A Review on Dye Sensitized Solar Cells (DSSCs): Present status and future prospects

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Abstract

The pursuit for the discovery of abundant and sustainable resource of energy has been of interest to many scientists due to accelerated depletion in non-renewable energy resources and environmental concerns. This draws attention to photovoltaic technology which converts solar radiation to electrical energy. Photovoltaic devices like inorganic, organic and hybrid solar cells have been invented for the past several years using several methods. The issue with traditional Silicon-based Solar Cell is the manufacturing costs and environmental problems which restricts its pervasive use. Tremendously, among all organic solar cells, Dye Sensitized Solar Cell (DSSCs) been study as an alternative to Silicon base Solar Cells have received much attention since the first report of 7 % efficient cell in 1991. Its low cost and easily implemented technology. Affirmed record efficiencies of DSSCs is now 13.29 % for optimized CdSe-TiO_2 photo-anode. This review describes the present status, future prospects and the research challenges that must be addressed to continue the rapid commercialization of DSSC.

Keywords: Dye-sensitized solar cells, Photovoltaic, Solar Radiation, Efficiency, Photo-anode, Stability

1.0 Introduction

The history of sensitized cells dated back to the pioneering work of Brian O'Regan and Michael Grätzel, on the applications of nanosized TiO_2 porous film electrodes in dye-sensitized solar cells (DSSC); these devices convert solar radiation into electricity through the photoelectric effect (Praveen et al., 2020). DSSCs are low cost to manufacture, eco-friendly, and are considered to have a high photon-to-electricity conversion efficiency, so they soon became an intense field of research.

DSSCs can be fabricated from inexpensive oxide nanoparticles and coordination complexes or organic dyes without the expensive vacuum processing or high temperatures required for single crystal or thin film solar cell production. Not only did the DSSC have potential for inexpensive and efficient conversion of sunlight to electricity, but it was also relatively easy for research groups to enter the field and contribute in many areas. As a result, the amount of work on DSSCs has literally grown exponentially over the past two decades.

Due to numerous investigations, DSSCs have now reached an efficiency of approximately 13 %, which has made them potential candidates to produce clean and renewable energy (Aneesiya & Louis, 2020).

The DSSCs imitates the process of photosynthesis in plant to produce energy. DSSCs have a photo-anode which is sensitized with a dye. DSSCs basic components are photo-anode, a sensitizer, an electrolyte and a counter electrode. The photo-anode is made up of a semiconductor nanostructures. There are several nanostructures such as nanotubes, nanorodes, nanowires, nanocones, nanosheets or a combination of them manufactured on a transparent conducting glass (Fadhilah et al., 2019).

DSSCs are devices that uses photovoltaic effect by converting sun radiation in the visible region into electricity and are based on a porous, thin film of a wide band gap semiconductor oxide modified by dye molecules. This modification enhances light absorption and surface area. Electron injection and transparent determining the performance of DSSCs is affected by crystalline material (Kumar et al., 2019).

Typically, a DSSC consist of a transparent conduction oxide (TCO), semiconductor oxide, a dye sensitizer, an electrolyte and counter electrode. The electrode is a nanoporous semiconductor oxide that is deposited on a conducting glass which is separated from counter electrode by only a thin layer of electrolyte solution. The collection of lower-energy photons is aided by the extension of the photoelectrode dye. The dye is chemically absorbed on the semiconductor oxide surface. An ideal sensitizer should absorb a wide range of wavelengths and possess high thermal stability due to its strong binding to the semiconductor oxide (Rajamanickam & Ramachandran, 2020). A DSSC photoanode is typically constructed using a thick film (~10 μm) of TiO_2 or, less often, ZnO or SnO_2 nanoparticles. Light scattering as an important factor in the operation of DSSC is offered by TiO_2 film which has a large inherent absorptive surface area. One major challenge during the fabrication of DSSCs involves the matching of the material bandgaps and the structure design for each layer to give the maximum photoelectrochemical output and the maximum conversion efficiency (Aksoy et al., 2020). Typical architecture of a DSSC consists of a “sandwich” arrangement since it mainly has four parts, as shown in Figure 1: (a) working electrode (photoanode); (b) sensitizing dye; (c) electrolyte (d) counter electrode.

DSSCs have great advantages compared to conventional silicon-based cells. Their construction is simpler as well as their maintenance. Some of the materials used for the fabrication of DSSCc parts are very scarce elements in nature, leading to a very high price in its acquisition and, therefore, it affects the overall price of the cell, even if outputs are efficient, it is necessary to find a new material that addresses the requirements of low price and greater efficiency (Priyono et al., 2018). For this reason, dye-sensitized solar cells (DSSCs) have been innovating.

1.1 Working Electrode

The working electrodes are prepared by depositing a thin layer of oxide semiconducting materials such as TiO_2, Nb_2O_5, ZnO, SnO_2 (n-type), and NiO (p-type) nanoparickes of thickness of about 10 μm on a transparent conducting glass plate made of Fluorine-Doped Tin oxide (FTO) or Indium Tin oxide (ITO). The oxide semiconducting materials framework acts as electron acceptor and transport medium (Mehmood et al., 2020). These oxides have a wide energy band gap of 3– 3.2 eV.

1.2 Photosensitizer (Dye)

Dye is the component of DSSC responsible for the maximum absorption of photon in dye sensitized solar cell (DSSC) at visible light range, whose proprieties will have much effect on the light harvesting efficiency and the overall photoelectric conversion efficiency. The ideal sensitizer for dye-sensitized solar cells should absorb all light just below a threshold wavelength of 920 nm and firmly grafted to the semiconductor oxide surface and inject electrons to the conduction band (Chiba et al., 2006). An efficient photosensitizer has the following characteristics:

1) They absorb excellently in the visible region (400 nm to 700 nm);

2) Adsorb strongly on the surface of the semiconductor;

3) They have high extinction coefficient;

4) They are stable in its oxidized form allowing it to be reduced by an electrolyte;

5) They are stable enough to carry out ~108 turnovers, which typically correspond to 20 years of cell operation;

6) They possess more negative lowest unoccupied molecular orbital (LUMO) than the conduction band of the semiconductor and more positive highest occupied molecular orbital (HOMO) than the redox potential of the electrolyte.

In general, dyes are divided into two groups namely:

1) Synthetic.

2) Natural Dyes.

1) Synthetic Dyes Ruthenium(II) polypyridyl complexes are most commonly used as sensitizer in DSSC due to its high stability, excellent redox properties, broad absorption spectrum in the visible light region (Grätzel, 2005). They have good photoelectric properties, but have some drawbacks such as high cost, scanty resources of Ru and biological toxicity. Therefore organic dyes, for example chlorophyll, coumarin, polyene, merocyanine, indoline and anthocyanins, have been tested as sensitizers. We have three classes of photosensitizers; they are: metal-free organic sensitizers, natural sensitizers and metal complex sensitizers (Grätzel, 2003).

i) Metal Complex Sensitizers Metal complex sensitizers are made up of Anchoring Ligands (ACLs) and Ancillary Ligands (ALLs). The photosensitizers adhesion to the semiconductor is highly dependent on the properties of ACLs. Ancillary Ligands (ALLs) can be used for the tuning of the overall nature of sensitizers, polypyridine complexes of metal ions possess very high Metal to Ligand Charge Transfer (MLCT) bands in the visible region (Grätzel, 2004).

ii) Metal-Free Photo Sensitizers Metal free organic sensitizers can be used to replace the expensive ruthenium based sensitizers and to improve the electronic properties of devices. Even though, the efficiency of these sensitizers is still low when compared to devices based on ruthenium-based dyes, the efficiency and performance can be improved by the proper tuning of the designing components.

2) Natural Sensitizers Natural dyes have also been used in dye sensitized solar cell (DSSCs) as a photosensitizer due to their low cost advantage, easy extraction, nontoxicity in reaction, and the environmentally friendliness (Hardin et al., 2012). Natural dye colorants from chlorophyll, betalain, carotenoid and anthocyanin have been employed as photosensitizers in DSSC (Okoye et al., 2021). These can be found in flowers, fruits and vegetables.

To avoid the aggregation of the dye over the TiO_2 surface, co-absorbents like chenodeoxycholic acid (CDCA) and anchoring groups like alkoxy-silyl (K. Sharma et al., 2018), phosphoric acid (Zaban et al., 1998), and carboxylic acid group (Hagberg et al., 2008) were inserted between the dye and TiO_2. This results in the prevention of dye aggregation and thus limits the recombination reaction (Neale et al., 2005) between redox electrolyte and electrons in the TiO_2 nanolayer as well as results in the formation of stable linkage.

1.3 Electrolyte

This is a solution containing a suitable redox couple in a high concentration, as well as some additives that improve solar cell performance. The most common redox couple used in DSC is iodide/tri-iodide. Electrolyte (such as I^-/I^-_3, Br^-/Br^-_2 (Ferrere *et al.*, 1997), SCN^-/SCN_2 (Oskam *et al.*, 2001), and Co(II)/Co(III) (Nusbaumer et al, 2001). The electrolyte has five main components, i.e., redox couple, solvent, additives, ionic liquids, and cations. The following properties should be present in an electrolyte:

1. Redox couple should be able to regenerate the oxidized dye efficiently.

2. Should have long-term chemical, thermal, and electrochemical stability.

3. Should be non-corrosive with DSSC components.

4. Should be able to permit fast diffusion of charge carriers, enhance conductivity, and create effective contact between the working and counter electrodes.

5. Absorption spectra of an electrolyte should not overlap with the absorption spectra of a dye. I^-/I^-_3 has been demonstrated as a highly efficient electrolyte (Gao et al., 2008), but there are certain limitations associated with its application in DSSCs. I^-/I^-_3 electrolyte corrodes glass/TiO_2/Pt; it is highly volatile and responsible for photo degradation and dye desorption and has poor long-term stability (Wu et al., 2008).

1.4 Counter Electrode (CE)

Counter electrode (CE) in DSSCs is an electrode with good catalytic activities for electron transfer to the redox electrolyte. CE in DSSCs are mostly prepared by using platinum (Pt) or carbon (C). The counter electrode is used for the regeneration of the electrolyte. The oxidized electrolyte diffuses towards the counter electrode where it receives electrons from the external circuit.

2. The principle of operation of DSSCs

The principle of operation of the cell consists of the capture of photons of solar radiation by the dye, hence, the sensitizing molecule must have an intense absorption in the visible region of the electromagnetic spectrum where the radiative intensity of the sun is greater.

$hv + D \rightarrow D^*$

Then, the dye, which is adsorbed on the photoelectrode, is excited by promoting an electron from its electron-filled level, called HOMO, to its first empty level, called LUMO.

$D^* + TiO_2 \rightarrow D^+ + e^-cb\ (TiO_2)$

The electron is then transferred to the mesoporous TiO_2 conduction band, which has a large surface area; this facilitates the injection of large amounts of charge carriers. This electron is then transferred to the transparent conductive oxide and transported to an external circuit until it reaches the counter electrode, which transfers the electron to the electrolyte so that the latter returns the electron to the dye that is, regenerates it and with this, the dye can absorb another photon from the medium and start the cycle again.

$2D^{+} + 3I^{-}$ -> $I^{-}_{3} + 2D$

the dye is regenerated in turn by the reduction of triiodide at the platinised counterelectrode

$I^{-}_{3} + 2e^{-}$ -> $3I^{-}$

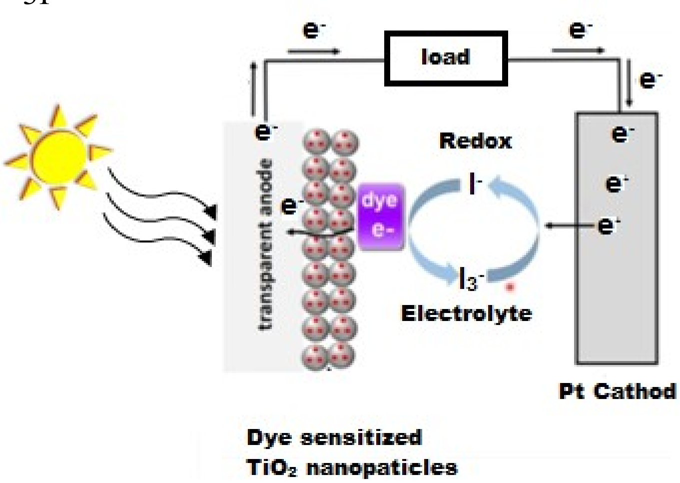

Figure 1: Typical component of a DSSC and functional mechanism

3.0 Previous and present Improvements in DSSCs

To fabricate low cost, more flexible, and stable DSSCs with higher efficiencies, new materials that are light weight, thin, low cost, and easy to synthesize are required. Thus, previous as well as further improvement in the field of DSSCs is included in this section. This section gives a brief account on the work done by the different researchers in the previous years and the results they observed for respective components of the DSSCs.

3.1 Working electrode

Grätzel *et al*. showed drastic improvements in the performance of DSSCs. Their work showed efficiency of 7–10% under AM 1.5 irradiation using nanocrystalline (nc) TiO_2 thin-film electrode with nanoporous structure and large surface area, and used a novel Ru bipyridyl complex as a sensitizer and an ionic redox electrolyte at EPFL (K. Sharma et al., 2018). The conduction band level of TiO_2 electrode and the redox potential of I^{-}/I^{-}_{3} as − 0.7 V versus saturated calomel electrode (SCE) and 0.2 V versus SCE has been evaluated ((Hagfeldt & Graetzel, 1995) and (Kalyanasundaram & Grätzel, 1998)). Some reports have shown that incorporating carbon nanotube (CNT) in TiO_2 by hydrothermal or sol–gel methods greatly improved the cell's performance (Lee et al., 2009). Sun *et al.* (2010) reported that the DSSCs incorporating graphene in TiO_2 photoanode showed a PCE of 4.28 %, which was 59% higher than that without graphene (Sun et al., 2010). An efficiency of 8.30 % was demonstrated by Qiu *et al.* (2010) for the DSSC based on double-layered anatase TiO_2 nanospindle photoanodes (Qiu et al., 2010).

Hu *et al.* (2011) observed that the performance of the DSSCs with graphite-P25 composites as photoanodes was significantly enhanced by 30 % improvement of conversion efficiency compared with P25 alone. They found an enhancement in the value of J_{SC} from 9.03 to 12.59 mA/cm^2 under the condition of 0.01 wt % graphite amount and attained the conversion efficiency of 5.76 % (Hu et al., 2011). An excellent efficiency of 7.5 % was demonstrated for a polymerized ionic liquid (PIL)- based

DSSC with a heterostructured photoanode consisting of 400-nm-thick organized mesoporous TiO_2 interfacial (om-TiO_2 IF) layer, 7-μm-thick nc-TiO_2, and 1.2-μm-thick om-TiO_2 BS as the bottom, middle, and top layers, respectively, which was again much higher than that of nanocrystalline TiO_2 photoanode with an efficiency of 3.5 %.

In 2013 Sharma *et al.* showed the improvement in the PCE value from 7.35 to 8.15 % of the co-sensitized solar cell using modified TiO_2 (G-TiO_2) photoanode, instead of pure TiO_2 photoanode (G. D. Sharma et al., 2013). Usually, mesoporous TiO_2 nanoparticle films are used in WE fabrication because they provide large surface area for efficient dye adsorption. However, there are certain limitations associated with them as short electron diffusion length (10– 35 μm) and random electrical pathway induced by the substantial trapping and detrapping phenomena that take place within excessive surface states, defects, and grain boundaries of nanoparticles and disorganized stacking of TiO_2 films which limits the electron transport (Wu et al., 2013). Park et al. (2014) prepared a mesoporous TiO_2 Bragg stack templated by graft copolymer for dye-sensitized solar cells. A binary oxide photoelectrode with coffee as a natural dye was demonstrated, in 2014 by Aye *et al.* $SnO_{2\,(x)}$–$ZnO_{\,(1-x)}$ binary system with two different SnO_2 composition (x = 3, 5 mol%) were prepared by solid-state reaction at high temperature and employed as a photoanode (Park et al., 2014). An improved efficiency was demonstrated for the larger SnO_2 composition and an overall power conversion efficiency (PCE) observed for SnO_2: ZnO device was increased from 0.18 % (3:97 mol%) to 0.26 % for a device with SnO_2:ZnO (5:95 mol%) photoanode. Gangishetty *et al.* (2013) synthesized core-shell NPs comprising a triangular nanoprism core and a silica shell of variable thickness. They found the incorporation of the nanoprism Ag particles into the photoanode of the DSSCs yielded a 32 % increase in the overall PCE (Gangishetty et al., 2013).

In 2014, Banerjee *et al.* demonstrated nickel cobalt sulfide nanoneedle-array as an effective alternative to Pt as a counter electrode in dye-sensitized solar cells (Banerjee et al., 2014). In 2014, plasmonic light harvesting of dye-sensitized solar cells by Au nanoparticle-loaded TiO_2 nanofibers was demonstrated by Naphade *et al.* because the surface morphology of a WE and a CE play a key role in the performance of DSSC (Naphade et al., 2014). Apart from NTs, bilayer TiO_2 hollow spheres/TiO_2 nanotube array-based DSSC also showed an effective efficiency of 6.90 % (Zhao et al., 2014). Efficiency can also be improved by incorporating SnO_2 as a shell material on a photoanode (Zhou *et al.*, 2014). The integration of SnO_2 as a shell material on ZnO nanoneedle arrays results in a larger surface area and reduced recombination rate, thus increasing the dye adsorption which plays a crucial role in the performance of a cell.

In 2015, Zhao *et al.* studied the influence of the incorporation of CNT-G-TiO_2 NPs into TiO_2 NT arrays and attained an efficiency of 6.17 % for the DSSC based on CNT-G-TiO_2 nanoparticles/ TiO_2 nanotube double-layer structure photoanode(Zhao et al., 2015). Maheswari & Venkatachalam (2014) reported various DSSCs employing zirconia-doped TiO_2 nanoparticle and nanowire composite photoanode film. They demonstrated highest efficiency of 9.93 % for Zirconia/TiO_2 nanowires (Zirconia/TNPW) photoanode with a hafnium oxide (HfO_2) blocking layer and observed that the combination of zirconia-doped photoanode with blocking layer possibly restrains the recombination process and increases the PCE of the DSSCs effectively (Maheswari & Venkatachalam, 2014).

Doping of metallic cations and non-metallic anions in TiO_2, treating FTOs (Sharma *et al.*, 2018), applying 1-D nanostructures like nanowires, nanorods, nanosheets, nanoplates, and hollow spheres are approaches to modify the WE. However due to the low surface area, these 1-D nanostructures show poor dye loading (Yeoh & Chan, 2017).

Hossain *et al*. (2016) used the phenomenon of plasmonic with different amounts of silver nanoparticles (AgNPs) coated with a SiO_2 layer prepared as core shell Ag@SiO_2 nanoparticles (Ag@SiO_2 NPs) and studied the effect of SiO_2-encapsulated Ag nanoparticles in DSSCs. They found the highest PCE of 6.16 % for the photoanode incorporated 3 wt% Ag@SiO_2; the optimal PCE was 43.25 % higher than that of a 0 wt% Ag@SiO_2 NP photoanode (Hossain et al., 2016).

Huang *et al*. (2018) synthesized mesoporous TiO_2 spheres of high crystallinity and large surface area and applied it as a WE in the device. An excellent efficiency of 10.3 % was achieved for the DSSC-employed TiO_2 spheres with long-term stability due to the terrific dye-loading and light-scattering abilities as well as attenuated charge recombination. Further, the efficiency was improved by performing the $TiCl_4$ treatment (Y. Huang et al., 2018). Recently in 2018, a study was carried out to determine the effect of microwave exposure on photoanode and found an enhancement in the efficiency of the cell upon exposure. For the preparation of the DSSC, a LiI electrolyte, Pt cathode, TiO_2 photoanode, and Alizarin red as a natural sensitizer were used. An efficiency of 0.144 % was found for the cell, where 10 min of microwave exposure was carried upon the photoanode (Swathi et al., 2018). Sim *et al*. (2018) applied a novel 3-D transparent photoanode and scattering center design to increase the energy conversion efficiency from 6.3 to 7.2% of DSSC (Sim et al., 2018). A study on incorporation of Mn^{2+} into CdSe quantum dots was carried out by Zhang and group. An improved efficiency from 3.4 % (CdS/CdSe) to 4.9 % (CdS/Mn-CdSe) was achieved for the device upon the addition of Mn^{2+} into CdSe. (Zhang et al., 2018). However, in QDSCs (quantum dot-sensitized solar cells), there is an inefficient transfer of electrons through the mesoporous semi-conductor layer, because their application on a commercial level is still far off (Surana et al., 2018).

Gupta *et* al. (2020) carried out work in photovoltaic measurements, under simulated solar irradiation, the DSSC based on Cu/S co-doped TiO_2 with 0.3 at % Cu and 0.05 at % S exhibited the best power conversion efficiency (PCE) of 10.44 % with significantly improved short circuit current density (Jsc) of 22.05 mA/cm². In contrast, the undoped TiO_2 NPs based DSSC has displayed a PCE of 6.37 % with Jsc of 14.85 mA/cm² (Gupta et al., 2020). Atanacio-Sánchez *et al*. (2020) modified ZnO photo catalyst with graphene oxide (GO) by means of high energy milling. The anode of the flexible dye-sensitized solar cell was fabricated by electrophoretic deposition of the photo catalyst onto flexible electrodes. The obtained results demonstrate that ZnO–GO cell have higher efficiency compared with the ZnO cell (Atanacio-Sánchez et al., 2020).

In 2022, Halil *et al*., studied the effects of Cu doping and the dye adsorption time on the ZnO DSSC. ZnO nanostructures were obtained by hydrothermal synthesis method at different Cu doping ratio (0 %, 0.1 %, 1 %, 3 %) and used as photoanode in DSSC. The maximum cell efficiency of 2.03 % was achieved in the DSSC when photoanode was fabricated by using 0.1 % of Cu doped ZnO nanopowder dipped in N719 solution for only one hour. The efficiency of DSSC with Cu doped ZnO photoanode has improved by 20 %, and the dye adsorption time was decreased by three times (Esgin et al., 2022).

Recently Jae-hun *et al*.(2022) studied the impacts of different ultrasonic treatments on TiO_2. The particles were determined and they were used for the manufacturing of photoelectrodes of a DSSC. The energy conversion efficiency of the ultrasonic horn DSSC was measured to be 3.35 %, which is about 45 % increase in comparison to that of the non-ultrasonic treated DSSC (2.35 %) (Bae et al., 2022).

Many ideas do not achieve great efficiency initially but at least embed different ideas and aspects for the synthesis of new materials for the production of photoanode is still carried out by researchers to increase the performance efficiency of the DSSCs.

3.2 Counter electrode

Calogero *et al.* (2011). invented a transparent and low-cost counter electrode based on platinum nanoparticles prepared by a bottom-up synthetic approach. By using a special back-reflecting layer of silver, they improved upon the performance of a counter electrode based on platinum sputtering and achieved an overall efficiency of 4.75 % under 100 $mWcm^{-2}$ (AM 1.5) of simulated sunlight (Calogero et al., 2011). Li *et al.* (2011) reported that the transition metal nitrides Molybdenum nitrate (MoN), Tungsten nitrate (WN), and Fe_2N show Pt-like electrocatalytic activity for dye-sensitized solar cells, where MoN showed superior electrocatalytic activity and a higher PV performance with an efficiency of . In the case of WN and Iron nitrate (Fe_2N) electrodes, they obtained an efficiency of 3.67 % and 2.65 % respectively (Li et al., 2011).

Anothumakkool *et al.* (2014) showed a highly conducting 1-D aligned polyethylenedioxythiophene (PEDOT) along the inner and outer surfaces of a hollow carbon nanofiber (CNF), as a counter electrode in a DSSC to enhance the electrocatalytic activity of the cell. They showed that the hybrid material (CP-25) displayed a conversion efficiency of 7.16 % compared to 7.30 % for the standard Pt counter electrode, 4.48 % for bulk PEDOT and 5.56 % for CNF, respectively. By using carbon-coated stainless steel as a CE for DSSC, prakash *et al.* (2014) showed an efficiency of 1.98 % (Anothumakkool et al., 2014).

The fabrication of different samples by varying the sintering temperature of the CEs and obtaining the maximum efficiency of 3.62 % at 600 °C of temperature has been reported (Tsai et al., 2015). In the queue of developing new materials, Maiaugree *et al.* fabricated DSSCs employing carbonized mangosteen peel (MPC) as a natural counter electrode with a mangosteen peel dye as a sensitizer and achieved efficiency of 2.63 % (Maiaugree et al., 2015).

Guo *et al.*(2017) synthesized an $In_{2.77}S_4$@conductive carbon ($In_{2.77}S_4$@CC) hybrid CE via a two-step method and achieved efficiency of 8.71 % for the DSSC with superior electrocatalytic activity for the reduction of triiodide and, also, comparable to the commercial Pt-based DSSC that showed PCE of 8.75 %. In 2017 (Guo et al., 2017), Liu *et al.* fabricated DSSCs employing $Co(bpy)_3{}^{3+/2}$ + as the redox couple and carbon black (CB) as the CE. The observation revealed superior electrocatalytic activity of a well-prepared CB film compared to that of conventional sputtered Pt (Liu et al., 2017).

Ho *et* al. demonstrated the first report on Ag nanoparticles doped on Graphene - Ba_2GaInO_6 (GBGI@Ag), which was synthesized by a simple hydrothermal process for improving the counter electrode (CE) in dye-sensitized solar cells (DSSCs). The use of different atomic percentages of Ag (2–6 wt%) on G-BGI@Ag was studied. The 6 % G-BGI@Ag showed an excellent power conversion efficiency (PCE) at 9.90 %, which was similar to the Pt CE under the same conditions (Oh et al., 2019).

A novel nanoporous NiS film with inverse opal structure and outstanding electrocatalytic properties was prepared by a facile template-assisted electrodeposition method (X. Chen et al., 2020). Compared with the flat NiS/FTO electrode, this kind of nanoporous NiS film with inverse opal structure has higher catalytic activity and can be used as a cheap and efficient Pt-free electrode to replace the traditional

Pt/FTO electrode. The nanoporous structure has unique advantages compared with the flat NiS/FTO electrode and the Pt/FTO electrode. The corresponding PCE of the CE of NiS/FTO is 6.30 % which is lower than that of the flat Pt/FTO electrode of 6.69 %. For the nanoporous NiS electrode, the PCE is 6.77 % (X. Chen et al., 2020).

Recently, Mahato *et al*. (2022) use the influence of lyophilization on the electrochemical properties of hydrothermally synthesized tin (Sn) doped molybdenum sulfide (MoS_2) nanostructures. The lyophilized tin doped MoS_2 used as counter electrode (CE) in dye-sensitized solar cells (DSSCs) showed high efficiency and better stability (Mahato et al., 2022). Power conversion efficiency (PCE) of 7.14 % is achieved using lyophilized 2.5% Sn-doped MoS_2 as CE in DSSCs, which is much higher than devices made of CE comprising oven air annealed samples (5.74 %). Akman & Karapinar (2022) prepared porous activated carbon (AC) from fruit peel wastes via chemical activation technique. The fabricated DSSC with a CE using Se@AC:3@5 showed a power conversion efficiency (PCE) value of 5.67 % which is close to the performance of the fabricated DSSC with the Pt-based CE (6.86 %) (Akman & Karapinar, 2022).

The use of other material as counter electrode to reduce the fabrication cost of DSSCs aside the platinum based has not yield high efficient output and hence platinum is the best counter electron material so far.

3.3 Electrolyte

The DSSCs employed pure water-based electrolyte and were tested under a simulated air mass 1.5 solar spectrum illumination at 100 $mWcm^{-2}$ and found the highest recorded efficiency of 3.45 % and 6 % for flexible and glass cells, respectively (Nazeeruddin et al., 1993).

Therefore, more research was carried over the developments and implementation of gel, polymer, and solid-state electrolytes in the DSSCs with various approaches, such as the usages of the electrolytes containing p-type inorganic semiconductors (Kumara et al., 2002), organic hole transporting materials (HTMs) (Bach et al., 1998), and polymer gelator (PG) (J. H. Wu et al., 2007).

Due to the low cost, thermal stability, and good conductivity of the conductive polymers based on polytiophenes and polypyrroles, they can be widely applied in DSSCs despite using ILs (Murakoshi et al., 1998). For the application point of view, the ionic liquids (ILs) should have a high number of delocalized negative charge and counterions with a high chemical stability. Also, the derivatives of imidazolium salts are one of the best applicable in DSSCs.

When 1-ethyl-3-methylimidazolium dicyanamide (EMIM) (DCA) with a viscosity of only 21 mPas was combined with 1-propyl-3-methylimidayolium iodide (PMII, volume ratio 1:1), an efficiency of 7.4 % was observed and, after prolonged illumination, some degradation was also found (MacFarlane et al., 2001).

The effect on the addition of SiO_2 nanoparticles to solidify the solvent was also studied as to increase the cell efficiency, where only inorganic materials were applied in this technique. However, there are certain limitations associated with the addition of organic solvents within a liquid electrolyte, i.e., this leads hermetic sealing of the cell and the evaporation of solvents at higher temperature, and thus the cells do not uphold long-term stability (H. Wang et al., 2005). However, ILs with lower viscosity and higher iodine concentration are needed as to increase J_{SC} by increasing iodine mass transport. Laser transient measurements have been attempted and revealed that the high iodide concentration present in the pure ILs leads to a reductive quenching of the excited dye molecule.

A cell with a binary IL of 1-ethyl-3-methylimidazolium tetracyanoborate in combination with PMII showed a stable efficiency of 7 % that retained at least 90 % of its initial efficiency after 1000 h at 80 °C in darkness and 1000 h at 60 °C, at AM 1.5 (Kuang et al., 2006).

L-cysteine/L-cystine redox couple was employed in DSSC by Chen *et al.* which showed a comparable efficiency of 7.70 %, as compared to the cell using I^- /I_3^- redox couple (8.10 %) (Cheng et al., 2012).

Chen *et al.* (2013) fabricated a solid-state DSSC using PVB-SPE (polyvinyl butyral-quasi-solid polymeric electrolyte) as an electrolyte. They measured the efficiency approximately 5.46 %, which was approximately 94 % compared to that of corresponding liquid state devices, and the lifetime observed for the devices was over 3000 h (K.-F. Chen et al., 2013).

Application of solidified electrolytes obtained by in situ polymerization of precursor solution containing monomer or oligomer and the iodide/iodine redox couple results in a completely filled quasi-solid-state electrolyte within the TiO_2 network with negligible vapor pressure (Komiya et al., 2004). They obtained initial efficiency of 8.1 %. Moudam and Villarroya-Lidon. (2014) studied the effect of water-based electrolytes in DSSC and demonstrated a highly efficient glass and printable flexible dye-sensitized solar cells upon application and found the highest recorded efficiency of 3.45 % and 6 % for flexible and glass cells, respectively (Moudam & Villarroya-Lidon, 2014).

In 2016, Huang *et al.* studied the effect of liquid crystals (LCs) on the PCE of dye-sensitized solar cells. They observed that the addition of minute amounts of LC decreases the J_{SC} because it reduces the electrochemical reaction rate between the counter electrode and an electrolyte. Also, it delays the degradation rates of the cell because of the interaction between cyano groups of the doped LCs and organic solvent in the liquid electrolyte (C.-Y. Huang et al., 2016).

Puspitasari *et al.* (2017) investigated the effect of mixing dyes and solvent in electrolyte and thus fabricated various devices. They have used two types of gel electrolyte based on PEG that mixed with liquid electrolyte for analyzing the lifetime of DSSC. They also changed solvents as distilled water (type I) and ACN (type II) with the addition of concentration of potassium iodide (KI) and iodine, and achieved better efficiency for the electrolyte type II (Puspitasari et al., 2017).

Iwata *et* al. (2018) showed the increase in the ratio of iodide to tri-iodide in the electrolyte rather than to the decomposition or the coupling reactions of the constituent materials (Iwata et al., 2018).

The use of iodide/triodide as an electrolyte corrodes glass/TiO_2, highly volatile and responsible for photo degradation and dye desorption and has poor long-term stability but still the best currently based on its high efficient performance.

3.4 Dyes

However, a different trend to optimize the performance of the DSSCs has been started by adding the energy relay dyes (ERDs) to the electrolyte (Margulis et al., 2013); inserting phosphorescence or luminescent chromophores, such as applying rare-earth doped oxides (Han et al., 2015) into the DSSC; and coating a luminescent layer on the glass of the photoanode. In the process of adding the ERDs to the electrolyte or to the HTM, some highly luminescent fluorophores have to be chosen. The main role of

ERD molecules in DSSCs is to absorb the light that is not in the primary absorption spectrum range of the sensitizing dye and then transfer the energy non-radiatively to the sensitizing dyes by the fluorescence (Forster) resonance energy transfer (FRET) effect (Forster 1959). An improvement in the external quantum efficiency of 5 to 10 % in the spectrum range from 400 to 500 nm has been demonstrated by Siegers and colleagues (Siegers et al., 2007).

Chang *et al.* (2013) achieved an efficiency of 1.47 % when chlorophyll dye (from wormwood) and anthocyanin dye (from purple cabbage) as natural dyes were mixed together at volume ratio of 1:1, whereas the individual dyes showed lower conversion efficiencies (Chang et al., 2013).

Lim *et al*. (2015) have achieved a 0.085 % of efficiency when mixing the chlorophyll and xanthophyll dyes together (Lim et al., 2015).

Puspitasari *et al*. (2017) fabricated different DSSCs by mixing the three different natural dyes as turmeric, mangosteen, and chlorophyll. The highest efficiency of 0.0566% was attained for the mixture of the three dyes (Puspitasari et al., 2017).

Bakr *et al*. (2017) have fabricated Z907 dye-sensitized solar cell using gold nanoparticles prepared by pulsed Nd:YAG laser ablation in ethanol at wavelength of 1064 nm. The addition of synthesized Au NPs to the Z907 dye increased the absorption of the Z907 dye, thus achieving an efficiency of 1.284 % for the cell without Au NPs and 2.357 % for the cell incorporating the Au NPs (Bakr et al., 2017). Lin et al. showed the doping of 1,8-naphthalimide (N-Bu) derivative fluorophore directly into a TiO_2 mesoporous film with N719 for application in DSSCs (L. Zhang & Konno, 2018) in which the N-Bu functioned as the FRET donor and transferred the energy via spectral down-conversion to the N719 molecules (FRET acceptor). An improvement of the PCE from 7.63 to 8.13 % was attained by the cell. Similarly, (Pratiwi et al., 2017) fabricated a DSSC by adding a synthetic dye into the natural dye containing anthocyanin (from red cabbage). They prepared two different dyes at different volumes, i.e., anthocyanin dye at a volume of 10 ml and combination dyes at a volume of 8 ml (anthocyanin): 2 ml (N719 synthetic dye), respectively. They showed an enhancement in conversion efficiency up to 125 %, because individually the anthocyanin dye achieved a conversion efficiency of 0.024 % whereas for the combination dye 0.054 % conversion efficiency was achieved .

Zhang and Konno (2018) studied the PV characteristics of DSSCs by mixing different dyes and observed highest efficiency of 3.03 % for the combination dye “D358 + D131,” (Zhang & Konno, 2018).

Recently, Castillo-Robles *et al.* reviewed four important aspects, with two related to the dye, which can be natural or synthetic. Herein, only natural dyes and their extraction methods were selected. Their review shows development of three highly rigid quinoxaline-based dyes (LY01, LY02, and LY03) which their performances showed that the LY03 dye had the best efficiency of this group with 7.4 % (Castillo-Robles et al., 2021). On the other hand, they discussed the nanostructures used for DSSCs, the TiO_2 nanostructure being the most reported; it recently reached an efficiency level of 10.3 %.

The use of natural plants as dye as extensively been reviewed in the field of DSSCs but the output is still very low compared to the synthetic dyes, hence they are still the most efficient dye for the production of DSSCs.

4. Future prospects in DSSCs

To improve on the efficiency as well as the stability of the DSSCs, researchers have to focus on fundamental fabrication methods and materials, and working of these cells. Different ways to improve the efficiency of DSSCs are discussed below.

1. To increase the efficiency of DSSCs, the oxidized dye must be firmly reduced to its original ground state after electron injection. In other words, the regeneration process (which occurs in the nanosecond range) should be fast as compared to the process of oxidation of dye (the process of recombination (0.1 to 30 μs) (K. Sharma et al., 2018). As the redox mediator potential (I^- ion) strongly effects the maximum photovoltage, thus the potential of the redox couple should be close to the ground state of the dye.
2. To improve the efficiency of the DSSC circuit, light absorption from organic dyes must reach the maximum visible and near infrared spectrum values (Grifoni et al., 2021).
3. One promising approach to improve DSSC performance is to improve the spectral response of sensitizers with metal nanoparticle-based surface plasmon resonance (Selvapriya et al., 2022).
4. The design of high-performance early transition metal decorated carbon-based multiple active-site catalysts is of high significance for improving the efficiency of energy utilization (Huang et al., 2021).
5. By increasing the porosity of the TiO_2 nanoparticles where the maximum dye absorption takes place for TiO_2 based solar cell .
6. Reducing or prohibiting the formation of the dark current by depositing a uniform thin layer or under layer of the TiO_2 nanoparticles over the conduction glass plate (Wang et al., 2022).
7. By promoting the use of different materials in the manufacture of electrodes like nanotubes, nanowires of carbon, graphene; using varied electrolytes instead of a liquid one like gel electrolyte and quasi-solid electrolytes; providing different pre-post treatments to the working electrode like anodization pre-treatment and $TiCl_4$ treatment; using different types of CEs (J. Wu et al., 2017) and by developing hydrophobic sensitizers, the performance as well as the efficiency of these cells can be tremendously improved.
8. By inserting phosphorescence or luminescent chromophores, such as applying rare-earth doped oxides into the DSSC (Chander et al., 2015), coating a luminescent layer on the glass of the photoanode (Han et al., 2015), using plasmonic phenomenon (Bakr et al., 2017) and adding energy relay dyes (ERDs) to the electrolyte (Rahman et al., 2015).

5. Conclusions

This review has shown extensive study on the efficiency offered by working electrode, dye, electrolytes and counter electrode, hence, a comprehensive approach needs to be used to improve the efficiency of the DSSC by choosing appropriate conditions of electrolyte (most stable electrolyte which provides better electron transportation capability), optimum dye, photoanode and counter electrode. In terms of their commercial application, a DSSC needs to be sustainable for more than 25 years in building-integrated modules to avoid commotion of the building environment for repair or replacement and a lifespan of 5 years are sufficient for portable electronic chargers and accessories.

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