

The Quantum Dot-sensitised Solar Cells (QDSSCs): A Review on Recent Achievements (2010-2021)

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Abstract

Over the past few decades, quantum dots sensitized solar cells (QDSSCs) have attracted significant attention due to the quantum dots sensitiser's unique properties, including, its non-precious synthesis, size-tuneable bandgaps; excellent photostability, the ability to generate multiple excitons, and high absorption coefficient that led possible to increase power conversion efficiency (PCE) to more than 15% due to their higher molar extinction coefficient and tuneable photo-response. This review article outlines a comprehensive overview of the development of the performance of QDSSCs including their components fabrications and highlights the challenges and limitations of the QDSSCs' components such as narrow absorption areas and the charge recombination happening at the photoanode/electrolyte interfaces and discusses the prospects for the development of highly efficient and stable QDSSCs.

Keywords: Quantum dots sensitised solar cells, Quantum dots, Counter electrode, stability.

1.0 Introduction

Third-generation solar cells are inherently different from the previous two generations because they do not rely on the p-n junction design of the others. Its concept is an increase in efficiency and the reduction of the production cost of the second generation (Kanemitsu, 2011). This new generation of solar cells is being made from a variety of new materials besides silicon, including nanomaterials, silicon wires, and solar inks using conventional printing press technologies, organic dyes, and conductive plastics. This generation exhibited due to the high costs of first-generation solar cells and toxicity and limited availability of materials for second-generation solar cells, a new generation of solar cells emerged. Three primary types of third-generation solar cells have been commercially developed: Dye-sensitized solar cells (DSSCs), Quantum dots sensitized solar cells (QDSSCs), and Perovskite solar cells. Initially, the material used to fabricate quantum dots sensitized solar cells (QDSSCs) was researched similarly to that used to fabricate DSSCs which was proposed by O'Regan and Grätzel in 1991 when they released their first publication on the principles of the new system introduced to photovoltaic (PV) conversion by dye-sensitized solar cells (Gopi, Venkata-Haritha, Lee, & Kim, 2016; Hosseinpanahi, Abbaspour-Fard, Feizy, & Golzarian, 2017; Shitta, Ogedengbe, Familoni, & Ogundipe, 2021; Yusuf, Mustafar, Borines, Kusumawati, & Hashim, 2022) but the difference between them is replaced organic dyes with inorganic nanosized semiconductors quantum dots (QDs) having the same mechanism as that of the DSSC (Hosseinpanahi et al., 2017).

In recent years, numerous researchers from various fields have attracted QDSSCs, including three fields, the first is the physical field which is developing novel types of materials for QDSSC fabrication, optimizing, and comprehending the photophysical mechanism of QDSSCs, and the second is the chemical field which is pioneering suitable light-harvesting materials, and finally, engineering field which is constructing novel device architectures for QDSSCs (Abate & Chang, 2018; Bhambhani, 2018; Mora-Seró, 2020). The chemistry between these researchers may have a

significant impact on further advances in QDSSCs in the future. In fact, of point, high-performance solar cells require materials that should harness a wide range of the solar range, superior light-harnessing material, and can be capable of effectually converting light into electricity. Better charge generation, charge separation, and charge extraction material with low defects in charge recombination are required to develop economically profitable and realistic PV technologies. Nonetheless, the use of most of the materials is limited because of their high production costs and the need for high-boiling point solvents, which causes rapid injection methods to produce these materials (Abate & Chang, 2018; Mora-Seró, 2020; Peng et al., 2018a; Sotodeian & Marandí, 2021). In contrast, using QDs sensitized cells can provide several advantages, including improved charge generation, charge separation, and charge extraction all within the same material, making them excellent candidates for solar cells (S. Fu et al., 2021; Thiruvengadathan et al., 2015; Zhu, Yang, Song, Rodríguez-Cordoba, & Lian, 2011). In QDSSCs, the charge generation process usually occurs in QDs, and the charge is then quickly introduced into two different transport media, reducing the electron-hole recombination process. QDs' dielectric confinement effect and MEG ability make QDSSCs so efficient. As a result, QDSSC technology is quickly acquiring traction in the global science and technology community (Chai & Jun, 2019).

The fabrication of QDSSCs has advanced significantly in recent years, showing that QDSSCs technology has attracted significant interest from a variety of scientific and technological disciplines. Due to the evolution of technology has resulted in significant performance enhancement and the discovery of novel types of QDs, which has led to rapid advancement in the CE, photoanode, electrolyte and QDs as shown in Figure 1, has been reflected in the increased number of publications and the related field through published book chapters and peer-reviewed journals of QDSSCs since the middle of the last decade. However, because of limited efficiency and performance stability issues, progress in QDSSCs technology has slowed significantly in 2020–2021, and large-scale application and commercialization of QDSSCs technology are restricted globally.

As a result, it's critical to understand what solutions are available to address the issues with QDSSCs' performance and stability. As shown in Figure 1, the number of research papers published on QDSSCs per year has exploded over the last 11 years, showing that QDSSCs are one of the best candidates for the PV industry. In this review, the discussion starts with a brief description of the QDSSCs operation. Then, introduces the fundamental structure and reaction mechanism of QDSSCs and their status of performance with an emphasis on QDSSCs stability and instability. Also, this study focuses on the strategies for obtaining highly efficient QDSSCs by presenting a discussion of QD sensitizers, redox electrolytes, and counter electrodes. Furthermore, the challenges and limitations discuss the ways which lead to QDSSCs' poor performance and how to improve performance stability. Finally, the progress and future challenges are discussed, which explain that developing new low-cost technologies for high-efficient QDSSCs is an effective method for overcoming current energy and environmental problem.

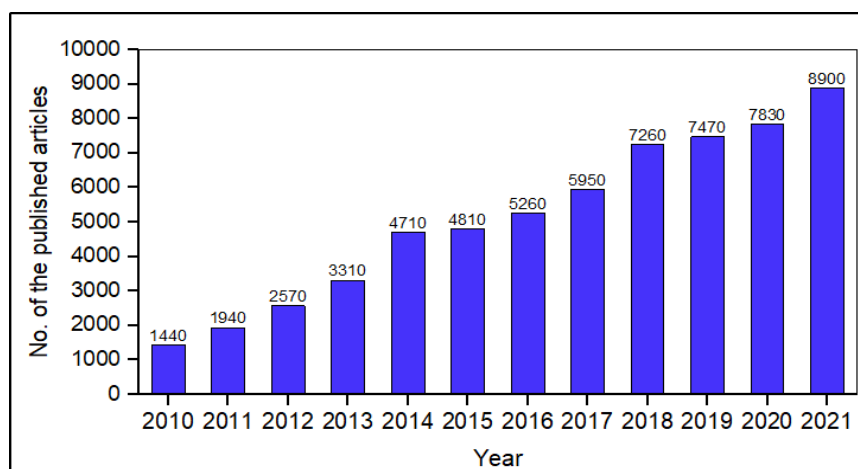


Figure 1: The number of articles published per year was extracted from the search terms "quantum dot sensitized solar cells" from 2010 to 2021.

2.0. Fundamental structure and reaction mechanism of QDSSCs

The quantum dots sensitised solar cells (QDSSCs) consist of four essential components, semiconductor QD sensitizers include group II-VI (CdS, CdSe, CdTe) [15], III-V (InP, InAs) (Yu et al., 2006), IV-VI (PbS, PbSe) photosensitizers (Basit, Abbas, Jung, Bang, & Park, 2017), and I-III-VI₂ QDs (CuInS₂, AgInS₂, CuInSe₂, and AgInSe₂)

(G. Wang et al., 2017). The semiconductor quantum dots are used as photosensitizers, converting absorbed photons to excitons. They have several advantages, including size-tunable bandgaps, excellent photostability, a high absorption coefficient, a long carrier lifetime, a high dipole moment that defines how far into a material light of a specific wavelength can penetrate before it is absorbed, a long carrier lifetime, a large intrinsic dipole moment, and the ability to generate multiple excitons from a single photon which is called as multiple excitons generation (MEG) (Goodwin, Jellicoe, Davis, & Böhm, 2018; Gopi, Srinivasa Rao, Kim, Punnoose, & Kim, 2015; Kim, Yeo, et al., 2014; Manjceevan & Bandara, 2018; Pan, Rao, Mora-Seró, Bisquert, & Zhong, 2018). Because of these excellent properties, they can achieve a theoretical efficiency of up to 44% beyond the Shockley-Queisser detailed limit of 33% for thin-film solar cells (Pawar et al., 2016), and considerably higher than its rival, dye-sensitized solar cells (DSSCs) with 31%, which has prompted researchers to focus more on QDSSCs as compared to DSSCs (Yeh et al., 2011). However, due to poor stability and corrosion resistance, QDSSCs' power conversion efficiency lags far behind that of DSSCs (Manjceevan and Bandara 2018), also, most of the inorganic QDs utilized in QDSSCs suffer from stability issues in electrolytic conditions (Ghosh, Sarkar, Devi, Kim, & Kumar, 2021).

QDSSC is composed of a transparent conducting oxide (TCO) glass substrate, a mesoporous semiconductor oxide layer such as (TiO_2 , ZnO , SnO_2), semiconductor quantum dots (QDs) such as (CdSe , CdTe , CdS , PbS , PbSe , InAs) as photoanode, a counter electrode such as (Pt , Transition metals chalcogenide (TMC)), and electrolyte (polysulfide, iodide/triiodide) the I^-/I_3^- redox couple electrolyte has been applied to QDSSCs, but with limited success due to the photolysis of QDs in the presence of highly corrosive iodine as shown in Figure 2 (Hwang & Yong, 2015; Sun, Jiang, Zhong, Hu, & Wan, 2017; Vignesh et al., 2019). Therefore, the ideal electrolyte is the polysulfide electrolyte ($\text{S}^{2-}/\text{S}_x^{2-}$), which effectively stabilizes metal chalcogenide QD sensitizers, accomplish efficient charge separation, and provides good PV performance (Kim et al., 2015; Thulasi-Varma et al., 2015).

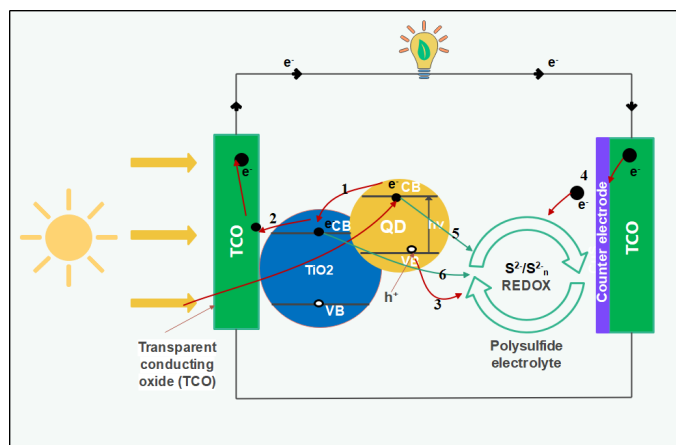
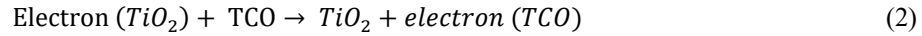
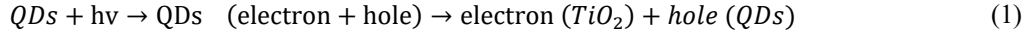


Figure 2: Schematic of QDSSCs

The fundamental operating mechanism, which is dependent on the driving force of electron circulation, is the energy difference between the aligned Fermi levels of the QDs/semiconductor oxide layer and the electrolyte's redox potential (G. Chen, Seo, Yang, & Prasad, 2013). When light passes through the clear FTO and reaches the QDs, photons are caught by the QDs, resulting in electron-hole pairs that swiftly separate into electrons and holes at the interface between the nanocrystalline oxide and the QDs. Electrons are injected into the conducting oxide sheet, while holes are scavenged to the CE via the polysulfide electrolyte's hole carrying the redox pair (Gopi, Srinivasa Rao, et al., 2015).

Understanding the mechanism of the various photo-sensitization processes in QDSSCs might facilitate the implementation of design principles for future successful applications. A conventional QDSSC is composed of a photoanode sensitized by QDs, an electrolyte and a counter electrode. A photoanode is manufactured by printing a mesoporous semiconductor oxide layer on a transparent conductive oxide (TCO) substrate with a thickness of around 15-25 μm with 50-60% porosity. Then sensitized by semiconductor QD. Polysulfide solution ($\text{S}^{2-}/\text{S}_x^{2-}$) redox couple is mostly used as the liquid electrolyte. Noble metals, carbon-based materials, polymer-based materials, and metallic compound materials are all examples of counter electrode materials. When QDSSCs are exposed to sunlight. The radiation penetrates TGO and QDs absorb photons from this radiation of certain energy and generate electrons from

the QD valence band (VB) to the conduction band (CB). The excited electrons on the CB of QDs inject into the CB of semiconductor oxide (e.g., TiO₂) as shown in (1). Then transfer from TiO₂ to the TCO layer and flow to the external circuit as shown in (2). The exciton electrons leave behind holes in QDs which transfer to the redox couple that leads to regenerating QDs' original state, as shown in (3). Concurrently, electrons transfer to CE by the external circuit and reach the oxidized (S_x²⁻) ions on the CE surface to reduce it to (S²⁻) as shown in (4). In addition, improper processes may happen such as carrier recombination, as shown in (5) and (6).



The essential working mechanism depends on the driving force of the electron circulation which is the energy level varies between the aligned Fermi levels of QDs/semiconductor oxide and the redox potential of the electrolyte (G. Chen et al., 2013; Sun et al., 2017). Figure 2 shows a schematic diagram of the reaction mechanism in QDSSCs. (1 and 2) reaction (1), (3) reaction (2), (4) reaction (3), (5) reaction (4), (6) reaction (5), and (7) reaction (6).

Consequently, QDSSC generates electrical power when irradiated with sunlight. The power Conversion Efficiency η of a solar cell can be estimated by dividing the generated electrical power density (P_{max}) by the incident solar power (Smets, Jäger, Isabella, van Swaaij, & Zeman, 2016).

$$\eta = \frac{P_{max}}{P_{in}} = \frac{J_{sc} * V_{oc} * FF}{P_{in}} * 100 \quad (7)$$

Where P_{max} output power, P_{in} is input power density at the operating point (also known as radiance, which indicates the solar radiation per surface unit (W/m²)), J_{sc} is short-circuit current density, V_{oc} is the open-circuit voltage and FF is filled factor of the solar cell. J_{sc} depends on the incident light intensity, the number of photons absorbed and mobility of charge carriers, while V_{oc} is affected because of different recombination processes of charge carriers. The input power for efficiency calculations is 1 kW/m² or 100 mW/cm² (1000 W/m²) Thus the input power for a 100 × 100 mm² cell is 10 W and for a 156 × 156 mm² cell is 24.3 W.

3.0 QDSSCs Fabrication Techniques

In QDSSCs, the synthesis technique is an important area for optimizing solar cell performance. Several methods are available to deposit films of semiconductors; chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) method are of special interest because they represent simple and efficient approaches. CBD is influenced by several parameters, including the concentration of reactants and complexing agents, pH, deposition time, annealing, temperature, and substrate spacing. Overall, this approach has a huge use in PV. To improve the QDSSCs' performance, a solution-based SILAR approach was introduced. The synthesis of QDSSCs assembly involves several steps: conductive glass substrate cleaning. Identify the conducting side and apply two parallel strips of tape on the edges of the substrate with the conductive side facing up; Apply a little amount of TiO₂ paste between the two pieces of tape towards the top border of the transparent conductive oxide (TCO) glass; spread the paste across the substrate using a doctor blade. In the furnace, sintering the titania layer at 450°C for 30 minutes; QD sensitizers (CdS/CdSe) are soaked into the electrode. Preparing the counter electrode with a metal sulphide oxide layer; connecting the two electrodes Finally, the electrolyte gap between the two plates is filled and sealed.

3.1 Photoanode fabrication techniques

In QDSCs, the QDs act as photosensitizers, which are usually anchored on the metal oxide surface. The semiconductor quantum dots are used as photosensitizers, converting absorbed photons to excitons. They have several advantages, including size-tunable bandgaps, excellent photostability, a high absorption coefficient, a long carrier lifetime, a high dipole moment that defines how far into a material light of a specific wavelength can penetrate before it is absorbed, a long carrier lifetime, a large intrinsic dipole moment, and the ability to generate multiple excitons from a single

photon which is called as multiple excitons generation (MEG) (Goodwin et al., 2018; Gopi, Srinivasa Rao, et al., 2015; Kim, Yeo, et al., 2014; Manjeevan & Bandara, 2018; Pan et al., 2018).

The strategies of QDs synthesis are SILAR, and CBD, which are both methods of in-situ growth, and electrophoresis deposition and linker-assisted binding are ex-situ growths. The pre-synthesized QDs can be subsequently loaded by ex-situ methods such as linker-assisted binding, which were effective in loading QDs on TiO₂ films, and hot injection led to easily producing QDs with uniform and controllable diameters and high crystallinity. Ex-situ methods struggle with non-tailored QD sizes and poor crystallinity due to the huge QD size relative to the pore size in TiO₂ mesoporous film and the lengthy alkyl ligands capped on QDs surface, which causes QDSSCs with low power conversion efficiencies. However, this problem was overcome by the linker-assisted assembly approach for QD deposition, which uses a hot injection to easily produce QDs with uniform and controllable diameters and high crystallinity (W. Li & Zhong, 2015; Md. Akhtaruzzaman & Vidhya Selvanathan, 2022).

The second component of the photoanode is called the functioning electrode in QDSSCs. The anode includes wide-band-gap semiconducting metal oxides (TiO₂, ZnO, SnO₂, NbO₅, or SrTiO₃) deposited on a TCO substrate, typically fluoride doped tin oxide glass (FTO) or indium tin oxide (ITO) glass (C. Chen, Ling, & Li, 2017; W. Li & Zhong, 2015; Peng et al., 2018b) However, ITO films display ideal transparency over 80% and resistivity (10⁻⁴ Ω cm), while FTO has attracted great interest because of its wide energy gap, inexpensive, thermal stability, chemical inertness, resistivity (4.3×10⁻⁴ Ω cm), and transparency 86% (Spray et al., 2019). The resistivity of the ITO increases with annealing while FTO does not. The resistivity of the ITO substrate increases after 300°C, but for FTO, the resistivity has little changed up to 500 °C (Ahmadi, Shoushtari, & Farbod, 2019). In QDSSC applications, FTO glass is recommended over ITO substrates because it is non-precious.

3.2 The Counter Electrode fabrication

There are two primary approaches to nanostructure synthesis: top-down and bottom-up methods as shown in Figure 3. The top-down method involves the breaking down of bulk materials through external forces applied to the material into smaller particles and the bottom-up method often refers to building up nanoparticles from their atoms in the form of gas or liquid state through the transformation of molecular condensation. In the top-down method, there is the absence of surface structure has a significant effect on the physical and chemical properties of nanomaterials. As a result, even with great energy consumption, it is difficult to generate nanoscale structures. Additionally, this method results in a considerable crystallographic loss for the treated forms (Khan, 2020). Counter electrodes are responsible for collecting electrons from the external circuit and catalyzing oxidized polysulfide electrolytes at the electrolyte/CE interface and they can be synthesised from precious metals and non-precious metals.

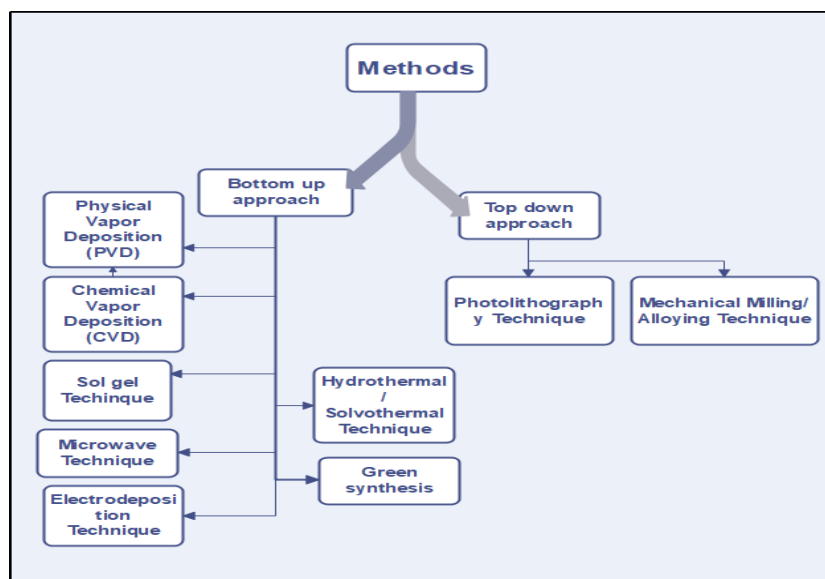


Figure 3: Flowsheet for methods of nanostructures synthesis

3.2.1 Precious Metal Catalysts

Ding et al., (2019) stated that precious metal catalysts, the most active and reliable catalysts, are expensive (Ding et al., 2019). They include platinum, palladium, rhodium, ruthenium, rhenium, iridium, osmium, silver, and gold and their alloys were used in a variety of industries due to their outstanding corrosion resistance, good electrical conductivity, excellent corrosion resistance, and most active catalysts for a fuel cell or solar cell. Platinum (Pt) is an extremely expensive noble metal (Thomas et al., 2014), widely used as a CE in DSSCs because of its low resistance, high electrical conductivity, and high electrocatalytic activity in the reduction of iodide/triiodide (I^-/I_3^-) electrolyte, but when using Pt as CE in QDSSCs results in poisoning of the Pt CE surface because of sulfur species adsorption caused by the polysulfide redox couple (S^{2-}/S_x^{2-}) and which inhibits its catalytic activity, and finally, it reduces the efficiency of the QDSSCs (Faber, Park, Cabán-Acevedo, Santra, & Jin, 2013; D. M. Li et al., 2014; Seol, Ramasamy, Lee, & Yong, 2011; Yang, Chen, Liu, Li, & Chang, 2011; X. Zhang et al., 2013) Also, Pt is not an effective CE active material for redox couples such as cobalt-complexes, T_2/T (Kakiage et al., 2015). Another noble metal, such as gold (Au), shows remarkable activity and stability, but they are insufficiently catalytic, generating substantial overpotentials for electrolyte regeneration, lowering the solar cell's power conversion efficiency (Kiyonaga, Akita, & Tada, 2009; Tachan et al., 2011).

3.2.2 Non-precious Metal Catalysts

Prakasam, (2020) suggested that, due to their superior catalytic performance, non-precious metal catalysts such as carbon, nickel, copper, iron, cobalt, chromium, manganese, molybdenum, and tungsten have been extensively used as photoconversion catalyst materials (Prakasam et al., 2020). Also, their first-row transition metal alloy catalysts, such as iron, nickel, and cobalt, are plentiful, affordable, and comparatively harmless. Thus, substituting low-cost materials for precious metal catalysts would drastically cut the cost of hydrogen generation (Bernskoetter & Hazari, 2018; Tiwari & Titinchi, 2015). Countless researchers are developing and improving electrode materials to suit the requirements of energy storage devices and generation systems while also safeguarding the environment and lowering fossil fuel use through the use of nanotechnology and renewable energy sources (Hussein, 2015; Ierides et al., 2019; Jain & Jain, 2016; Mao, Shen, & Guo, 2012; Serrano, Rus, & García-Martínez, 2009). As a result, significant effort is being made to develop non-precious metal catalysts such as available transition metals (metal carbides, sulfides, oxides, and nitrides) were unique forms of energy storage materials. (Al-Enizi et al., 2019; Fadil et al., 2014; Kulkarni, Nataraj, Balakrishna, Nagaraju, & Reddy, 2017; Shombe et al., 2020; Tang & Yang, 2019). Transition metals sulfides (TMSs) are efficient materials used in most energy storage applications due to their excellent electrochemical characteristics and facilitate electron transfer in sulfides' structure due to the small value of the electronegativity for S metal (Qingyong Zhang, Mei, Cao, Tang, & Zeng, 2020). In addition, TMSs have a high ratio between the surface area and the volume of the particle because the catalytic process is located on the surface and possesses excellent properties related to the sulfur-specific morphology of their surfaces in terms of posing unique shapes (nanosheet, nanorod, a nanoplate, nanobud, nanowires and others) (de León, Kumar, Antúnez-García, & Fuentes-Moyado, 2019; Shen et al., 2015; Theerthagiri et al., 2020).

4.0 Current status of performance in QDSSCs

QDSSCs efficient performance depends on its components' performance which is counted by PV performance parameters such as (power conversion efficiency (PCE), open circuit voltage (V_{oc}), short circuit current density (J_{sc}), Fill factor (FF), and charge transfer resistance (R_{ct})). The power conversion efficiency is a significant PV parameter that reflected the extent of the quality of the QDSSCs performance. The solar cells' performance is influenced by many indoor and outdoor factors such as (Temperature, Time, components' fabricated materials, humidity, and geographical location).

4.1 Efficiency

Several advancements have happened towards the front of both photovoltaic performance and fundamental comprehension of this technology. In the initial advances, the design and fabrication of devices were two key elements that were primarily investigated to attain high PV several improvements have occurred along this voyage, both in terms of PV performance and fundamental understanding of this technology. The design and fabrication of devices were two major factors that were initially researched to achieve high PV performance.

After the sensitization concept was developed, a variety of light-harvesting semiconductors such as Bi_2S_3 , CdS, CdSe, and PbS were used as sensitizers in photoelectrochemical applications. The authors could fix CdS on metal oxide (TiO_2) for the first time, which resulted in higher photocurrent, because of the longer spectrum absorption. After the

sensitization concept was discovered, a variety of light-harvesting semiconductors were used as sensitizers in photoelectrochemical applications, such Bi₂S₃, CdS, CdSe, and PbS (Pan et al., 2018; Sato et al., 1988). Vogel et al., (1990) attempted to build photoelectrochemical cells utilising QDs sensitised semiconductors. For their device, they got a FF of 0.75%, V_{oc} of 0.395 V, and a J_{SC} of 175 mA/cm² (Vogel, Pohl, & Weller, 1990).

Figure 4 shows that QDSSCs have remarkable increase in power conversion efficiencies over the previous two decades, going from less than 1 %to over 15%. Plass et al., (2002) obtained an efficiency of 0.49% under 0.1 sun illumination as shown in Figure 4 (a) (Plass, Pelet, Krueger, Grätzel, & Bach, 2002), before 2010, several researchers boosted the PCE of QDSSCs such as Yu et al., (2006) attained a PV performance of 0.3% for QDSSCs based on indium arsenide (InAs) QDs sensitised TiO₂ photoanode. Despite the poor power conversion efficiency, the gadget showed greater stability in open-air situations for up to a week, as shown in Figure 4 (b) (Yu et al., 2006), Diguna et al., (2007) added a broad semiconductor (ZnS) passivation layer over the CdSe sensitised TiO₂ metal oxide and subsequent F⁻ ions deposition. Due to the efficiency advancement, QDSSCs technologies have piqued the interest of the scientific community and solar sectors by 2.7% (Diguna, Shen, Kobayashi, & Toyoda, 2007), and 4.22% (Y. L. Lee & Lo, 2009) as shown in Figure 4 (c,d), respectively. Zhang et al., (2011) achieved a structure of TiO₂ based on CdS/CdSe QDs as a photoanode electrode system, giving the best efficiency of 4.92% as shown in Figure 4(e) (Quanxin Zhang et al., 2011). Soel et al., (2013) designed a set of new catalytic electrodes by combining Mo-compound particles (Mo₂N, Mo₂C, and MoS₂) with carbon nanotube/ reduced graphene oxide (rGO) supports for use as counter electrodes in QDSSCs led to increasing the PCE to 5.41% as shown in Figure 4(f) (Seol et al., 2013), and on the same year, Wang et al., (2013) used CdTe/CdSe QD-based regenerative sandwich solar cells exhibit a record PCE of 6.76% (J. Wang et al., 2013) as shown in Figure 4 (g), respectively. From 2016 to 2019, there was a development in the PCE values from 9.73%(Ren et al., 2016), 11.91% (Du et al., 2016), 12.45% (Jiao et al., 2017), 12.75% (W. Wang et al., 2018), and over 13% (Pan et al., 2019), as shown in Figure 4 (h, i,j, k, l), respectively. In 2021, Song et al.,(2021) developed a new photoanode (TiO₂/QD/Mg/QD) instead of TiO₂/QD that increased QD loading and concomitantly improved light harvesting capacity and decreased charge recombination, photocurrent, photovoltage and FF had been remarkably improved, and the PCE increased from 13.54% to 15.31% as shown in Figure 4 (m) (Song et al., 2021). Furthermore, a new certified PCE record of 15.20% has been obtained for liquid-junction QDSSCs.

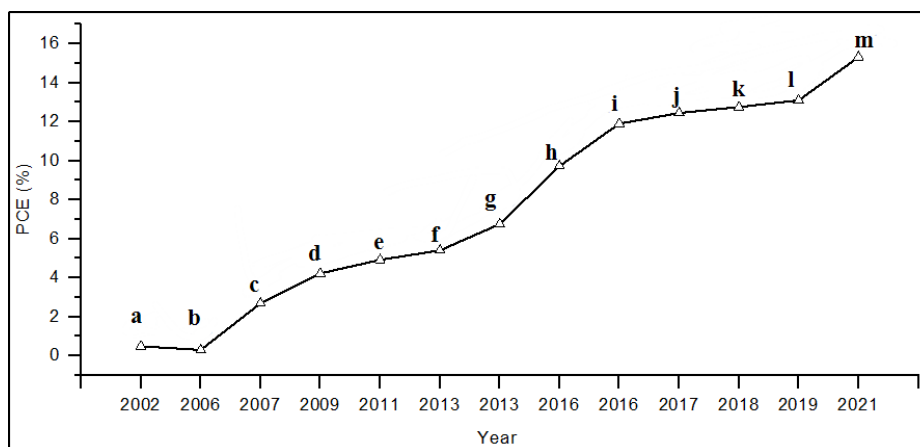


Figure 4: The power conversion efficiency (a) 0.49% (Plass et al., 2002), (b) 0.3% (Yu et al., 2006), (c) 2.7% (Diguna et al., 2007), (d) 4.22% (Y. L. Lee & Lo, 2009), (e) 4.92% (Quanxin Zhang et al., 2011), (f) 5.41 (Seol et al., 2013), %, (g) 6.76% (J. Wang et al., 2013), (h) 9.73% (Ren et al., 2016), (i) 11.91% (Du et al., 2016), (j) 12.45% (Jiao et al., 2017), (k) 12.75% (W. Wang et al., 2018), (l) Over 13% (Pan et al., 2019), and (m) 15.31% (Song et al., 2021) of QDSSCs vs years (from 2002 to 2021).

An extensive research and development effort that began in the physical and material sciences has resulted in a dramatic enrichment in the conversion efficiencies of QDSSCs since 2014. Until this year, the electrode sensitization method, which was fully performed using the CBD or SILAR method, yielded the best PCE results. Nonetheless, the QDs made with the other techniques demonstrated the potential of light-harvesting materials that could be made by using colloidal quantum dots as sensitizers. Chiang et al., (2018) focused on using novel and simple methods to assemble Cu–In–S QDs as sensitizers to reduce surface defect states in Cu–In–S QDs and electron recombination at

the interface. High-quality QDs were synthesised for this purpose using simple and inexpensive microwave-assisted techniques (Chiang et al., 2018). When applied to QDSSCs applications, this method was found to be capable of uniformly and quickly delivering QDs that provided a TiO₂ semiconductor with a quick, homogeneous, and better surface coverage of uniform crystals. Thus, a higher PCE of 8.0% was attained for these high-quality and defect-free Cu–In–S QDs which was a more auspicious performance in comparison with its reference devices (Chiang et al. 2018).

On the other hand, in the absence of prior methods of immobilizing pre-synthesized QDs, the secondary deposition relying on the electrostatic interaction approach has become the preferred means for immobilization of these QDs on mesoporous TiO₂ films that deliver higher efficiencies (K. M. Lee, Chiu, Lu, & Hsieh, 2011). Additionally, this strategy is incorporated, allowing the different QDs to be loaded onto TiO₂ films irrespective of the type of light-harvesting QDs utilized (McDaniel, Fuke, Makarov, Pietryga, & Klimov, 2013).

Even though numerous QDSSC designs have been suggested, the cell efficiency of the QDSSCs (around ~15%) is still lower than the PCE of the DSSCs due to QD loading and charge recombination having remarkably affected the efficiency and other PV parameters. To improve the efficiency of QDSSCs, research on novel electrocatalytic materials for their counter electrodes is necessary.

4.2 Performance Stability

Most PV systems are constructed using solar modules, which are considered to be the most reliable components. Under typical operating conditions, PV modules should be able to perform adequately for 30 years (Achey, 2016). As a consequence, when the solar cells have good efficiency, effectively performance, and excellent stability commercialization will happen. Long-term performance stability, according to this hypothesis, encompasses both internal and extrinsic difficulties associated with devices functioning under varying settings. A well-designed aptitude is critical for achieving predictable long-term performance stability in a variety of environmental conditions, including heat, light, humidity, and air moisture, among others. These devices must remain in perfect functioning to deliver substantial performances in the future.

The majority of device component stability research focuses on photoanodic corrosion and chemical stability of QDs, type of substrate, nature of adhesive material, electrocatalytic activity of CE material, and evaporation and volatilization of electrolytes, among other things, with the primary goal of investigating device performance stability in terms of temperature and atmospheric moisture. Many people believe that PV technology's long-term stability is unknown at this time. There has been little research into the effect of polysulfide electrolytes on QDSSC device stability. The chemical and environmental stability of QDs towards heat, light, and humidity are all factors that affect the performance stability of QDSSCs devices.

In terms of electrolyte preference, the organic iodide/triiodide (I⁻/I₃⁻) redox couple electrolyte is preferred in the DSSCs application; Nevertheless, due to the instability of QDs, it is not applicable in the QDSSCs application. While the polysulfide electrolyte with the S_x²⁻/S²⁻ redox pair has been proven to be suitable for stabilising the frequently used chalcogenide QDs, the polysulfide electrolyte would provide far more stable devices. Nonetheless, (Kamat & Bang, 2009; Malashchonak et al., 2017) observed that the high redox potential of polysulfide electrolytes produces photo-corrosion of QDs, which could potentially compromise the device's performance stability. Consequently, the CEs' stability (both electrochemical and mechanical stability) can affect the device's overall stability. For instance, QDSSCs often use transition metal sulphide and chalcogenide-based CEs, which suffer from severe corrosion to the polysulfide electrolyte, which eventually seeps out and causes ongoing corrosion of the CE, reducing the device's performance stability (Meng, Chen, & Thampi, 2015).

TMCs CEs have a large number of redox sites, unique crystal structures, high electrical conductivity, and exceptional electrochemical capabilities, and a significant proportion of them have a layered, two-dimensional structure that increases their electrochemical properties. It is mostly used to refer to sulphides, selenides, tellurides, and polonides, the latter of which are typically semiconducting in nature, rather than other elements. (FeS₂, MoS₂, WS₂, MoSe₂, and WSe₂, NiS, etc.). Moreover, TMC has remarkable thermal stability and optical absorption properties because of its tuneable indirect bandgap energies, high absorption coefficients, and unique physiochemical properties that enable the catalysts to absorb visible light, which is abundant in solar radiation. The energy difference between the aligned Fermi levels of the QDs/semiconductor oxide layer and the electrolyte's redox potential is the essential working mechanism, and it is dependent on the driving force of electron circulation (H. Y. Chen et al., 2013).

Currently, despite significant advances to QDSSCs, the issue of device performance stability has not been successfully solved. The main challenge to QDSSCs devices being used on a large scale is their difficulty to maintain stability, which is hindering future development. Other issues such as intrinsic and component stabilities, containing photochemical stability of QDs, substrate type, adhesive material, electrocatalytic activity of CE material, sealing disability, and evaporation or volatilization of electrolytes, are the most challenging roadblocks to overcome in the future.

5.0 The Major reasons for QDSSCs instability

In the QDSSCs system, the stabilities are directly associated with the stabilities of various device components such as the type of QDs used, photoanode, electrolyte, and the electrocatalytic behaviour of the CE. Due to the different degradation mechanisms related to the different device components of QDSSCs. Many factors cause degradation to decrease the degradation it is not easy to estimate the processes that affect the performance stability of QDSSCs (Akash S. Rasal, Yadav, Kashale, Altaee, & Chang, 2022). CE has a significant impact on device performance stability. In long-term stability assessments, fast degradation or corrosion of electroactive CE materials causes device ageing, which affects CE material stability. The chemical reactivity of electroactive CE materials with the electrolytes to prevent corrosion by redox couple adsorption on the CE surface is called electrochemical stability, and the separation of the catalyst CE from the conductive substrate glass as a result of poor adhesion, causing mechanical detachment of the two separate chemicals to form that is called mechanical instability; finally, the back transfer of photoinduced electrons in QDSSCs operation, CE nanostructures and TiO₂ electrodes by redox couple electrolytes which in turn reduce the values of J_{sc} , V_{oc} , and FF, that is called charge recombination dynamics (Mastroianni et al., 2014; Yun, Lund, & Hinsch, 2015).

Luo et al., (2015) investigated FeS₂ nanocrystals (NCs)/polymer solid solar cells and QDSSCs with a liquid electrolyte and observed that FeS₂ NCs/polymer had high stability, with 83.3% of its initial PCE remaining after 105 days of exposure in air and quite stable performance between 20°C and 80°C using the light soaking test (Luo, Luan, Yuan, Zhang, & Jin, 2015). Hessein et al., (2016) and Hessein et al., (2017) reported in Cu_xS/rGO and CuS Nps, respectively, as CEs in QDSSCs exposed for a certain time under the light soaking test, then compared them with Pt CEs. Their results were good photostability, efficient performance, and a highly stable electrocatalytic activity for polysulfide electrolyte reduction owing to the synergistic effect between Cu_xS nanocrystals and conductive rGO sheets in the case of Cu_xS/rGO, and have high PCE values for each of them, while Pt CEs suffered from the dissociation of their thin film from the substrate by the action of the continuous reaction between the Pt and Cu₂S and the polysulfide electrolyte causes poisoning of the photoanode and results in severe degradation of the QDSSC device. as shown in Figure 5 (Hessein, Wang, Masai, Matsuda, & Abd El-Moneim, 2016, 2017).

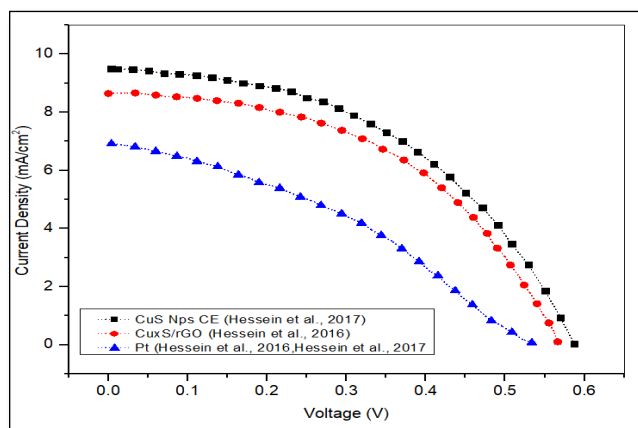


Figure 5 J–V characteristic curves between the fourth counter electrodes (Hessein et al. 2016, 2017).

In another type of TMC-based catalyst materials, a work done by Gopi et al., (2015) presented that NiS/PbS CE in QDSSCs had outstanding stability with no measurable degradation of the initial performance in the light soaking at room temperature under AM 1.5G illumination at 1000 W/m² for 600 min. After light soaking, the PV performance of the QDSSC significantly increases due to the improved penetration of the polysulfide electrolyte through the entire thickness of the electrode and the activation of the complete electrode. However, PbS CE has a too large value of R_{ct}

compared to the value of R_{ct} of metals sulfides and it has an unsatisfactory stability value due to the slow reduction reaction (Gopi, Venkata-Haritha, et al., 2015).

Several researchers investigated that Cu_2S CEs suffer from mechanical instability and uncertainty due to the reaction of copper and the electrolyte and pointed out that CoS may poison the surface of the photoelectrode thereby reducing total cell efficiency and stability of the system (Gopi, Venkata-Haritha, et al., 2015; Hessein et al., 2017; Hodes, Manassen, & Cahen, 1980). Furthermore, Cu ions are harmful to human health, and Cu is not very abundant. Several other researchers have reported that PbS demonstrated similar high electrocatalytic activity to CuS and CoS CEs and Cu_2S CE indicated superior activity and stability, but these CEs were not satisfactory due to their issues over long periods when utilized in conjunction with photoanodes (Gopi, Venkata-Haritha, et al., 2015; Hodes et al., 1980; Hwang & Yong, 2015; Radich, Dwyer, & Kamat, 2011). Meanwhile, Kim et al., (2014) reported that NiS is abundant and demonstrates superior PV performance compared to a CoS CE (Kim, Kim, et al., 2014).

In addition to the high energy conversion efficiency, the catalyst materials should also have good adhesion strength to the FTO substrate glass to support the stability of the solar cell device (Wu et al., 2017). Therefore, QDSSCs stability is affected by the delamination or detachment of CE catalyst films from FTO substrate glass resulting from poor adhesion at the interface of CE films and the substrate, where the separated CE catalyst particles reach the photoanode through the redox couple electrolyte, resulting in decreased PV parameters of J_{sc} , V_{oc} and FF. Kim et al., (2014) demonstrated good adhesion of NiS layers when the synthesis parameter was optimized at various temperatures and found the optimum synthesis temperature was between 80°C and 100°C. The deposition temperature of the NiS layer on FTO substrate glass above 100°C showed that NiS started to peel off from the FTO substrate due to its effect on morphology, particle size and thickness of CE (Kim, Yeo, et al., 2014). The degree of adhesion of the catalyst's material on FTO utilized as CE is the critical factor to determine the PCE of the QDSSCs. If the catalysts material of CE did not properly adhere to the FTO, it might be peeled off from the FTO substrate and fell into the electrolyte, thereby reducing the PCE of the QDSSCs (Punnoose, Kim, & Chung, 2015).

6.0 The strategies for improving the performance stability of QDSSCs

Researchers have proposed various good techniques to address the issue of poor performance stability, all of which have been utilised to reinforce device/enlarge and increase device stability, and then all of these have been combined to strengthen it, and these goals can be realized by these mentioned effective strategies such as (semiconductor quantum dots (QDs), redox electrolyte, counter electrodes materials).

6.1 Quantum Dots (QDs) Sensitiser

The semiconductor QD sensitizers include group II-VI (CdS, CdSe, CdTe) (Nideep, Ramya, & Kailasnath, 2020), III-V (InP, InAs) (Yu et al., 2006), IV-VI (PbS, PbSe) photosensitizers (Basit et al., 2017), and I-III-VI₂ QDs (CuInS₂, AgInS₂, CuInSe₂, and AgInSe₂) (G. Wang et al., 2017), QDs are used as photosensitizers, converting absorbed photons to excitons. They have several advantages, including size-tunable bandgaps, excellent photostability, a high absorption coefficient, a long carrier lifetime, a high dipole moment that defines how far into a material light of a specific wavelength can penetrate before it is absorbed, a long carrier lifetime, a large intrinsic dipole moment, and the ability to generate multiple excitons from a single photon which is called as multiple excitons generation (MEG) (Goodwin et al., 2018; Gopi, Srinivasa Rao, et al., 2015; Kim, Yeo, et al., 2014; Manjceevan & Bandara, 2018; Pan et al., 2018). Because of these excellent properties, they can achieve a theoretical efficiency of up to 44% beyond the Shockley-Queisser detailed limit of 33% for thin-film solar cells (Pawar et al., 2016), and considerably higher than its rival, dye-sensitized solar cells (DSSCs) with 31%, which has prompted researchers to focus more on QDSSCs as compared to DSSCs (Yeh et al., 2011). However, due to poor stability and corrosion resistance, QDSSCs' power conversion efficiency lags far behind that of DSSCs (Manjceevan & Bandara, 2018), also, most of the inorganic QDs utilized in QDSSCs suffer from stability issues in electrolytic conditions (Ghosh et al., 2021).

To improve the photochemical and thermal stability of light harvesting QDs, many techniques have been suggested, including surface treatment and internal alteration. The proposed solutions have already resulted in considerable improvements in the QDSSCs' performance and stability. Many effective methods have been developed up to now to resolve the issues with QDSSCs such as an optimal design of QD sensitizers to balance sunlight absorption and electron injection (Chang, Li, Chiang, Chen, & Li, 2016; Elibol, Elibol, Cadirci, & Tutkun, 2019; Liu, Chen, & Lee, 2016; Rahman et al., 2021), and achieving good sensor coverage by immobilizing pre-synthesised QDs on semiconductor oxides, (Alavi, Rahimi, Maleki, & Hosseini-Kharat, 2020; Y. Fu et al., 2017; Goodwin et al., 2018; Halder, Ghosh, Ali, Sahasrabudhe, & Bhattacharyya, 2018; Manjceevan & Bandara, 2018).

6.2 The electrolytes

An electrolyte is responsible for conducting electricity through the external circuit by transferring charges. It plays a vital role in the QDSSCs process, and an ideal electrolyte should have the following characteristics: a suitable redox potential to achieve high V_{oc} for devices, low photo-corrosion towards QD-sensitizers, high ion conductivity, suitable chemical stability towards QD-sensitizers, and capable of regenerating QDs throughout the QDSSCs process. The increased temperatures of the solar cells due to the device's internal heating influence the liquid electrolyte which leads to affects the device's overall performance. To solve this issue developed the electrolyte status which has three forms of electrolyte categories solid electrolytes, and quasi-solid-state electrolytes, addition to liquid electrolytes (Elibol, 2020; Luo et al., 2015; Patel & Gohel, 2019; A. S. Rasal et al., 2021). At present, an aqueous polysulfide electrolyte is often used in QDSSCs due to QDs are not stable in the conventional triiodide electrolyte.

6.3 The Counter electrode materials

The counter electrode is a critical component in QDSSCs due to its ability to catalyse the redox couple's reduction reaction. The significant characteristics of a CE material are non-precious, superior electrical conductivity, high catalytic activity, and stable stability. Although precious metal-based CEs have high activity, their high running costs are the primary drawbacks for commercial use. Another difficulty with Pt CE is that it is particularly sensitive to the redox electrolyte, which can affect not only their stability but also the stability of the overall PCE. For these reasons, looking at alternative Pt CEs for devices that are less expensive, effective, and durable can help not only improve device stability and cost-efficiency but also lower the entire cost of QDSSCs. Nonetheless, there are limited publications on the effect of Pt and Au on QDSSCs stability because S^{2-} species have been observed on the surface of Pt or Au, decimating device lifetime. As a result, a lot of work and effort has gone into producing CEs that are inexpensive, efficient, and stable in QDSSCs (Itzhaik, Niitsoo, Page, & Hodes, 2009). The combination of two or more different materials is one of the essentials methods to improve the issues of CE instability, for instance, Akman et al., (2020) observed that Cu_2S /single-layer graphene (SLG) nanocomposite CE on FTO in QDSSCs had high electrochemical stability by remaining the J_{sc} value 98%, compared with J_{sc} value of Cu_2S CE 85%, and higher mechanical stability than Cu_2S CE, due to the SLG framework which was critically important to protect the Cu_2S structure from S^{2-}/S_x^{2-} penetrating electrolyte and that led to an increase in the adhesion of the Cu_2S structure on the surface and accordingly (Akman et al., 2020), and adding reduce graphene oxide to any TMSs was observed that the electrocatalytic activity and stability, as well as mechanical stability, are enhanced further through the synergistic effects of highly catalytic TMSs compounds nanostructures and electrically conductive rGO (Hessein et al., 2016; Prakasam et al., 2020).

7.0 Challenges and Limitations

The performance of QDSSCs is limited by insufficient electrocatalytic activity and stability of counter electrodes, both of which are critical but lack research proof. Rasal et al., (2021) stated that there is no proportionality between the number of studies on QDSSC and the rising quantity of research on its stability (A. S. Rasal et al., 2021). The majority of the leading research laboratories have obtained power-to-conversion efficiencies of 15% or above (Song et al., 2021), but the study on the electrochemical and mechanical stability under high temperatures are issues that are found to be problematic for large-scale application of QDSSCs. This is confirmed by, (Yun et al., 2015) reported that data for CE stability evaluation was only obtained from the sole test in most cases, and not from multiple tests that can perform a systematic assessment. Indeed, the increase of research in CE development publications does not match the number of publications on the research on CE stability. As a result, the important knowledge for assessing CE stability in QDSSCs is still lacking, as each characterization technique has distinct advantages and disadvantages, and integrated assessment tests have not been performed in the majority of situations to assess CE stability (Yun & Lund, 2018).

Therefore, the development of these CE materials is driven mainly by overcoming the disadvantages of Pt, by being replaced by transition metal sulfides (TMS) which are forcefully considered emerging candidates, owing to their unique physical and chemical properties. Owing to their non-precious, excellent electrochemical activity as well as mechanical and thermal stability, transition metal sulfides have exhibited promising potential. QDSSCs fabricated with TMS CEs, such as Cu_2S (Krishna Prasad, Jo, Kang, & Ahn, 2021), PbS (Gopi, Bae, et al., 2015), NiS (Gopi, Srinivasa Rao, et al., 2015), CoS (Reddy et al., 2017), FeS (R. & Balakrishna, 2019) demonstrated remarkable improvement in the PV operation. However, some researchers investigated that Cu_2S and CoS CEs suffer from mechanical instability and uncertainty due to the reaction of copper and the electrolyte that lead to poisoning the

surface of the photoelectrode (Hodes et al., 1980; Zeng, Chen, Wang, & Jin, 2015). Therefore, the development of these CE materials is driven by replacing some TMS CEs to overcome the disadvantages of these CEs and integrate them with conductive graphene hosts has enabled the significant improvement of the electrochemical performance of devices among the materials studied for energy generation applications.

The stability of the catalyst materials deposited on the CE in QDSSCs consists of electrochemical stability and mechanical stability. CE is among the most critical factors that define the device its efficient performance, especially for non-precious metals and their alloys. In the mechanical design aspect, enhancement of CE catalyst stability can be achieved directly by strong adhesion of the catalytic material layer to the conducting substrate which is the electrode. The study of temperature stability of CE is important since solar cells are exposed to the outdoor temperature, which will influence the energy conversion efficiency.

8.0 Conclusion and Future Perspective

Numerous research publications have been published on the general stability of QDSSCs, but little is understood about the physical and chemical events that cause cell degeneration, or their relationship to the levels of stress that cause the damage. Generally, stability investigation articles evaluate the time-dependent current density-voltage (J-V) characteristics of devices at ambient temperature or in an inert atmosphere. Therefore, to make major advancements in QDSSCs will need rational techniques to raise cell device J_{sc} , V_{oc} and FF values.

Some publications analyse stability impact using chemical or spectroscopic techniques, providing experimental evidence of chemical changes or molecular alterations, whereas most simply measure chemical parameters. In addition, most research reported only the affirmative stability data, while unfavourable results are rarely disclosed to expedite publication. As a result, to improve QDSSCs' overall stability, all degradation processes and mechanisms must be studied and explored. The most crucial part of carrying out the QDSSCs experiment expansion is providing physical and chemical information for QDSSCs techniques to analyse the tested material.

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