A Review on the Impacts of Materials on the Efficiency of Dye-Sensitized Solar Cells

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Abstract

In the pursuit of clean and renewable energy sources, the third-generation photovoltaic cells known as Dye Sensitized Solar Cell (DSSC) have been forecasted as a potential solution for future applications. In comparison to thin film solar cells, it is comparatively simple, low cost, lightweight, flexible, highly efficient with high-throughput synthesis for harvesting solar energy. However, it suffers several challenges including light absorption, charge transferring, dye degradation and stability issues. The DSSC, though invented in 1988, is still at the stage of development and there exist several areas open for improvement in its current technology. As the function of devices basically depends upon their constituents, the improvement of DSSC over the past years strongly depends upon modification of the involved materials. This paper is dedicated to providing a comprehensive overview on the efforts reported by researchers worldwide in order to modify Counter Electrodes (CEs), electrolyte, dye and semiconducting photo electrode used in DSSC.

Keywords: Dye Sensitized Solar Cell, Counter Electrode, Efficiency, Electro Catalytic Activity.

Introduction

The depletion of conventional energy sources had become increasingly more alarming until modern photovoltaic devices were developed prepared in the current century. The harvesting of solar energy is now being attempted by using a number of mechanisms including chemical, biological and physical mechanics to produce highly efficient solar cells free from drawbacks. It has been witnessed during the last decade that the improvement in efficiency of the solar cells is largely dependent on the material side of the devices. The evolution as well as ongoing research in the field of Dye Sensitized Solar Cells (DSSC) is centring over the enhancement of the efficiency along with the better performance of the DSSC (Nurazizah et al., 2023). Though, the efficiency as well as performance of every type of solar cell depends upon the materials. However, the DSSC are specifically material dependent as physical and chemical processes rely exclusively on functioning of its

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component materials. The technological development of engineering solutions and material fabrication techniques has motivated the material scientists to improve the existing literature and explore further potential materials in this regard. Despite the availability of books, review articles and related stuffs on DSSC at different forums, the reports on its material side are not frequent (Antu et al., 2025; Mariotti et al., 2020). This review addresses the properties, improvements witnessed, future challenges and the expert's opinions on the materials of DSSCs thereby giving a comprehensive look into the published literature.

Dye Sensitized Solar Cell (DSSC)

The DSSC, a well-known device for harvesting solar energy in simple but efficient manner, also known as Grätzel cell as it was first introduced by Michael Grätzel. The DSSC are principal research and industrial consideration because of their less manufacturing cost and high efficiency in contrast to other conventional silicon-based solar cells. The typical components of DSSC are semiconducting nanoparticles, dye molecules, electrolyte and Counter Electrode (CE). In general, titanium dioxide (TiO_2) is used as semiconducting component, but in alternative, zinc oxide (ZnO) can also be used as semiconducting component. This is because, it has matching properties like band gap as well as high carrier mobility of electrons (Zhang et al., 2009). An extremely ordered spongy TiO_2 layer is attracting growing interest because of its three dimensional (3D) periodic arrangement and comparatively higher refractive index difference between TiO_2 as well as ambient air. Furthermore, band gap in specific and detectable range depends upon the size as well as shape of 3D structure (Seo et al., 2011; Thomas et al., 2014). The construction, functioning and material properties of the components of DSSC are discussed briefly in the following sections.

Components and Functioning of DSSC

The components of DSSC include photoanode with conductive glass, semiconducting nanoparticles and dye, the CE (usually platinum (Pt)) and electrolyte (usually iodide). The most significant part of DSSC is semiconductor TiO_2 in which electron-hole (e-h) pairs are generated upon absorption of sunlight. Its surface is made mesoporous and contains nanoparticles, which appears to enhance the efficiency. The thickness at which it deposited on conductive glass ranges from 10-12 μm and having porosity of 50-60%. Though, the light can directly produce e-h pairs in TiO_2 but it offers limited absorption of incident radiations due to which a photo-sensor known as dye is coated on surface of semiconductor (Qadir, 2016).

The fundamental function of dye is the absorption of light from spectrum of radiations available in sunlight. The absorbed radiations then sensitize semi-conductor material which have large band gap (Hao et al., 2006; Susanti et al., 2014). The quantity of light absorbed by dye depends upon its properties that are strongly based on the respective material used. Hao et al. (2006) have utilized many natural dyes which have been extracted from black rice and capsicum, as well as erythrina kelp as dyes. The dyes prepared from black rice showed maximum photo-sensitized impacts because of best interaction among carbonyl and hydroxyl groups of anthocyanin particle on black rice. Chang, et.al have reported the usages of ipomoea fruit and spinach extracts as dyes for DSSC and consequently, obtained the efficiencies of 0.257 % and 0.131 % respectively (Chang et al., 2010; Kakiage et al., 2015; Saranya et al., 2015).

Operational Principle

The operating principle of a DSSC is as sketched in Figure 1. The basic principle of DSSC involves photo excitation of carriers in semiconductor. In order to initiate the process, light is incident on dye molecules, which act as sensitizer. The dye molecules have two important levels known as Highest Occupied Molecular Orbit (HOMO) and Lowest Unoccupied Molecular Orbit (LUMO). When light falls on the dye, molecules of the dye become excited as a result of which electrons are transferred from HOMO of dye to its LUMO. From where those excited electrons are injected to the Conduction Band (CB) of semiconductor (usually TiO_2). This transportation of excited electrons into the CB takes place in the time range of tens of a femtosecond to hundreds of a picosecond. The electrons then move to the external circuit (towards the load) and hence to the CE in the time range of micro to millisecond (Asbury et al., 1999; Benkö et al., 2002). The electrons from CE will move towards the electrolyte, which transport the electrons to dye causing its regeneration. The oxidized dye gained its original state in nanosecond timeframe by the transfer of electron from electrolyte. The regeneration of the dye by iodide stops the recapture of the injected electrons in the CB by the oxidized dye. The triiodide ions (I_3^-) formed by the oxidation of iodide (I^-) diffuse through the CE usually composed of islands of finely divided Pt (Hailu et al., 2017; Teuscher et al., 2014).

The process of regeneration of dye involves change of I_3^- into I^- ions. Under light brightness voltage is produced with respect to variance of Fermi level of the e^- in metal oxide and the redox potential of the electrolyte (Grätzel, 2003; Hagfeldt et al., 2010). The mechanism of electron-transfer in DSSC is as sketched in Figure 2.

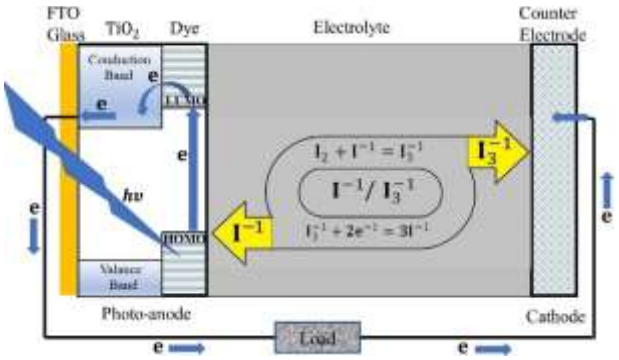

Figure 1: Schematic diagram of DSSC representing procedure of different components (Majid et al., 2020).

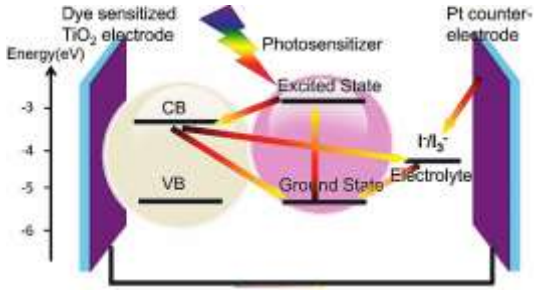

Figure 2: The Process of sequence of electron-transfer (Xu et al., 2018).

The overall reactions involved in working of DSSC are described below:

$$S + hv \rightarrow S^*(Photo\ excitation) \quad (1)$$

$$S^* \rightarrow S + hv^1\ (Emission\ ) \quad (2)$$

$$S^* \rightarrow S^+ + e^-\ CB(TiO_2\ charge\ injection\ ) \quad (3)$$

$$2S^+ + 3I^- \rightarrow 2S + I_3^-\ (regenration\ of\ S) \quad (4)$$

$$I_3^- + 2e^- \rightarrow 3I\ (regenration\ of\ I^-) \quad (5)$$

$$S^+ + e^-(TiO_2\ ) \rightarrow S \quad (6)$$

$$TiO_{2\_}\ S^+ + e^- CB \rightarrow TiO_{2\_}\ D(recombination\ process) \quad (7)$$

The commercial dye sensitizers present over here claim that dye has an important role in the absorption and a global air mass 1.5 of sunlight. These complexes are also one of the most effective sensitizers because of their high efficiency, good chemical stability, favourable photo electro chemical properties and deep charge transfer absorption in the wide visible range.

Materials for DSSC

The properties and efficiency of DSSC depends upon processes involved and materials used in different components of the cell. The basic components of DSSC include CE, dye, electrolyte and semiconductor.

Counter Electrode (CE)

CE, the fundamental part of the DSSC, primarily performs two tasks: (a) behaving as a catalyst using the reduction couple, and (b) collecting the holes generated by the material. The fundamental task of a CE is the reduction of the redox couple acting as the mediator within the regenerating the sensitizers as the electron injection takes place within the DSSC (Wei et al., 2014). For a material to be used as an efficient CE, the following characteristics should be present: high catalytic activity, low charge transfer resistance, and high energy conversion efficiency.

A competent CE should be catalytically active for fast reactions and decrease the over-potential. Besides these, the charge transfer resistance should be ~1 Ωcm^2 to obtain the fast charge transfer rate. Recently, the Pt is widely used as the CE because of the desired properties but due to higher cost as well as limited availability of the material restrict its practical usage. Considering this, it is need of an hour to embellish the Pt-free CEs to be utilized in DSSC. Several materials have been taken into consideration as a possible substitution/replacement of the Pt, which includes the various metal oxides, transition metal carbides, sulphides, nitrides and carbon-based materials. Some representative materials are discussed briefly in the upcoming sections.

For direct assessment of the various CEs considered in DSSCs, the Table 1 sum-up the salient photovoltaic performance parameters i.e. Power Conversion Efficiency (PCE), short circuit current density (J_{SC}), fill factor (FF) and open-circuit voltage (V_{OC}) in addition to the qualitative analysis of long-time stability and cost-effectiveness among various CE classes of materials. The next section briefly describes various materials used as CE.

Carbides

Carbon Black: Carbon black is principally obtained by partial ignition of petroleum products and is used as toners on a very large scale. Carbon is considered an outstanding material since it offers anti-corrosion and provides high FF as well as less charge resistance (R_{CT}). Due to which, it can also be used as best CE material because of its excellent characteristics such as best conductivity, electro catalytic activity as well as its maximum surface-to-volume ratio (Kamau, 1988; Wroblowa & Saunders, 1973). All carbon materials contain the active positions at edges of crystal for catalysis. When this material utilized as CE, the thickness of layer should be controllable because it directly disturbs resistance as well as catalysis of material. Murakami et al. (2006) considered the different black carbon materials and modified the thickness of deposing layer. It has also been reported that if the thickness of the carbon layer increases, the

FF also increases and, consequently, the R_{CT} decreases. These features indicate that thick carbon materials offer high or maximum electro-catalytic activity. By considering the thickness of layer 14.4 μm provided the efficiency 9.1% as well as good J_{SC}, and voltage. Besides these, one parameter which is also important, is charge transfer resistance and depends upon surface area i.e. when the surface area of carbon layer is high ~ 2.96, there will be less resistance and all these properties make it low cost as well as corrosion free CE. Similarly, various prospects of the different forms of carbon are as given in Table 2.

Table 1: Summary of important photovoltaic matrices, stability along with corresponding cost among various CE material's categories in DSSCs.

CE Material's Class	Example	V_{OC} (V)	FF	J_{SC} (mA/cm^2)	PCE (%)	Corresponding Cost	Durability/ Stability
Noble Metals (standard)	Pt	0.70-0.78	0.65-0.75	14.0-17.5	7.0-8.5	High	Moderate (Corrodes in I/I_3)
CNTs/ Graphene	N-doped Graphene Nanoplatelets	0.73-0.80	0.65-0.73	14.5-18.0	6.8-9.05	Moderate	Excellent
Carbon Nanostructures	Carbon Black/AC	0.70-0.75	0.60-0.72	13.0-15.5	6.5-9.1	Very Low	High (Corrosion resistant)
Transition Metal Nitrides	TiN Nanotube Arrays/ Ni_3N_2 Foam	0.72-0.77	0.65-0.72	15.5-17.8	8.0-8.3	Low	High
Transition Metal Carbides	WC/MC Mesoporous Carbon	0.72-0.76	0.64-0.70	15.0-17.2	8.18-8.34	Low	High
Transition Metal Sulfides	CZTS	0.70-0.76	0.62-0.69	14.0-16.8	6.82-7.37	Low	Moderate to High
Transition Metal Oxides	WO_2 Nanorods/V_2O_5-Graphene	0.70-0.75	0.60-0.68	13.8-16.5	6.17-7.75	Low	Moderate (Requires carbon matrix)

Abbreviations: Activated Carbon (AC), Carbon Nanotubes (CNTs), Copper Zinc Tin Sulphide (CZTS), Counter Electrode (CE), Fill Factor (FF), Molybdenum Carbide (MC), Nickel Nitrides (Ni_3N_2), Open-Circuit Voltage (V_{OC}), Platinum (Pt), Power Conversion Efficiency (PCE), Short-Circuit Current Density (J_{SC}), Titanium Nitride (TiN), Tungsten Carbide (WC), Vanadium Pentoxide (V_2O_5)

Mesoporous Carbon: Mesoporous carbon, a material that plays a vital role as electrode in DSSC because of its extraordinary properties like vast area of surface along with the desirable and controllable diameter etc. The Nanocasting or template synthesis is well known method that is utilized to prepare mesoporous materials (Srinivasu et al., 2011). Large porous carbon has been utilized in DSSC as CE and by the absorption of nitrogen on it, this material gave high efficiency as compared to silica because of high surface area. If the surface area of carbon would be even extended, it would help in penetration of best electrolyte and in this way efficiency enhanced (Plonska-Brzezinska et al., 2011).

Carbon Nanotubes (CNTs): Carbon is also available in the form of CNTs. On the basis of their structure, they have three types as single, double and multi-wall CNTs and these are considered as excellent CE because of their fascinating properties e.g. electrochemical activity as well

as thermal and mechanical properties (Javey et al., 2003; Pop et al., 2006). Due to several structures like random network and CNTs bundles etc., the basic and mostly used structure is random network because this structure transforms the behaviour of layer of the device. These layers which are deposited on electrode are transparent and are thin. Noureldine et al. (2012) prepares multiwall based CE using 20 sheets with different electrolytes and obtained the efficiency 4.2% which was much better as compared to the Pt.

Table 2: Several prospects of the carbon-based CE for DSSC (Samantaray et al., 2020).

SL. No.	CE Material	Synthesis	Fabrication	Remark
1	Carbon black	Combustion of petroleum products.	Doctor blade	Conductivity is low
2	AC	Alkali treatment and pyrolysis process	Doctor blade	Conductivity is low
3	Graphite	-	Doctor blade	TCO free substrate can be possible
4	CNF	Electrospinning	Doctor blade	Required high thickness.
5	CNTs	CVD	Doctor blade	Stability is low
6	Graphene	CVD	Doctor blade	Coating on TCO is difficult
7	Reduced graphene oxide+ CNTs	Microwave-assisted reduction	Electrophoretic deposition	Mass production is possible but toxic process
8	HACNF	Concentric electrospinning	Spray-coating	High performance compared with CNF-based CE
9	Graphite + AC	-	Bar coating method	-
10	AC + MWCNTs	Enzymatic dispersion	Doctor blade	High FF

Abbreviations: Activated Carbon (AC), Carbon Nanofiber (CNF), Carbon Nanotubes (CNTs), Chemical Vapor Deposition (CVD), Counter Electrode (CE), Fill Factor (FF), Hollow AC nanofiber (HACNF), Multi-Walled CNTs (MWCNTs), Transparent conductive oxide (TCO)

Graphene: Graphene, the monolayer or single layer of graphite having the atomic thickness, is 2D sheet forming a honeycomb structure. The said material shows exceptional properties like best carrier mobility as well as maximum surface area and thermal conductivity (Novoselov et al., 2005). This material has been utilized as CE because of its high area due to which charge transfer resistance decline and as a result, graphene Nano-sheets are used as CE (Unarunotai et al., 2010). The several exfoliation techniques such as oxidative exfoliation etc. of graphite have been utilized to prepare graphene nanosheets and the efficiency obtained was 6.8 %. Here, the efficiency is based on two factors, one is temperature that is 400^0 C (ideal temperature) and other is structure of graphene. Zhang et al. (2011) reported the R_{CT} by graphene is 11.7 Ω cm^2 and this is very near to CE of Pt.

Molybdenum Carbide (MC) and Tungsten Carbide (WC) Composite: All the materials using as CE retain the limited efficiency

ranges. To increase the efficiency range two materials can be used as CE; one is MC and other is WC.

Composite materials of both materials are used as ordered Nano-mesoporous carbon. The surface areas measured by using the Brunauer Emmett Teller (BET) method for Tungsten and Molybdenum 611 and 598 m^2g respectively and indicate high catalytic activity. The efficiency 8.34% and 8.18% have been gained for WC and MC respectively which is too much high from Pt (7.89%) (Wu et al., 2011a), and the similar example for TiO_2 efficiency can be found from Figure 3 for better understanding (Wu et al., 2011).

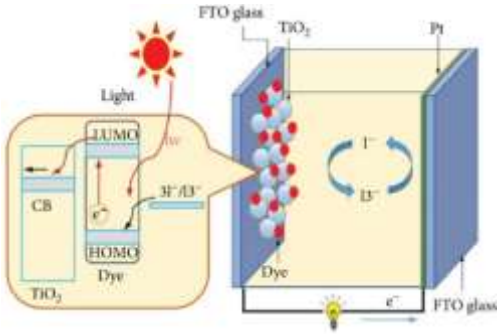

Figure 3: Schematics diagram representing the electron Transport Mechanism in DSSC (Patil et al., 2019).

Nickel Phosphide ($Ni_{12}P_5$)

To obtain the maximum efficiency of DSSC, several materials in place of graphene can be used like nickel (Ni) as well as cobalt (Co). These materials can be utilized with graphene. Nickel phosphide ($Ni_{12}P_5$**)** is used as composite material with graphene reported by Dou et al. (2012). They used hydrothermal method to prepare this composite.

This composite indicates the excellent electro-catalytic activity with reduction of Triiodide and shows efficiency of 5.7% as shown in Figure 4. If the efficiency is a little bit less but the basic purpose or benefit is there to enhancement in transfer of electrons at CE. For electro-catalytic this composite behaves as active site (Bajpai et al., 2012). This also work as spacer among graphene sheets. This spacer increases the speed of diffusion of electrolyte, so in this way graphene gives best connection of electrode and electrolyte. This is the reason electron-transfer enhanced at electrolyte as well as CE interface (Wang & Hu, 2012).

Nitrogen Doped Graphene Nano-Platelets

Using the nitrogen in graphene can provide a positive impact over the efficiency of DSSC. By using very finite quantity of nitrogen in the

form of thin layer was used and nitrogen doped graphene nano-platelets have been prepared which act as CE. For preparation of these platelets, the method used is Two-Step reaction. The dye utilized in that DSSC was organic and electrolyte was $Co(bpy)_3^{3+/2+}$. The prepared layers by Nitrogen with graphene indicate excellent result as CE. Excellent electrochemical stability has been attained. The charge transfer resistance appeared to be very less almost 1.73 Ωm^2 and compare to Pt it is very low. Using the Nitrogen Doped as CE provide the efficiency almost 9.05% which is very high to Pt (8.43%) (Ju et al., 2013).

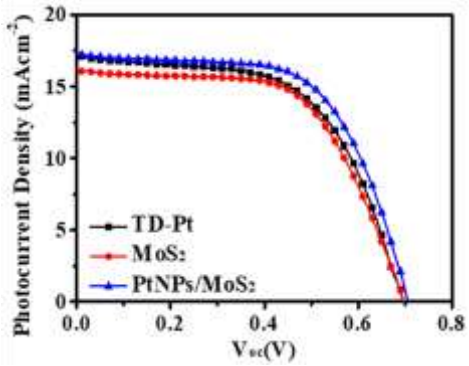

Figure 4: The Photocurrent voltage curves of DSSCs with several MoS_2, Pt and Pt NPS/MoS_2 CEs (Cheng et al., 2017).

Metallic Sulphides

The metallic sulphides are further divided into several classes that are going to discuss briefly in the upcoming section.

Copper (Cu) Tin (Sn) Zinc (Zn) Sulphide (CZTS/Cu_2ZnSnS_4): Copper sulphide, a class of material having vital role in DSSC as CE, like copper zinc tin sulphide (CZTS/Cu_2ZnSnS_4). This is also known as photovoltaic material and mostly utilized in thin layers' solar cell. This material offers the fascinating attributes such as less toxic, easily available in maximum quantity in crust of earth and most important contain high efficiency as compared to cadmium telluride (CdTe) (Ahmad et al., 2010; Habas et al., 2010). The CZTS possess the band gap in range of 1.5 eV enable their usage in DSSC as CE as an alternative of Pt. Due to the high absorption spectra, the material provides the maximum efficiency of power conversion by using the procedure of Spin coating which relate to Selenization. The reported value of power efficiency has been 7.37 %, which was higher as compared to the Pt (7.04%) (Xin et al., 2011).

Nickel Sulphide: To obtain the best alternative of Pt, several materials have been used as CE like NiS/Ni_3S_2. These materials have also been utilized with composite nano rods and directly deposit on the foil of

Ni by using the method of hydrothermal. The Ni_3S_2 has also been used as CE but NiS nanorods act as best CE and provided the higher efficiency of power conversion which has comparable to Pt CE at comparatively lower cost (Liao et al., 2015).

Several methods and techniques can be used for preparation of CE. For instance, for the preparation of nickel sulphide (NiS) as CE, two different techniques have been utilized and tested i.e. Potential Reverse (PR) and Potentio-static techniques (Franchini et al., 2013). The prepared CE by PR method exhibit excellent efficiency as well as catalytic activity for chemical reaction from I_3 to I^- in DSSC. By PR method efficiency obtained was 6.82%, that is very close to Pt CE (Sun et al., 2011).

To increase the efficiency as well as for replacement of Pt CE, Ni Co Nano-needles are utilized. By using the sulfurization method, Ni Co is deposited on the fluorine (F) doped tin oxide material. When these materials used as CE then they indicate excellent catalytic activity for catalyst I_3 or redox couple, and this exhibit high efficiency of power conversion 6.9% almost comparable to Pt 7.7% (Banerjee et al., 2014).

Metallic Oxides

Several metal oxides offer the fascinating properties to be used as CE; the details of some representative oxides are going to discuss in the coming section.

Nickel Oxide (NiO): NiO is a significant catalyst which is mostly used in many chemical process but also considered as potential candidate to be used in DSSC as CE catalyst (Guai et al., 2012). NiO has been considered due to its attractive attributes such as having good chemical stability, good capacity of charge and energy of valance band is almost 4.96 eV and the most important possessing the potential matching with redox couple that enhance the charge transfer. Besides many excellent properties, it also has one disadvantage i.e. it has less electrical conductivity and charge mobility. This is the reason that it has been used with combination of other materials. NiO has been used with sulphur and as CE it gave excellent results and good efficiency.

Due to the less electrical conductivity of NiO, it has been used with combination of poly materials like ploy(3,4 ethylenedioxythiophene) (PEDOT) and polystyrene sulfonate (PSS) (Wang et al., 2014). During this study, it has been revealed that there is weight proportion of NiO with poly materials has been reported 48:1. From this CE, the obtained efficiency was 7.58% and having good electrocatalytic activity. Guai et. al reported NiO with doping of sulphur offering high efficiency of power conversion which is 5.04% (Guai et al., 2012).

The NiO with graphene platelets (NiO-GP) have been reported as CE in DSSC (Bajpai et al., 2013). The properties of both materials are comparable to Pt like FF of NiO-GP is 0.61% and Pt having 0.63%. Similarly, the charge transfer resistances of NiO and GP has been reported 0.85Ω cm^2 and 0.63 Ω cm^2 respectively. Hence, the combination of both materials provides good CE with excellent stability as well efficiency.

Tungsten Oxide: Tungsten oxides are of great interest due to its properties specifically tungsten trioxide (WO_3) (Wu et al., 2011b). It has been utilized in many applications and still working on many applications like gas sensors, field emitters and as photo catalyst. But tungsten dioxide WO_2 nanorods have been reported as CE in DSSC. These materials provided the excellent catalytic activity for the reduction of triiodide. This is the reason that WO_2 can be considered as better replacement of expensive Pt in DSSC as CE. The efficiency attained was 7.25% which is almost comparable of Pt (7.57%). The WO_3 can also be used as CE but it is not much close to Pt as compare to WO_2. The Electro catalytic activity has been reported higher as compared to WO_3 while the charge transfer resistance has been evaluated by proposed method i.e. cyclic voltammetry.

As explained above, the WO_2 own the properties comparable with Pt, yet it has also been reported that use of WO_2 Mesoporous carbon as CE increases the catalytic activity as compare to Pt as shown in Figure 5 (Wu et al., 2011). The efficiency obtained was 7.75%, which was higher from Pt i.e. 7.55%.

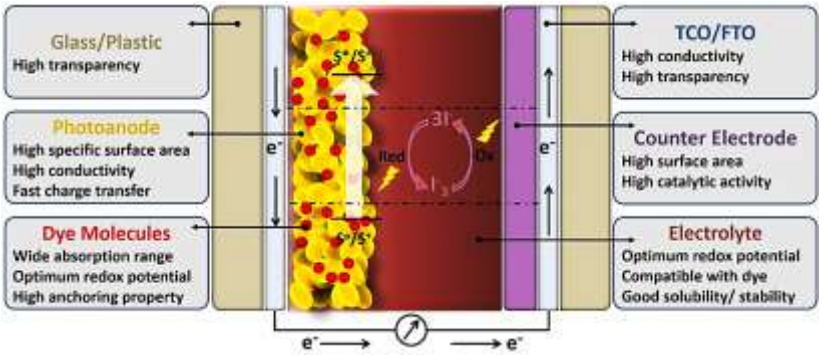

Figure 5: The diagram representing the Comparison of different CE (Shahzad et al., 2022).

Vanadium Oxide: Vanadium oxides have been considered as a good catalyst to be used as CE in DSSC and because of its attractive properties, it can be used in replacement of Pt. Lee et al. (2016) reported that vanadium trioxide (V_2O_3) as CE and the DSSC used was liquid type. The reported efficiency was 5.4%, hence, to increase the efficiency of CE,

the vanadium pentoxide (V_2O_5) has also been used along with graphene oxide Nano belts. The method that used for preparation of this type of CE was hydrothermal process and there was no usage of harmful solvents. These Nano belts have been used for the very first time in combination with V_2O_5, but showed the best properties in resemblance of Pt. The electro catalytic activity, charge transfer rate and PCE was very good. The reduction of tri-iodide molecule, which is very important factor in efficiency and presented in Figure 6. The PCE obtained was 6.17%, which was very close to Pt. Hence, it can be considered as best replacement of Pt.

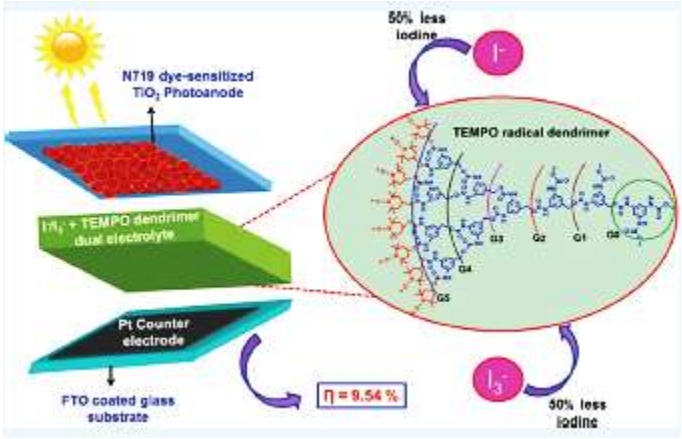

Figure 6: The reduction of iodide ions and impact on the efficiency of DSSC (Ali et al., 2020).

Metal Nitrides

In the upcoming sections, the brief description of use of metal nitride as CE is going to discuss.

Nickel Nitrides (Ni_3N_2): Many transition metals like titanium nitride (TiN), tungsten nitride (W_2N), nickel nitride (Ni_3N_2) etc. have been used as an CE in DSSC, but still the efficiency is limited (Jiang et al., 2010; Park et al., 2014). The Ni particles have been used on the surface of nickel film 200 μm in thickness and as a result obtained better efficiency. In most of the cases, the efficiency attained by nitrides was 8.3%. Although, the concept of using Ni nitride foam as CE has been presented initially, there exist the 3D porous surface structure that showed the better results as compared to the surface of particles. The said material indicates the excellent catalytic activity, which was comparable to metallic foil. The foam surface behaves as a good transporter for electrons from outer circuit to electrolyte and can be regarded as redox couple. This electrode provided several fascinating features such as good catalytic activity for the iodide

reduction and excellent conductivity in single film. The Nitridation method that has been adopted for the preparation of Ni nitride foam was in the presence of Ammonia.

The major benefit of the said electrode lies in the easy transportation of electrons in 3D and interconnected structure. Corrosion Resistance is also an important factor to consider and the said method of Surface Nitridation improves the resistance and provide the maximum possibility to escape the oxidation of metals in iodine (I) electrolyte (Jiang et al., 2010).

Titanium Nitride (TiN): Nitrides from the noble metals showed excellent properties as compare to Pt, hence, if nitrides are used as CE in DSSC, its performance can be enhanced (Gnanasekar & Grace, 2021). Because of having fascinating properties such as electrical conductivity in the range of 10^2 $(\Omega m)^{-1}$, good thermal conductivity, fascinating catalytic activity as well as radiation resistance besides the most important feature i.e. low temperature superconductors makes it excellent candidate for conducting devices. For the good charge transport as well as high surface area for CE in DSSC, all these requirements can be provided by TiN in combination of Nano tubes arrays.

The preparation method anodization has been used for TiN nanotubes array. It indicates that substitution of highly ordered TiN nanotube on layer of metallic foil provide amazing results. It offered the surprising catalytic activity, which was almost comparable to Pt. The charge transfer resistance was 1.51 Ω, which was very less as compare to Pt. The surface area was also greater (1.0710^4 F) which increases the absorption spectra (Jiang et al., 2009).

Boron Nitride (BN): Although, almost all other nitride materials reported to increase the charge transfer rate of CE. However, the hexagonal boron nitride, having a similar structure to graphite (Xu et al., 2013), yet it has been reported that BN is not good material to act as CE due to its high charge transfer resistance. The thickness of sheet used vary from 5-39 μm but its efficiency was not good and this was not suitable for reduction of Iodide. Therefore, all other factors depend upon the catalyst material properties, that's why all other parameters like operating voltage as well as FF are having low values.

Conducting Polymer

Just as metal sulphides, metal nitrides, carbides, metal oxides have been used as CE in DSSC, various conducting ploymers can be used as CE in DSSC. Conducting polymers are organic polymers with a π-conjugated structure. This structure provides the desired optical and electrical characteristics while maintaining good mechanical properties

(Nurazizah et al., 2023). The peculiar properties owened by the conductive polymer materials include excellent optical characteristics, good catalytic activity, lightweight and flexibility. The other's include higher conductivity, cost effectiveness, versitle process, enviornmental stability, and simple and easy prepartion.

All these properties indicate the conducting polymers as potential candidate as CE in DSSC (Gurunathan et al., 2003). Figure 7 indicating the importance of the conducting polymers and also showing that PEDOT conducting polymers are known as best CE as compare to other polymers.

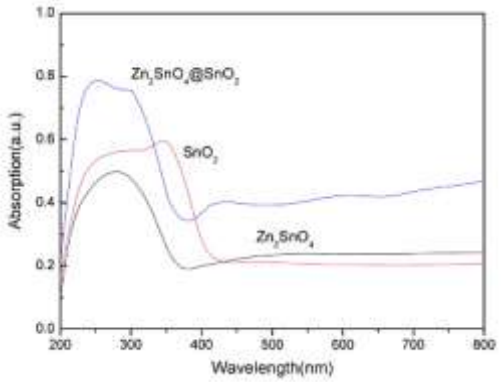

Figure 7: Comparison of different materials used as photoanode (Liu et al., 2012).

Polyaniline (PANI)

Polyaniline (PANI), a conducting polymer and basically belong to semi but flexibile rod polymer family. This is a versatile material and offer the excellent properties like outsatnding processability as well as good chemical and thermal stability. This material has been used in many energy storage electodes and devices like supercapacitors and energy storage batteries. Various types of PANI are utilized as CE in DSSC but mostly nano structre of PANI due to its large surface area (Li et al., 2008). PANI as CE for DSSC revealed the high catalytic activity for redox couple iodide has been attained because of high surface area. In order to increase the efficiency, several ions such as sulphate ion (SO_4^{2-}), perchlorate ion (ClO_4^-) etc. can be introduced in PANI. In general, the doping enhance the parameters including conductivity, porousity, morphology, and electrocatalytic activity.

By doping of the SO_4^{2-} anion, PANI SO_4 layer has been obtained which indicate the much higher porosity and very high reduction current with very low amount of charge transfer resistance (Li et al., 2009). Similarly, the doping of H_2SO_4 in PANI has also been reported, which is

used for prepartion was Electro Chemical Ploymerization (ECP) (Nunoo et al., 2019). Thus, the delocalization of electrons in higher order and high charge transfer rate are two important factors for consideration.

All other paramters indicated that the efficiency attained was very high as sulfamic acid was doped with PANI the highest photo conversion efficiency 27%. Its electrocatalytic activity is much higher as compare to all mtaerials.

Polypyrrole

Polypyrrole is also considered as good replacement of Pt in DSSC due to its attractive properties and good electro catalytic activity. The thermal stability is in good range as these materials offer thermal stability up to 150℃ in air (Xia et al., 2011). It can also be used in charge storage devices. Lu and co-workers described the use of polypyrrole as CE in DSSC. Polypyrrole nanoparticles used as CE, it indicate excellent results due to maximum surface area and good adhesion of material (Jeon et al., 2011).

To decrease the charge transfer resistance, polypyrrole has been used with nanoparticles having spongy and texture materials to increase the surface area along with the enhancement in the diffusion of electrons. Makris et al. (2011) reported the use of polypyrrole as CE by using the method of potentiostatic electro-depostion. The main focus has been given to investigate the size of thickness and effect of thickness on the performance of cell. The time of the deposion and effeciency would be increased by an enhacement in the thickness of the polypyrrole. Besides these, the decrease in thickness leads to low adhesion and low performance of Cell. The CE having the layer of polypyrrol like paper thickness and get good catalytic activity has also been investigated.

The usage of special type of polypyrrol has been reported and get the photo conversion efficiency 7.98% which is almost like Pt. The main issue with polypyrrole is its high charge transfer resitance which limits its performance and in turn their utilization in DSSC as CE.

Ploy(3,4 ethylenedioxythiophene (PEDOT)

PEDOT, a representative derivative of the polythiophene, which has been grabbing a lot of concentration because of the outstanding conductivity, narrow band gap, better transperancy, lower oxidation potential as well as superior stability. The said material is also considered as good candidate for replacment of Pt in DSSC as CE (Jonas & Schrader, 1991). Initially, the concept of using PEDOT in DSSC as CE was taken into consideration due to its properties such as electrochemical reverseability and chemical as well as sthermal stability.

Yohannes & Inganäs, (1998) explained first time the electrocatalytic properties while doping with PANI and indicated the better efficiency with eletrolyte containing aqueous solution. Although, most of the conducting polymers have showed good results and hence the potential candidate for the replacment of Pt CE, but among all of them, the PEDOT provided the best results and highest efficiency. Saito et al. (2002), reported initially PEDOT as CE and from 2002 to till now, a lot of work has been done and still continue on PEDOT. The two materials toluenesulfonate and poly styrenesulfonate has been doped by chemically polymerizing. Consequetly, the potential as well as the conversion efficiency have also been increased.

Zhang et al. (2013) reported the PSS on the glass material with combination of ethylene glycol (EG). The doping increases the efficiency and provided a good catalytic layer for DSSC as CE. The other main advantage is that this material offer less cost as compared to all other materials. The factor that can affect the conversion effecincy is the polymerization time. By the increase in time of polymerization, the photo conversion efficiency also increases. The PCE would also be changed by the combination of electrolyte type, like as the PEDOT used with electrolyte acetonitrile provided good efficiency of 8 %. The usage of Ionic liquid electrolyte leads the better outcomes such as the use of ionic liquid electrolyte with PEDOT CE has been reported by Li et al. (2014) and attained the excellent results due to its characteristics including high porosity, effective and suitable surface area, and hydrophobicity.

The other alternative materials have also been used with PEDOT to enhance the efficiency of DSSC. For instance, the one dimensional (1D) nano-tubes have been reported with PEDOT and obatined efficiency was 8.3%, which comes out to be much better and high as compared to simple use of PEDOT because of effective as well as high surface area along with better electro catalytic activity. The PEDOT with Nano-fibers have also been reported and in order to prepare this type of CE, the method of chemical oxidative polymerization has been used (Jeon et al., 2013). The obtained results showed low surface resistance, high catalytic activity and active sites, and good adhesion.

The 3D materials have also been used to enhance the efficiency of DSSC, but nano-structured materials are much better due to posrous surface area and low resistance.

Besides the above described materials, the PEDOT is soluble in various solvents because of the presence of the PSS, acting as the dopant (Nurazizah et al., 2023). The PSS play a leading role within the stability of the PEDOT:PSS dispersion due to the fact that the it contains the negative charge behaving as the counter ion as this is doped in the PEDOT.

Furthermore, the PSS contains the functional group of ester sulphate (SO_3H) acting as the hydrophilic part which aids the dispertion within the PEDOT:PSS. The PEDOT:PSS, in most of the cases, act as the CE owing the efficiency ranging from 2-7 % as reported in the literature (Wen & Xu, 2017; Yue et al., 2013). The performance of the DSSC varying the CE, electrolyte and dyes by using the PEDOT:PSS as the CE is given in Table 3, above (Diah et al., 2020). The performance of the DSSC has been based on various factors such as area/thickness (A) of materials, J_{SC}, voltage, FF, and efficiency. On contrary to this, the similar phenomenon has been observed, that PEDOT is dispersible within an aquous solution while the carrageenan was present. The carrageenan owing the ester sulphate (-SO_3H), that is simialar functional group as present within the PSS but now behaving as the anionic heteropolysacchrides extricated from the seaweed (Diah et al., 2020). Hence, the carrageenan would be a different dopent for the PEDOT to fabricate the PEDOT:carrageenan. Currently, this PEDOT:Carrageenan is mostly utilized as an electrolyte having the comparably lower efficiency.

Table 3: Performance of the DSSC on the basis of various parameters while using PEDOT with different combinations as CE (Nurazizah et al., 2023).

Materials	Photoanodes	Dyes	Electrolytes	*A* (cm^2)	*V*(*volt*)	*Jsc* (mA/cm^2)	*FF*	*η* (%)
PEDOT:PSS	TiO_2/ZrO_2	Z 907 (20 mg/L)	Liquid electrolyte (I)	0.5	0.61	5.04	0.29	1.77
PEG-PEDOT:PSS	TiO_2	N3	Liquid electrolyte (I^-/I_3^-)	0.2	0.73	10.11	0.60	4.39
PEDOT:PSS-TiO_2	TiO_2	N719 (5×10^{-4} M)	Liquid electrolyte	0.5	0.73	17.30	0.67	8.49
Ni-PEDOT:PSS	TiO_2	N719 (5×10^{-4} M)	Organic electrolyte (T_2/T^-)	0.5 × 0.5	0.66	8.86	0.38	2.25
$NiSO_4$-PEDOT:PSS	TiO_2	N719 (5×10^{-4} M)	Organic electrolyte (T_2/T^-)	0.5 × 0.5	0.65	8.79	0.54	3.05
NiS-PEDOT:PSS	TiO_2	N719 (5×10^{-4} M)	Liquid electrolyte I	0.5 × 0.5	0.76	16.05	0.67	8.18
PEDOT:PSS-Carbon	TiO_2	N719 (0.5 mM)	Liquid electrolyte I	0.5 × 0.5	0.81	13.6	0.69	7.60
PEDOT:PSS-Graphene	TiO_2	N719	Liquid electrolyte (I^-/I_3^-)	N/A	0.73	11.77	0.55	4.66
PEDOT:PSS/SWCNH	TiO_2	N719 (0.3 mM)	Liquid electrolyte I	0.5 × 0.5	0.68	14.06	0.52	5.10
MoS_2/SWCNTPEDOT:PSS	TiO_2	Z 907	Liquid electrolyte I	0.4 × 0.7	0.78	16.21	0.64	8.14

Abbreviations: Active Area (A), Fill Factor (FF), Molybdenum Disulfide (MoS_2), Nickel (Ni), Nickel Sulfate ($NiSO_4$), Nickel Sulfide (NiS), Open-Circuit Voltage (V), Poly(3,4-ethylenedioxythiophene):Polystyrene Sulfonate (PEDOT:PSS), Polyethylene Glycol (PEG), Power Conversion Efficiency (η), Short-Circuit Current Density (Jsc), Single-Walled Carbon Nanohorn (SWCNH), Single-Walled Carbon Nanotube (SWCNT), Titanium Dioxide (TiO_2), Zirconium Dioxide (ZrO_2).

Modification in Photoanode: Why Photoanode?

Photoanode, the fundamental part of DSSC, which mainly acts in two ways: the adsorption of dyes and as an electronic transport medium (Qohhar et al., 2020). The photoanode, performing dual functions assists the loading of sensitizer along with the transportation of the photo-excited electrons from the sensitizer towards the external circuits (Ye et al., 2015). Hence, the large surface area is required to secure the high dye loading. Furthermore, the rapid charge transport is necessary to certify the higher efficiency of electron collections. The above described characteristics determine the charge attributes/characteristics of the ideal photoanode.

The photoanode is fabricated over the surface of the transparent conducting oxides (TCO) that is basically the mesoporous semiconductor metallic oxides nanoparticles (Concina & Vomiero, 2015; Yeoh & Chan, 2017) In general, several semiconducting materials have been utilized as the photoanodes that includes ZnO, niobium pentoxide (Nb_2O_5) and TiO_2 etc. Initially, TiO_2 semiconductor have been utilized due to the fascinating properties such as being biologically and chemically inert, cost-effective, and environmentally safe (Gatou et al., 2024; Nagaraj et al., 2025). Besides this, the ZnO has been considered as the good subsitution of TiO_2 acting as the semiconducting material within the DSSC (Boro et al., 2018). Both ZnO and TiO_2 offer the similar band gap as well as the electron affinity. In addition to this, the ZnO offer much greater diffusivity of electrons as compared to the TiO_2, photo corrosion stability, higher mobility of electrons, cost-effectiveness and gretaer excitation binding energies (Cavallo et al., 2017). Similarly, the niobium penta oxides have attained a lot of attentions as it could be implemented to either cathode ot anode cells. Nb_2O_5 could also behave as the barrier layer, which in turn, have a great positive impact over the reducing electronic loss because of the recombination with the electrolytic materials.

Furthermore, the performance of the DSSC is directly related to the performance of the photoanode material in DSSC. If the performance of photoanode is good then overall PCE of DSSC will be high. In general, the most popular material for photoanode is TiO_2 because having good mobility of electrons (Awsha et al., 2021; Yeoh & Chan, 2017). Still there is need to enhance the efficiency of DSSC due to which different materials have been suggested as photoanode.

Metal Oxide

There are several metal oxides that may be considered as the photoanode, a major part of DSSC, but among all, the stannous (tin) oxide (SnO_2) is considered because of its suitable properties, such as high mobility of electrons, fast rate of diffusion, and large band gap.

There is an advantage of large band gap with low amount of oxidative electrons in valance band of material mentioned above because of which, the stability of DSSC increases. But there are some drawback of SnO_2 (Qian et al., 2009). There was high combination of valance electrones with oxidative dye and as result there was less absorption on dye. This less absorption on dye made performance of DSSC poor. To increase the efficiency, the nanoparticles of zinc stannate (Zn_2SnO_4) have been reported as photoanode in DSSC which is the modification in SnO_2 nano structure to improve the PCE.The method which have been employed to made this type of photoanode is spin coating. The size of

nanoparticles has been reported 20 nm which was an average size. Hence, the shell of Zn_2SnO_4 act as good resistor and resist acid etchant as well as recombination of electrones of CB with oxidized dye. This resistance showed two main aspects including better chemical stability and power conversion.

The above two properties were not good enough in SnO_2. The other drawback was less adsorption of dye. To solve this problem a layer was coated with different isolating oxides like ZnO, magnisium (Mg) oxide (MgO) etc. which indicate good results and improved efficiency of photoanode SnO_2 as shown in Figure 7.

Titanium Oxide (TiO_2)

The fundamental and most advanced improvemnets in material sciences are hierarchical as well as 1D strucutres (Sauvage et al., 2010). Using these two comparatively recent ideas, several nano structure can be preapred for the enhancemnt in the performance of photoanode. The TiO_2 nano-structured material has been prepared as photoanode by the combination of these two developments .The performance of conversion light has been increased as the diffusion length was maximum than the thickness of the TiO_2. It means that charge transport rate was increased and charge recombinantion would be less. Diffusion length should be maximum by the placement of Nano-tubes of TiO_2 vertically via using the electrochemical anodization method from Ti metal. This material was suggested as photoanode in DSSC and the dye that was used with TiO_2 was C101 and 4.9% efficiency has been obtained.

Zinc Oxide (ZnO)

Beside the other metallic oxides, ZnO can also be used as photoanode in DSSC for rapid charge transfer rate because of the properties including low trap density, suitable path for collection of electrons and rapid charge transfer due to 1D nano-structure. From all above properties, it has been expected that charge transfer rate would be increased and there will no effect on charge recombination. Due to the use of nano-rods as photoanodes, the efficiency increases 1.5% because of charge transfer rate. The nano-rods showed better results as compared to nanoparticles but the efficiency of ZnO is still restricted (Law et al., 2005). To solve this issue, the ZnO nano tubes with high surface area has been used as photoanode with anodic aluminum oxide (AAO). For deposition process, the atomic layer method has been used to coat the surface in well suitable way. This thing provide the eaxct and direct path for electron or charge collection and thickness tens of μm has been reported for this process. As these devices were compared with simple ZnO based devices,

hence, ZnO nano-tubes indicate high efficiecncy of 1.6% which is a good increment in the performance of DSSC (Martinson et al., 2007).

Strontium Titanate ($SrTiO_3$)

To enhance the photovoltic performance of DSSC, several materials have been used in the replacment of TiO_2 photoanode but another alternative is also availabe, which is doping of other materials in TiO_2 like samarium (Sm^{3+}) ions (Li et al., 2015). Such materials offer less cost and efficient light converting material which can change ultraviolet rays into visibile light and dye can reabsorbe them. The nanoparticles of Gold coated with Silica used with TiO_2 has also been reported (Bhardwaj et al., 2018). The attained efficiency has come out to be the much higher and suitable for liquid and solid electrolyte for DSSC.

Similarly, the strontium titanate ($SrTiO_3$) can also be used with SiO_2 coating in different amounts as photoanode in DSSC (Beedri et al., 2017; Y. Li et al., 2015; Ou et al., 2012). This structure has special ability of down conversion and suppresing the recombination in DSSC. The photoanode can be prepared with composite materials such as in TiO_2, various amounts of nanoparticles of $SrTiO_3$ with SiO_2 (STS@SiO_2). The obtained efficiency from this composite photoanode has come out to be the (5.07%), which was ~36.6% higher than without (STS@SiO_2) DSSC.

Niobium Pentoxide (Nb_2O_5)

Nb_2O_5 has been reported as alternative of TiO_2 photoanode because of its fascinating favourable properties such as wide band gap, higher CB, efficient electron-transfer comparable to TiO_2, and better chemical stability.

To prepare the photoanode of Nb_2O_5, various methods have been considered such as spin coating, solvo thermal and soft chemical route etc. Among all the methods, soft chemical route is low cost and easily available. The output efficiency reported is comparatively much better by using this photoanode. Furthermore, the natural dye (Rose Bengal) has been used with this photoanode (Beedri et al., 2017).

The Nb_2O_5 nano-porous material has been used as photoanode and anodization method used for fabrication. The layer of Nb_2O_5 having thickness of 4 μm has been used and the efficiency obtained was 4.1%. This efficiency was much higher than photoanode of TiO_2 (2.7%). This photoanode offered the highest efficiency among all the photoanodes. The Figure 8 indicates the energy levels of Nb_2O_5 and showed at which energy level photoanode work better.

The Nb_2O_5 Nano-channels has also been considered as photoanode used in DSSC. Since the efficiency of the DSSC depends upon

the thickness of the layer, the thickness dependent studies have been performed from 5µm-25 µm in the presence of glycerol electrolyte. At the thickness of 10µm photoanode indicated the maximum efficiency which is 4.48%.

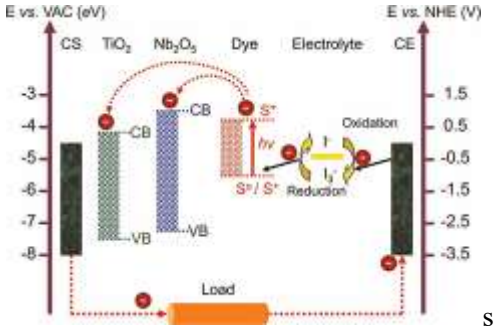

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Figure 8: Energy state diagram of Nb_2O_5 and TiO_2-based DSSCs (Ou et al., 2012).

Problems with Photoanode and Current Scenarios

A 10 μm thick films madeup of the 3D network of the arbitrarily dispersed spherical TiO_2 nanoparticles is generally implemented as the photoanode. Though, the larger surface area of ~50 m^2/gm of the nanoparticles leads towards the higher loading capacity of dye, the disordered network having countless grain boundaries impede the electronic mobility and consequently slow transport as well as weak recombination of the photo-excited electrons. This phenomenon highly limits the chief efficiency of these devices. The intrinsic problems related with the construction of the conventional photoanode require the exploration of the even more efficient nanostructure-based based photoanodes. Some representative cases can be discussed in details in the upcoming sections.

Manufacturing/Formation of Different Structural Motifs

In order to attain the efficient photoanodes, various techniques of the fabrication of films have been taken into consideration and implemented for the fabrication of the different combinations of the nanostructured semiconductor photoanodes (e.g. ZnO, TiO_2, Nb_2O_5 and SnO_2 etc.) (Ye et al., 2015). For instance, sol-gel method, atomic layer deposition, solvothermal/hydrothermal, spray pyrolysis, electrochemical anodization and electrospinning etc. have been implemented (Bao et al., 2013; Huo et al., 2013; Son et al., 2013; Wu et al., 2013). Various structure motifs include nanorods, 3D hierarchical, mesoporous structure, nanotubes and nanosheets etc. majority of such structures provides the

substantial improvement in the efficiency in comparison with the nanoparticle systems. For instance, the 1D semiconducting nanostructure show exciting charge transport properties (Lv et al., 2013). Besides these, the 3D mesoporous micro/nanospheres due to comparatively greater surface area offer the better properties regarding the scattering of light.

Ions doping

The doping of ions has been broadly utilized to adjust the band edge positions i.e. either Valence Band (VB) or CB of the semiconductors considered for the photocatalytic applications (Ye et al., 2015). In order to use within the DSSC, the doping of ions such as F, I, Cu, Mg etc. has been considered to decrease the recombination resistance along with enhancing the lifetime of the electrons within the photoanodes (AlDahoudi et al., 2017; Mahmood et al., 2013). Similarly, various cases such as doping of the silver (Ag) ions in TiO2 (Ramadhani et al., 2024) and rare earth ions e.g. La doping in ZnO (Shabbir et al., 2023) have also been considered and provide the valuable results but still some work is required for the better understanding of the mechanism.

Modification by the Metal Oxides

The surface modification of TiO_2 with an insulating layer like aluminium oxide (Al_2O_3), strontium oxides ($SrCO_3$) and lanthanum oxides (La_2O_3) and other semiconducting layers like silicon oxide (SiO_2), gallium oxide (Ga_2O_3), stannous oxide (SnO_2) and $SrTiO_3$ have been demonstrated to be efficient methods to enhance the efficiency of the DSSC. These coatings suppress the charge recombination within the hetero-structured photoanodes (Kim et al., 2012; Ye et al., 2015). Furthermore, the addition of the carbon materials such as graphene or CNTs within the semiconductor photoanodes assists the movement of the photo-generated electrons that in turn, increases the performance of the DSSC (Dembele et al., 2013).

Coating with the Down/Up Conversion Materials

Since the typical sensitizers generally used within the DSSC involve the Ruthenium (Ru) complexes or organic dyes absorb only visible portion of the sun light. Hence, the alternative method for enhancing the light harvesting abilities into the near-infrared regions had been considered through the synthesis of the up-conversion nanoparticles that shift the near infrared light to the visible light for the sensitizer's absorption. Currently, some of the down-conversion nanocrystals like $LAVO_4:DY^{3+}$, have been narrated as down-converter ultra-violet light to the visible light in order to enhance the J_{SC} of the DSSC. The hetero-

structures photoanodes of the semiconductors up conversion materials have proven to be potential candidates for their capability to enhance the light harvesting efficiency of the DSSC and hence improve the efficiency.

Noble Metal Decoration

The surface plasmon resonance effect initiated by the decoration of the noble metal i.e. Ag, Au nanoparticles has been considered to localize the incident light as well as enhance the optical path length. This attribute has been considered within the photoanodes in order to enhance the light harvesting efficiency of DSSCs. The related research showed that the decoration of gold (Au) nanoparticles could enhance the electron-transfer along with the scattering as well as the plasmonic impact. These parameters are dependent over the size of nanoparticles and superior for some specific sizes. For instance, the $SiO_2/Ag/TiO_2$ nanostructure has been fabricated, in which the coating of the SiO_2 saved from the corrosion of the Ag nanoparticles through the I^{-1}/I_3^{-1} electrolyte and leads towards the improved surface plasmonic as well as the light scattering impact, as a result the enhanced light absorption. Furthermore, the impact of the noble metal nanoparticles within the DSSCs is still under progress and a lot of work is required to highlight their specific role in DSSCs.

Modification in Dyes

Dye, another elementry component of DSSC, which have a great impact over the performance of the cell. The dyes basically can be either synthetic or natural. The synthetic dyes of inorganic type are usually utilized. The dye consisting of Ru complexes are very famous but these may have adverse impacts on the environment. Moreover, Ru complexes have the tendency to degrade in the presence of water. There have been widespread discussion on preparation and mechanism involved in dyes but still a lot of work need to be done. In some cases, the natural dyes indicate the high reuslts but in some cases inorganic dyes showed best efficiency but this all depends upon the cost as well as availbility of dyes, but to find out such a dye that has low cost (Al-Ghamdi et al., 2014). Other requirement for the dye to be used in DSSC includes excellent stability, absorption in visibile range of solar spectrum, high electron-transfer rate, high surface area for absorption, and ability to inject electrons in CB.

From all aobve characteristics, the best dye could be choosen easily for better performance of DSSC.

Inorganic Dyes

The basic difference between organic and basic difference is that organic dyes contain carbon atoms, whereas inorganic dyes do not i.e.

absence of carbon atoms. The efficiency of both dyes depends on different factors, such as stability of dyes, absorption of light, and electron ejection characteristics.

Inorganic dyes also known as organomettalic dyes. Recently the most competent DSSCs are made of Ruthenium(Ru) organometallic dyes, which includes N3, N719, Z907 etc. These dyes gained a lot of attraction due to attractive PCE of 10-11% (Nath et al., 2013).

Organic Dyes

Along with the use of inorgainc dyes in DSSC, the organic dyes are also used to enhance the performance of DSSC and several research groups are currently working on these materials. Campbell et al. (2007) prepared a DSSC in which green porphyrin dye was used, in which, basically two groups are participating: aryl group and malonic acid group behaving as electron donor and acceptor respectively. Similarly, the DSSC with the dye pi-conjugated oligo phenylenevinylene has also been reported by Hwang (2011), in which the same concept of electron donor and acceptor has been used. The obtained efficiency has been reported to be ~ 9.1% which is much better as compared to other materials.

Matar et al. (2008) reported the use of Ru based on polypyridyl dye which is also knownTG6 and compared with N719 dye. They reporteed that at specific limits TG6 is more efficient than N719 because of high light absorption in visible range.

Natural Dye

The important aspect of natural dyes are their easy availability from natural sources like fruits, flowers and becteria (Chang & Lo, 2010). These dyes showed different colors and many pigments, which can be extracted from fruits and can be easily applied in DSSC as a dye. The various types of the natural dyes are discussed in details in upcoming section. The main purpose of choosing these dyes include, high surface area and absorption in visibile region, easy preparation, environemnt friendly, available in high quantity, cost effective, and reduction of noble metals (Hemalatha et al., 2012). The natural dyes are evaluated on the basis of parametrs such as FF, J_{SC}, and efficiency of light conversion.

Chlorophyll: Chlorophyll can be defined as a green pigment which is usually found in green plants. Chlorophyll is classified in six different classes but the most consuming type is Chlorophyll α. Its structure contains cholorine ring along with the Mg center having various hydrocarbon chains. The range of light absorption usually lies in red, blue and violet wavelenght and all the colors are derived by refelction of green color (Wang et al., 2005). The main functions of chlorophyll includes

absorbing solar light, transfering of electrons, and conversion of solar light into chemical energy.

Chlorophyll and the respective derivatives are used in DSSC as photo sensitizer due to high light harvesting efficiency. The use of chlorine in DSSC has also been reported, which has more capacity as compared to TiO_2 and ZnO surfaces. Maximum absorption range of Chlorine is 670 nm in visible range (Amao & Komori, 2004).

Anthocyanin: Anthocyanin, a natural group providing the colors to various flowers and fruits etc., supplying the colors in purple to red range (Chang & Lo, 2010). Anthocyanin belongs to carbonyl and hydroxyl groups and stuck on the surface of the TiO_2. This dye excite the electrons and then electron-transfer in CB of the TiO_2. Anthocyanin as obtained from different sources offered different efficiency performance, such as the blue violet Anthocyanin as photo-senstizer extracted from Jaboticaba as well as Calafate has been reported and the maximum power conversion obtained was 1.9 $mWcm^{-2}$ and short circuit current 9.0 mA cm^{-2} (Polo & Iha, 2006). Similary, Adedokun et al. (2016) prepared a DSSC, consists of Anthocyanin dye taken from Kopsia flavida fruit and presented the better reuslts regarding the efficiency. The anthocyain dye as obtained from Rosella as well as blue pea has also been used in DSSC as sensitizer (Hamad, 2016; Ludin et al., 2014; Wongcharee et al., 2007). The two dyes blue pea and Rosella was mixed and used as dye in DSSC. Since both have different absorption spectra and offered the more effective performance than mixture of anthocyain and chlorophyll. Similarly, Li et al. (2013) reported use and restrictions for red cabbage as sensitizer to enhance the performance of DSSC.

Flavonoid: The term, flavonoid is generally reffered as the collection of natural dyes consisting of carbon structure C_6-C_3-C_6 carbon. Similar to other dyes, these materials can be divided in different categories on the basis of their chemical structures, such as flavonoids (2 phenylbenzopyrans), isoflavonoids (3 benzopyrans) and neoflavanoids (4-bezopyrans).

Although, almost all the flavonoids offer similar structure yet all Flavonoids do not have capacity to absorb visible light (Narayan & Raturi, 2011), because of which the pigments of different colors have been used to solve this issue. Flavonoids have less energy to excite the molecules to LUMO. The Adsorption spectra of Flavonoids is greater than TiO_2. The Flavonoids sensitizer has also been extracted by Botuje and used in DSSC to enhance the DSSC efficiency and normally an increment of ~0.12% in efficiency has been observed by using this type of Dye.

Carotenoids: Basically, the Carotenoids has been reported as organic pigment, which is easily available in plants in addition to their

presence in various micro-organisms. Sometimes, the anthocyanin, flavonoids and carotenoids are available in asme organs. The Carotenoids pigmnets are well known for yellow –orange colors and are light absorbing pigments, playing the vital role in photosynthesis fortification (Kishimoto et al., 2005). The Raw natural dyes are considered much better as compared to commercial dyes due to natural extracts availbility like organic acids and alcohols having different charatcteistics such as assistance in dye adsorption, prevention electrolyte recombination, and reducation in dye accumulation.

The conversion efficiency of Kerria japonica (caroteniod dye) has been reported which is ~ 0.22% (Tiwari et al., 2024). In short, it can be written that Carteniods dyes are high light harvesting dyes offering the enhanced efficiency of DSSC. There may be many factors that have impactover the performance of DSSC and the main factor is decrease in interaction of excited state dye molecules. Yamazaki et al. (2007) reported the use of different natural dyes and crocetin presented the best reuslts as sensitizer. The conversion efficiency is 0.56%, which is 3 times higher than Crocin(0.16%).

Natural Dye's Stability Constrictions and Degradation Mechanisms

In-spite of the greater absorption, cost-effectiveness as well as eco-friendliness, the natural dyes suffer from the in-build chemical instability under various functional solar circumstances, restricting the corresponding long-term performance in DSSC. The main degradation ways involve each of the following.

UV Instability and Photodegradation: Natural chromophores (for instance anthocyanins, chlorophylls and betalains) represents the immense conjugate π-systems, which radially absorb solar radiation (Dutta et al., 2025). Nevertheless, the exposure of UV-radiations for the long time initiates the photo-oxidation, referring to the irreparable cleavage of the main chromophores e.g. anthocyanin's pyrylium ring cleavage. This refers the corresponding loss of the light-producing efficiency.

Structural Isomerization and pH Sensitivity: Natural pigments are more reactive towards the environmental pH (Negi, 2025). For instance, anthocyanins experience the structural transformation among various pH ranges i.e. of stable red flavylium cation at smaller pH to colorless chalcone or hemiketal conversion pseudo bases at neutral-alkaline pH. The said variation in structure changes the respective energy-level alignment comparative to the TiO_2 CB as well as liquid electrolyte.

Thermal Desorption: The heat produced during the operational exposure to sun (>45℃) diminish the comparatively weaker hydrogen as

well as ester bonds in between the dye's carboxyl or hydroxyl groups. This leads the easy desorption to the TiO_2 surface (Reynal & Palomares, 2011).

Photo-Isomerization: The heat as well as light activate the cis-trans isomerization in dyes based on the carotenoid disturbing the molecular geometry along with the efficiency (Telegina et al., 2023).

Improving Stability and Mitigation Realities

To deal said degradation mechanisms and approach to commercial viability, various engineering techniques are recently being used.

Molecular Blending and Co-Sensitization: By combining two complementary natural pigments neutralized the inter-molecular aggregation and hence widening the spectrum of light absorption by protecting the independent dye molecules form the photo-induced degradation.

Complexation of Metallic Ions: Metal ion's chelation e.g. Al^{3+}, Mg^{2+} or Zn^{2+} with carbonyl and hydroxyl groups of the natural pigments strengthen the molecular backbone for the photo-oxidation. This results in reinforcing the anchoring to the metallic oxide photoanodes.

Solvent Optimization and Encapsulation: By utilizing quasi-solid state or solid-state polymer gel electrolytes remarkably suppress the solvent evaporation and dye leaching than the typical liquid I^-/I_3 electrolytes, improving the total functional lifespan (Islam et al., 2024).

Rationale and Future Perspectives of Natural Dyes

Feasibility of Dyes on Economic and Environmental Grounds: The natural dyes does not need any harmful or costly synthetic procedure, leading to the safe, cost-effective and totally biodegradeable substitutes to the expensive metallic based (Pt/Ru) complexes.

Indoor and Lower-Light Implementation: The natural sensitizers function exceptionally well in indoor as well as ambient and diffuse fluorescent lighting. In these cases, the PCE value is critically smaller as compared to the smaller cost of production along with the environmental safety (Blakesley et al., 2023).

Scaling of Green Energy: These systems issue an accessible and simple framework for smaller power electronics, off-grid, disposable sensors as well as educational photovoltaic kits, in which the expensive processing and toxicity of noble metals are forbidden.

Sustainable Design's Template: The recent research carried out on natural pigments highlights the eco-friendly designs of metal-free organic dyes providing the drafted structure for the safe, stable bio-friendly solar cells.

Academic Truth vs Commercial Prospects

Feasibility of Niche Market: Though the natural dyes are inappropriate for the grid-scale installation, yet they owe the capability for smaller- power implementations, for instance, smart packaging, indoor Internet of Things (IOT) etc. in which the sensitivity of low light along with the safe to the environment exceed the absolute peak efficiency.

Eco-Sourcing and Circular Economy: In contrast to the various synthetic or metal-organic Ru-complexes, the natural sensitizer presents the non-zero embodied energy, simple routine of extraction of biowastes, zero toxicity from heavy metals. This line up directly with circular economy and green chemistry banderole.

Cost Effective and Roll-to-Roll Fabrication: The unavailability of the high-purity fabrication suppresses the costs of the raw material leading highly inexpensive, continuous roll-to-roll printing over plastic substrates flexibility for the disposable energy producing applications.

Electrolyte

Electrolyte is the fourth basic part of DSSC. This is called Redox couple (Ye et al., 2015). The two basic functions of electrolyte include regeneration of oxidized dye and acting as electrically conducting medium. It can be divided into three classes on the basis of nature of electrolyte, such as liquid, solid, and polymer.

Liquid Electrolyte

In the most competent DSSC, the liquid electrolyte has been reported (Wang et al., 2005). Iodide has been reported as best liquid electrolyte among all electrolytes because of having characteristics like very fast dye regeneration, slow recombination within the conducting layer, and low recombination.

These are the characteristics of an ideal best electrolyte. The main drawback of liquid electrolyte is corrosion. Iodine showed corrosive behaviour towords metals, which are used as CE in DSSC. Many other materials like bromine (Br), tribromide ion (Br_3^-), rhodanine (SCN^-), thiocyanogen (SCN_2) have been studied as electrolyte in DSSC. An alternative electrolyte disulfide/thiolate (T_2/T^-) have been reported and the novel DSSC made by using the said electrolyte obtained efficiency of ~6.44% (Hilmi et al., 2014). Similarly, Wang et al. (2010) synthesized new DSSC by using L-cysteine redox couple.

This is the newly redox couple and exhibited the efficiency 7.70%, which is almost comparable to Iodide I_3^-(8.10%). The new DSSC have also been fabricated using the hybrid electrolyte benzoquinone (BQ). This type

of DSSC showed the efficiency of 8.40% which is much better and higher than Iodide electrolyte (Cheng et al., 2012).

Solid Electrolyte

The main issue with liquid electrolytes is lack of stability (Wu et al., 2007). To resolve this issue, many new developments have been in solid state electrolyte. Several materials are used as solid electrolyte including inorganic p-type semiconductor, organic hole trasnporting electrolytes, ionic liquids, and polymer gelators. $CsSnI_3$ used as electrolyte in DSSC attained efficiency of 10.20%.

Polymer Gelators Electrolyte

Polymers electrolyes have achieved much attention due to fast charge transfer rate and better as well as time lasting stability (Wu et al., 2007). These polymer electrolytes contains the following, poly(ethylene glycol), poly(acrylonirtrile), poly(methyl metharcy-late), poly(vinylidene fluoride). Wu et al. (2007) prepared a thermoplastic gel as electrolyte for use in DSSC and obtained an efficiency of 7.22%.

Material Selection

Considering a material with the required properties from a wide range of available materials is difficult and challenging. For this, the complete perception of the functional of each component and the analysis of several important factors are needed for the development of detailed engineering designs (Baghel et al., 2014). Accounting all the properties at the same time within the material selections is not an easy task, therefor, the systematic approach towards the selection process of the material is needed to screen as well as the selection of the optimal material for the application within the device. For this purpose, various strategies have been considered, e.g. the Multiple-Criteria Decision-Making (MCDM) methods, multiple-attribute decision-making (MADM), and Multi-Objective Decision-Making (MODM) techniques etc. various methods have been come about on the basis of the MADM technique, for example Technique for Order Preference through Similarity to Ideal Solution (TOPSIS), linear assignment method, VlseKriterijumska Optimizacija Kompromisno Resenje (VIKOR), Prefrence Index (PSI) method, Elimination Et Choix Traduisant la Réalité (ELECTRE), graph theory and matrix approach, Preference Ranking Organization Method for Enrichment Evaluations (PROMETHEE) and Complex Proportional Assessment (COPRAS) etc.

As discussed above, the metallic oxide semiconductors are widely utilized for thr conversion of the solar energy. The useful attributes of

several matal oxide semiconductors involving TiO_2 have been considered that are needed for the formation of the higher performancee photo-sensitive devices (Kurda et al., 2024).The performance of the photovoltaic of the solar cell is strongly based on the semiconductor materials used. Furthermore, the transportation of the injected electrons via nanostructures network is one of the most important process having impact on the performance of the device. The near infrared absorption study has been conducted over the nano-crystalline thin films formed by the variety of materials shows comparable spectral response, though dyes having the similar Ru complex dyes showed different injection times. The transport kinectics is seemed to be the function of the electronic density within the films that are normally elaborated through the trapping and detrapping ratewithin the band gap.

The attributes of the various metal oxide semiconductors i.e. band gap as well as the mobility of the photoelectrochemical conversion of solar energy (Maggard, 2021).The greater electronic mobility within the respective nanostructures films can be attained, if the electronic mobility within the bulk single crystal phases is higher that would possibly lessen charge recombination loss at the electrolyte interface that is made up of the oxidized redox species and therefore improve the device performance. The broad band gap semiconductor having the better carrier mobility is second most important requirement for the photoelectrode.

The ultimate target of any novel solar cell technology is to attain commercialization as well as competing with other existing technologies within the photovoltaic market. The value of the silicon photovoltaic device has been decreased from 4 US$/W in 2008 to 1.25 US $/W within the 2011 owing the module efficiencies fro, 15-20%. Contrary to this, the CdTe based thin films have attained the efficiencies of 14% at the cost of ~ 0.50 US $/W. In near future, the DSSC require to enhance the power conversion effiency having the lower cost formation methods as well as having the good stability. The smaller device cost of DSSC could consider them as the attractive alternate energy sources, hence, the cost is considered to be the third most important factor affecting the commercialization probabilities.

Besides these, the effective masses of the electrons from the CB is another crucial parameters defining the electronic structure of the CB of the metallic oxide semiconductor film. The accessible Density of States (DOS) is based on the effective masses (Lany, 2015). The higher value of DOS enables faster electronic injection. The electronic DOS has more impact over the performce of device, whereas the bulk dielectric constant have merely the secondary impact.

By study, it has been deduced that TiO_2 has been proved to be the most appropriate material out of the selected metal oxides (i.e. SnO_2, In_2O_3, and ZnO) for the utilization as photo-electrode in DSSC. Furthermore, the assessment of the performance of the solar cell is based on various parameters, e.g., FF as well as the energy conversion efficiency. The PCE for TiO_2 have been attained to be ~11.5 %, that is much greater than its related potential candidate i.e. ZnO and SnO_2.

Critical Analysis of Reported Efficiencies

A well-known hindrance of presenting the material-to-material analysis as provided above is that the published PCE values for a CE under consideration, electrolyte, dye or photoanode could not be compared directly across the investigations without providing the remaining device stack. A DSSC formed with the excellent CE, but combined with the smaller efficiency dye and incompatible electrolyte would definitely underperform and vice versa. This section is designed to couple the efficiencies provided in the review through material's class and through benchmark, where feasible (conventionally Pt for the CE or TiO_2 benchmark for the photoanode) utilized in the similar investigation, to provide the comparison that genuinely reflects the corresponding performance instead of the absolute numbers extracted from the context.

Amid the various CE materials, the metal phosphide i.e. $Ni_{12}P_5$ presented the maximum efficiency given in this review at 9.05% surpassing the taken Pt control i.e. ~8.43% that shows the stronger in-build catalytic activity for the I_3-/I-redox reaction (Sun et al., 2018). The electrodes based on the carbides i.e. WC and MC tracked at 8.34 % and 8.18% respectively against the Pt-control, hence exceeding the Pt in the similar investigation, greatly ascribed towards the greater surface area as well as the stable catalytic performance. The metal oxide electrode's i.e. V_2O_5 and tungsten oxide showed the performance which is 7.75 % vs Pt 7.55 % and 7.25 % vs Pt 7.57% respectively followed the trend closely yet not very constant behavior to the respective Pt benchmarks. These also require hybridization with the graphene or other carbon-based nano-structures to attain the corresponding rates of the charge transfer. Similarly, the electrodes based on the conducting polymers i.e. PANI, PEDOT presented the broader range i.e. from 2%-~8% based on the doping as well as the synthesis technique (Cai et al., 2026; Murtaza et al., 2026). The results showed that this class is much more sensitive to deal with as compared to the respective inorganic counterparts. Conclusively, the pattern around the CE materials is such that the efficiency imprints the catalytic behavior towards the tri-iodide reduction as well as the surface area, irrespective of the material's abundance or cost. This is more exactly

why various of the cost-effective choices match above or outperform the Pt in-spite of the fact that Pt is the typical benchmark.

Photoanode materials, however, represents the issue directly as compared to previously described CE. The TiO_2 extend the efficiencies to ~11.5 % as presented in one of the investigations in this paper. Nevertheless, the TiO_2 alone was presented at only 2.7%within another paper utilized as benchmark for the comparison of the Nb_2O_5, in which the Nb_2O_5 reached the efficiency up to 4.1% (Elrahoumi et al., 2026). Likewise, the composite of $SrTiO_3$ as photoanode extends the efficiency to 5.07 % i.e. ~ 36.6% betterment over the considered TiO_2 benchmark within the similar study. Such figures could not be aligned together over a single scale of efficiency and compared as the benchmark TiO_2 fluctuates almost greater than fourfold i.e. 2.7% to 11.5% in the various investigations considered in this study because of the variation on the thickness of the film, electrolyte formulation, the choice of dye instead of the photoanode material alone. What is about to compare and what are the highlights of this study is the comparative improvement every transition generated on the respective benchmark in the similar study.

The dye materials represent a distinct and stable ranking system. For instance, the inorganic, Ru-based dyes provided the maximum efficiency of the dyes discussed in this paper, within the range of 10-11% after organic donor acceptor dyes at ~9.1% (Carella et al., 2018). Similarly, the naturally occurring dyes i.e. carotenoid, anthocyanin and flavonoid modified well behind <1%, the individual published data states 0.56%, 0.12% and 0.22% respectively. The said gap is in accordance with the chemistry behind it instead of the just an arbitrary number, i.e. synthetic dyes are made-up of the anchoring groups, which, in turn, are bind more strongly to the surface of TiO_2 and with the tailoring donor-acceptor architectures. This results in expansion and shifting of absorption ranges. However, the natural dyes depend upon the functional groups as well as chromophores provided by the plant sources owing the weaker surface anchoring along with the shorter absorption ranges. The natural dyes are, however, cost-effective and environmentally safe make them attractive. However, the efficiency gap vs synthetic dyes presented in varies studies are consistent as well as large and not marginal (Saxena & Raja, 2014).

The electrolyte systems, resist the simple classifications devoid of context. An electrolyte based on $CsSnI_3$ provide the greatest efficiency described in this study at 10.20 % (Shah et al., 2020). Whereas the various liquid redox couples varies from 6.44-8.40% against the standard iodide with 8.10% efficiency representing that several novel redox couples either matched or somehow exceeded the typical iodide systems as compared to

the others that fell short (Li et al., 2015). The polymer gel provided here get to 7.22% i.e. smaller as compared to the extraordinary liquid systems that reflects the standard alternative in the described class, the polymer gel offers some ionic conductivity. Hence, some efficiency as a result suppress volatility as well as the comparatively better operation stability for long-term, an exchange the liquid electrolytes cannot offer.

Among the presented four classes of materials, there exists several factors, which are responsible for the performance. First, the effective participation of various components in charge separation or transfer at the particular interface. For instance, the catalytic activity at the CE, electron mobility and injection at the photoanode, surface anchoring for the dyes and ionic conductivity for the electrolytes. Second, the reality of the reported increase in the efficiency in the study in which it was measured. The broad ranges within the TiO_2 threshold efficiency alone i.e. 2.7%-11.5% in the studies reported in this review is the direct proof that the complete fabrication choices instead of the single component is responsible for the large part of efficiency modification perceived in the literature. Thus, this review paper is structured differently depending on the specific requirements of each reporting destination.

Summary

This review emphasize on the importance the engineering of materials in improving the DSSC performance, cost, balancing efficiency along with the stability analysis for CE, photoanodes and sensitizerd. Whereas the synthetic Ru-based dyes and Pt CE are considered as standard, the extensible commercialization depends upon the emerging cost-effective materials. The viable aternatives like metal carbides/nitrides, carbon nanostructures and targated natural sensitizers for niche in-door implementation. Among all four classes of materials, no class could independently surpass on each metric. The stability or increase in cost are conventional counterbalence by efficiency drop. This is the reason, that choice of materials must be corresponding to the targeted application instead of only considering the peak PCE value. To narrow the gap between the lab-scale testing and commercial feasibilty, the future research should emphasize on MCDM structure for choice of materil in addition to the solid state electrolytes to control te long-term environmental degradation.

Above the material's selection, the switching from the laboratery-scale towards the commercially feasible modes would also need the standard testing protocols along with the long-term outdoor verification. This is because the fact that the accelerated ageging tests does not provide the reliable real-world performance dissipation in controlled conditions.

The techno analysis, which deal with the abundance of raw materials, encapsulation cost, procesing temperature in addition to the stability and efficiency will give the more reality check for selection of materials instead of only providing the efficiency records. In the near future, the hybrid structures combining the primary materials i.e. photoanode, electrolyte, sensitizer and CE might provide the more practical path towards the DSSC instead of optimizing every component. These devices will require to be simultaneously efficient, reliable, substantial and cost-effective for building the integrated Photovoltaics as well as indoor energy harvesting application.

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