity and higher corrosion resistance [94]. The transparent conductive oxide is normally prepared using two methods which include sputter deposition and chemical vapour deposition [96]. ITO has a high optical transparency and conductivity compared to FTO [95]

It is worth noting that the most crucial component of DSSCs is the dye sensitizer (DS) responsible for absorbing photons that excite its electrons excitation followed by a jump to

the conduction band starting the electricity generation process [8]. The efficiency of the DS is enhanced by the presence of several functional groups such as carboxyl and hydroxyl that enable anchoring onto the photoanode. The three common categories of DS include synthetic metal- and metal-free organic dyes, and natural dyes. Ruthenium complexes have found wide application since they have a high solar-to-electric energy conversion efficiency of 11% in the presence of sunlight at 1.5 AM standardized global air mass [97]. The commonly used ruthenium dyes include N719, N749 (black dye), and N3 (red dye) [98] with 10-11% efficiencies. The three ruthenium dyes have been used in numerous studies through the modification of their two bipyridyl moieties while leaving the rest of the molecule unchanged [99]. Grätzel et al described the synthesis of numerous ruthenium complexes and modification the substituents enhanced efficiency and interaction between the semiconductor and dye [19, 100]. The N-Chlorosuccinimide groups of ruthenium that help in diffusion of the surface holes and the bipyridyl ligands whose role is to carry out electron transport [101]. The methyl and phenyl groups have been found to increase the absorption coefficients of the metal-ligand once they are bonded at the appropriate positions [19, 100]. However, ruthenium dyes have major drawbacks such as tedious synthetic processes, high costs, and toxicity to the environment and living organisms [8]. Current research has shifted focus to natural dyes as photosensitizers for DSSCs because they are readily available, generally cheap, easy to extract, and have no detrimental effect on man and the environment. Commonly used dye extracts used in DSSCs contain anthocyanins [102], flavonoids [103], chlorophyll [104], and carotenoids [105]. It has been observed that natural dyes show absorb visible light (400-700 nm) [97]. Figure 5 shows the efficiencies of the commonly used dyes and the synthetic dyes have the highest conversions.

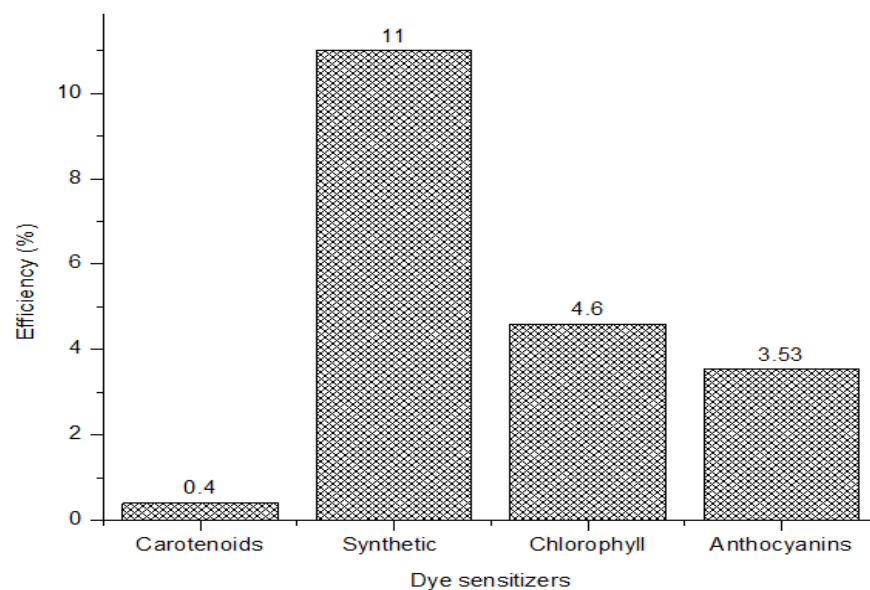


Fig 5. DSSC efficiency using synthetic [106] and natural photosensitizers Carotenoids [107], Chlorophyll [108] and Anthocyanins [109].

Chlorophylls have a magnesium ion in a porphyrin group containing four pyrrole rings [110, 111] responsible for the absorption of light facilitated by an extensive aromatic system [112]. Chlorophyll absorbs in the visible region 420-460 nm (Blue) and 650-700 nm (Red) and reflects green light observed by humans [70]. There are two types of chlorophyll which differ with methyl and acetyl groups attached to carbon at position 7 in chlorophyll a and b, respectively. Recently, Mejica et al [113] used chlorophyll extracted from *Strobilanthes cusia* as a dye photosensitizer and the recorded V_{oc} , J_{sc} , FF, and η values were 0.306 V, 0.0155 mA cm⁻², 0.462, and 0.039 %, respectively which were relative low compared to the synthetic dye N719 [98]. In similar research works Jaafar et al used chlorophyll extracted from *Spinacia oleracea* and the obtained V_{oc} , J_{sc} , FF, and η were 0.33 V, 3.74 mA cm⁻², 0.47 and 0.58%, respectively [114]. In both works, the low J_{sc} is likely due to the weak attachment of the dye to the semiconductor caused by long hydrophobic chain alkyl group which decreases the chances of electron injection into the conduction band and due to the high possibility of the electron combining with the cation of the dye. Other chlorophyll extracts from brown seaweed [108], moss bryophyte [115], cream leaves [116], *Pandanus amaryllifolius* [117], *Azadirachta*

indica [118], *Zizyphus* sp leaves [119], *Ficus rectus linn* [120], and microalgae [121] have been used in DSSCs (Table 3). The measured parameters J_{sc} , V_{oc} and FF vary with each component of the DSSC making it difficult to attribute the overall performance on any one due to the uncorrelated fluctuations in values with respect to the efficiency. Nevertheless, some factors such as the FF can be ruled out in determining the overall efficiency and to a fair prediction, high J_{sc} values result to higher efficiencies as observed with the different classes of photosensitizers, electrolytes and electrode materials in Tables 1-3.

Table 3. Photochemical parameters of chlorophylls

| Chlorophyll | J_{sc} (mA/cm ²) | V_{oc} (V) | FF | η (%) |
|---------------------------------|--------------------------------|--------------|------|------------|
| Microalgae | 2.53 | 0.551 | 0.65 | 0.90 |
| Brown sea weed | 13.80 | 0.57 | 0.58 | 4.60 |
| Moss bryophite | 5.96 | 0.58 | 0.58 | 2.00 |
| Cream leaves | 2.28 | 0.61 | 0.44 | 0.61 |
| <i>Pandannus amaryllifolius</i> | 0.40 | 0.55 | 0.61 | 0.10 |
| <i>Azadirachta indica</i> | 0.43 | 0.40 | 0.40 | 0.72 |
| <i>Zizyphus</i> sp leaves | 1.50 | 0.68 | 0.40 | 0.40 |
| <i>Ficus rectus linn</i> | 7.85 | 0.52 | 0.29 | 1.18 |

Natural dyes containing flavonoids have also been used in DSSCs. They have phenolic structures with low molecular weight and are abundant in fruits, flowers, and a few beverages [122]. Anthocyanins have the longest absorption 500-600 nm which lies in the visible range [123]. They are substituted glycoside salts of phenyl-2-benzopyrilium whose chromane bears another aromatic ring B at carbon 2 where the hydroxylated points are attached to sugar molecules [124-126]. These pigments have loosely bound electrons that easily jump to the semiconductor electrode thus enhancing the conversion efficiency [127]. The hydroxyl groups of anthocyanins strongly anchor the DS onto the semiconductor electrode (Figure 6) [128] facilitating the transfer of electrons into its conduction band [129].

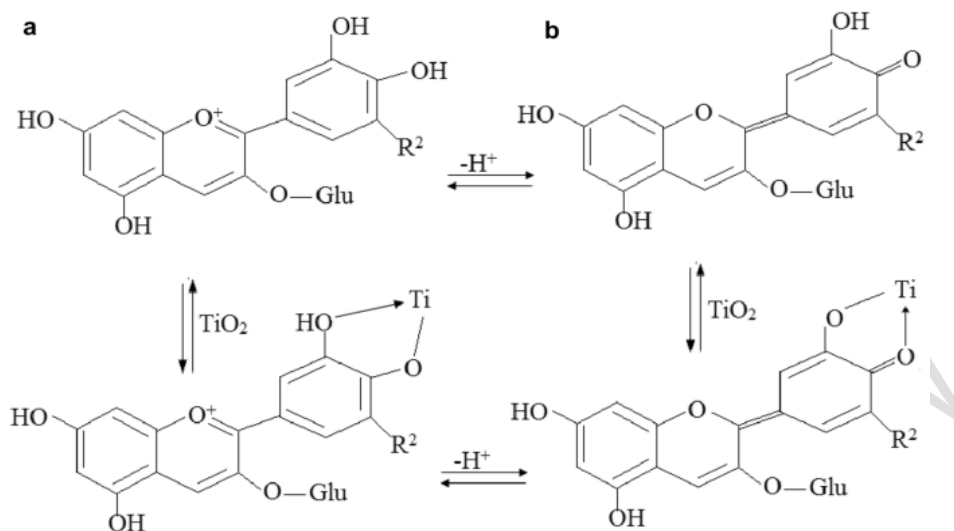


Fig 6. Schematic representation of the interaction between cyanidine-3-glucoside (anthocyanin) and TiO_2 [130].

Al Batty et al investigated Ber and Blackberry fruits containing anthocyanins and managed to obtain the highest efficiency of 1.194 % with J_{sc} of 5.71 mAcm^{-2} , V_{oc} of 0.4 V, and FF of 0.523% using Ber extract compared to an efficiency of 1.059 % with a J_{sc} of 5.25 mAcm^{-2} , V_{oc} of 0.4 V, and FF of 0.504 using the Blackberry fruit extract (Table 4) [131]. The higher performance of the Ber extract is attributed to the high anthocyanin concentration. Other anthocyanin extracts Poinsettia bracts [132], dragon fruit [133], Rose myrite [109], pomegranate [134], spinach [135], *Opuntia dillenii* [136], red sicilian orange [137] and hibiscus flowers [138] used as photosensitizers in DSSCs are shown in (Table 5).

Table 4. The Photochemical parameters of a combination of Blackberry/Ber [131]

| Combination of dyes | J_{sc} (mA/cm^2) | V_{oc} (V) | FF | η (%) |
|-----------------------|-------------------------------|--------------|------|------------|
| Blackberry: Ber (1:1) | 3.50 | 0.35 | 0.46 | 0.57 |
| Blackberry: Ber (1:2) | 4.50 | 0.36 | 0.51 | 0.83 |
| Blackberry: Ber (2:1) | 2.70 | 0.32 | 0.41 | 0.35 |

Table 5. Photochemical parameters of anthocyanins

| Dyes | Jsc (mA/cm ²) | Voc (V) | FF | η (%) | Reference |
|--------------------------|------------------------------|---------|-------|------------|-----------|
| Poinsettia bracts | 0.40 | 0.60 | 0.40 | 1.74 | [132] |
| Dragon fruit | 0.20 | 0.22 | 0.30 | 0.22 | [133] |
| Pomenganate | 12.20 | 0.39 | 0.410 | 2.00 | [134] |
| Spinach | 1.11 | 0.58 | 0.46 | 0.29 | [135] |
| <i>Opuntia dillenii</i> | 1.09 | 0.52 | 0.69 | 0.47 | [136] |
| Rose myrite | 8.77 | 0.50 | 0.29 | 3.53 | [109] |
| Red sicilian orange | 5.13 | 0.33 | 0.59 | 1.01 | [137] |
| Hibiscus flower | 0.96 | 0.27 | 0.43 | 0.11 | [138] |
| Blueberry | 0.96 | 0.39 | 0.47 | 0.17 | [139] |
| <i>Tamarindus indica</i> | 0.35 | 0.53 | 0.67 | 0.14 | [136] |

Carotenoids are also another important group of natural pigments used in DSSCs. They are normally found in the chloroplast and chromoplast and are responsible for the orange, red, and yellow colour which are characteristic of most fruits and flowers [70]. They have a C₄₀ backbone structure [140] and are grouped into the xanthophylls that contain oxygen, and carotenes with only hydrogen and carbon (Figure 7) [141]. Carotenoids are derivatives of lycopene which are produced through reactions such as dehydrogenation, methyl migration, cyclization, hydrogenation, chain elongation and hydrogenation [142]. Table 6 shows the performance of DSSCs using carotenoid extracts from achiote seeds [105], *Curcuma longa* [143], golden trumpet [107], gardenia yellow [144], tomatoes [145], *Syngonium* sp [146], walnuts [147] and Gardenia blue [144] as photosensitizers. The relative poor performance of DSSCs containing carotenoids as DS is likely due to the extensive conjugated double bond system that can hold the excited electron by formation of many stable resonance forms there by reducing the chance of electron jump to the photoanode.

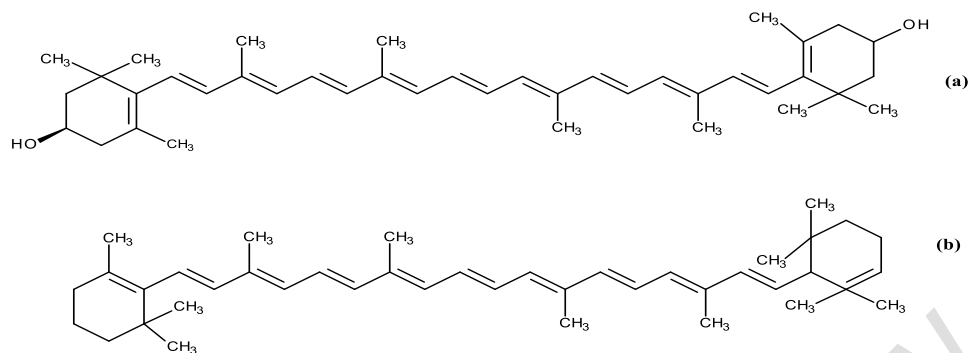


Fig 7. The structure of xanthophyll (a) and carotene (b) molecules

Table 6. Photochemical parameters of carotenoids

| Carotenoids | Jsc (mAcm ⁻²) | Voc (V) | FF | η (%) | Reference |
|----------------------|---------------------------|---------|------|-------|-----------|
| Achiote seeds | 1.10 | 0.57 | 0.59 | 0.37 | [105] |
| <i>Curcuma longa</i> | 0.20 | 0.28 | 0.65 | 0.36 | [143] |
| Golden trumpet | 0.88 | 0.41 | 0.54 | 0.40 | [107] |
| Gardenia yellow | 0.96 | 0.54 | 0.62 | 0.32 | [144] |
| Tomatoes | 0.51 | 0.14 | 0.37 | 0.03 | [145] |
| <i>Syngonium</i> sp | 0.27 | 0.40 | 0.69 | 0.07 | [146] |
| Walnuts | 0.73 | 0.30 | 0.39 | 0.01 | [147] |
| Gardenia blue | 0.53 | 0.44 | 0.69 | 0.16 | [144] |

CONCLUSIONS

Dye-sensitive solar cells are a promising cheap and green alternative energy source. The efficiency of the cells depends on the interdependent-components each playing a crucial role from the process of electron release and transfer to the load and back to the DSSC system. Synthetic dyes are better photosensitizer giving relatively higher efficiencies than natural dyes. The structure of the photosensitizer aid in its anchorage to the photoanodes that determines the extent of electron jump. In addition, it determines the chances of electronic release to the photoanode where photosensitizers with cations or conjugated pi-electron system can hold the excited electron causing the generally reduced low efficiencies of DSSCs. Photoanodes can be improved by metal doping to lower and expand the band gap increasing the chances

of electron reaching the conduction band. In general, the structural and electronic properties of individual components influence the performance of DSSCs. Functional groups of natural photosensitizers enable grip to semiconductors which enhances stability of the system and also facilitates electron transfer. The performance increases with concentration of DS while other factors such as pH and temperature directly affect electron release and recombination. For electrolytes, the performance of quasi solids lies midway between liquid and solid phase with that former having a slight edge.

ETHICS APPROVAL AND CONSENT TO PARTICIPATE

Not applicable.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

Not applicable.

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