



ADVANCED SOLAR CELL TECHNOLOGY: AN UP TO DATE REVIEW

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ABSTRACT

Generation of clean energy is one of the main challenges of the 21st century. Solar energy is the most abundantly available renewable energy source which could be supplying more than 50% of the global electricity demand in 2100. Solar cells are used to convert light energy into electrical energy directly with an appeal that it does not generate any harmful bi-products, like greenhouse gasses. The manufacturing of solar cells is actually based on the types of semiconducting or non-semiconducting materials used and commercial maturity. From the very beginning of the terrestrial use of Solar Cells, efficiency and costs are the main focusing areas of research. The definition of so-called advanced technologies sometimes described as including any technology capable of overcoming the Shockley–Queisser limit of power conversion efficiency (33.7%) for a single junction device. In this paper, some prominent solar cells technologies, their structural morphology, electrical and optical properties are elaborately discussed. The excellent state of the art technology, advantages and potential research issues yet to be explored are also pointed out.

Keywords: Solar Cells, Silicon, Thin film, organic, Efficiency, Perovskite, DSSC, CZTS Quantum Dots.

INTRODUCTION

Based on different technologies and materials, the solar cells can be grouped into three different generations. First generation or c-Si solar cells are most dominant PV technology even today for their good performance and better stability; typically demonstrate efficiency about 22%. However, rigidity, complex manufacturing processes and high costs still remains as bottleneck. The second generation or thin film solar cells demonstrate typical efficiency in 10-15%. Although the efficiency is less than the c-Si solar cells, but the cost effectiveness makes it an attractive alternative.

The third generation solar cells employ the most advanced techniques which is basically thin film based too, but the varieties of materials used to manufacture such cells introduces a new era of cell design. These cells are made of semiconducting p-n junctions ("first generation") and thin film cells ("second generation"). Common third-generation system techniques include multi-layer ("tandem") cells made of amorphous silicon or III-V compounds like gallium arsenide, frequency up down conversion, Intermediate band, hot-carrier effects and other multiple-carrier ejection techniques. [1][2][3][4]

In the most advanced PV technology, a wide range of materials, ranging from semiconducting, non-semiconducting, different polymers and even organic are incorporated which actually broadens the choice of materials to manufacture solar cell devices. Not only materials aspect, but also the uses of cutting edge technologies like tandem design of cells, Intermediate band concept, Hot carrier cell, Hybridization of both inorganic and organic materials shows a lots of promises in designing such cells.

Some examples of such cell design includes

- Perovskite solar cell
- Copper Zinc Tin Sulfide solar cell (CZTS), and derivatives CZTSe and CZTSSe
- Dye-Sensitized Solar Cell(DSSC), also known as "Grätzel cell"
- Quantum Dots Solar Cell

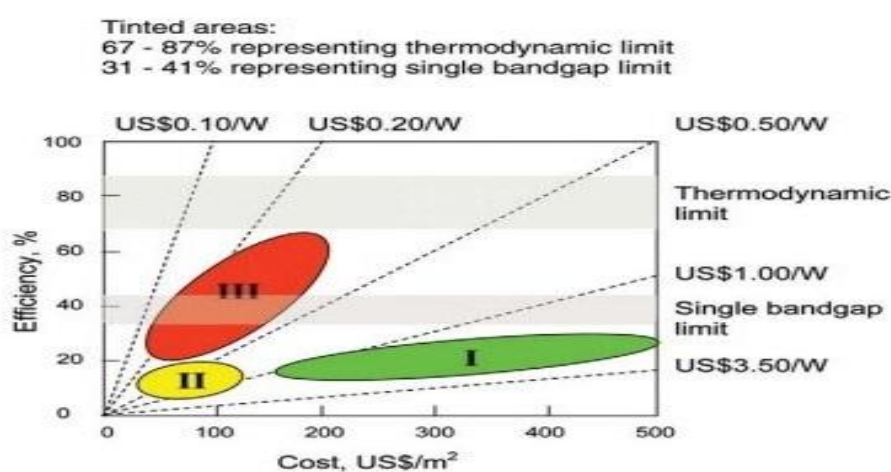


Figure-1 Efficiency and cost projections for first- (I), second- (II), and third generation (III) PV technologies (wafer-based, thin films, and advanced thin films, respectively)

Perovskite Solar Cell

A perovskite solar cell is a type of solar cell which includes a perovskite structured compound, most commonly a hybrid organic-inorganic lead or tin halide-based material, as the light-harvesting active layer. [5]

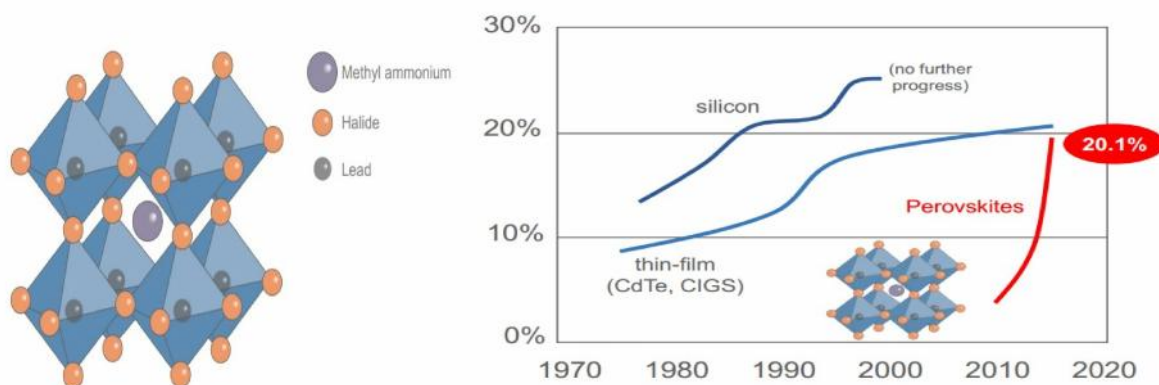


Figure-2 (a) Typical Perovskite Solar Absorber material **(b)** record breaking conversion efficiency scale

The efficiency has significantly rises from 3/8% in 2009[6] to 21.0% in 2015[7] by using methyl-ammonium lead halides ($\text{CH}_3\text{NH}_3\text{PbX}_3$) materials as absorber layer which are cheap and simple to manufacture. With the potential of achieving even higher efficiencies and the very low production costs, perovskite solar cells have become commercially attractive, with start-up companies already promising modules on the market by 2017. [8,9]

Traditional silicon cells require expensive, multistep processes, conducted at high temperatures ($>1000^\circ\text{C}$) in a high vacuum in special clean room facilities. [10] Meanwhile the organic-inorganic perovskite material can be manufactured with simpler wet chemistry techniques in a traditional lab environment.

Perovskite Solar Cell Materials, Structure and operating principles

The most commonly studied perovskite absorber is methylammonium lead trihalide ($\text{CH}_3\text{NH}_3\text{PbX}_3$, where X is a halogen atom such as iodine, bromine or chlorine), with an optical bandgap between 1.5 and 2.3 eV depending on halide content. So by introducing bandgap tailoring, the optical properties of this material can be optimized.

Incoming radiation from the sun is absorbed by the Halide perovskite which is integrated with mesoporous TiO_2 thin film. Electrons generated due to light absorption gets excited and move to the conduction band of perovskite and then jumps to the conduction band of TiO_2 and collected at the electrode. This missing electrons are replenished by a HTM (Hole Transport Material) mechanism.

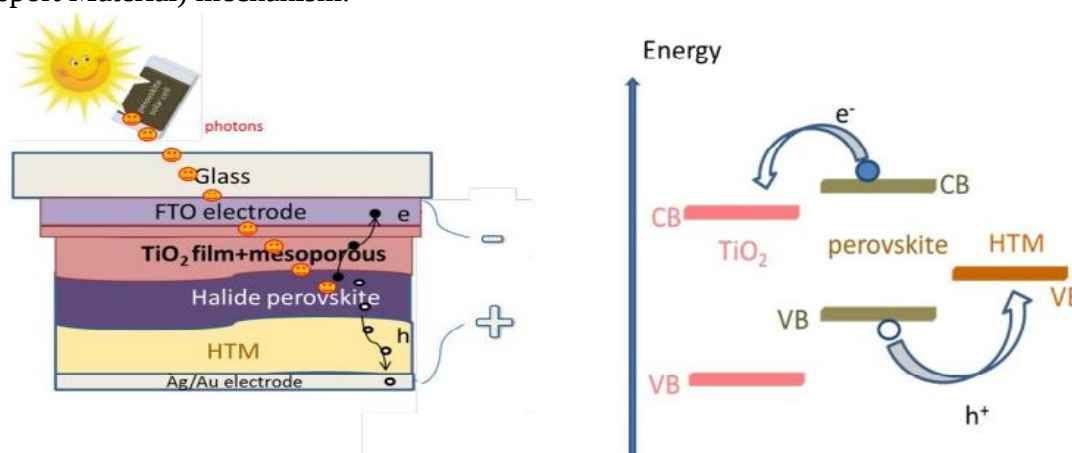


Figure-3 Perovskite Solar Cell structure and basic working procedure

There are some very prominent features which makes perovskite solar cell as one of the best emerging PV technologies, which includes-

- Simple manufacturing process (as compared to the dominant Si based PV technology) [11]
- Bandgap modification by changing the Halide components as well as their proportion. [12]
- Perovskite materials have very low recombination rate. So display a long diffusion length for both holes and electrons of over one micron [13,14]. The long diffusion length means that these materials can function effectively in a thin-film architecture, and that

charges can be transported in the perovskite itself over long distances.

- It has recently been reported that charges in the perovskite material are predominantly present as free electrons and holes, rather than as bound excitons, since the exciton binding energy is low enough to enable charge separation at room temperature.[15]

Although perovskite Solar Cells exhibiting higher conversion efficiency with relatively low costs, but there are some areas which need to be mastered -

The prime challenges for perovskite solar cells are inclusion of lead which is detrimental to the device performance and the aspect of short-term and long-term stability. The water-solubility of the organic constituent of the absorber material make devices highly prone to rapid degradation in moist environments.^[16] However, no long term studies and comprehensive encapsulation techniques have yet been demonstrated for perovskite solar cells.

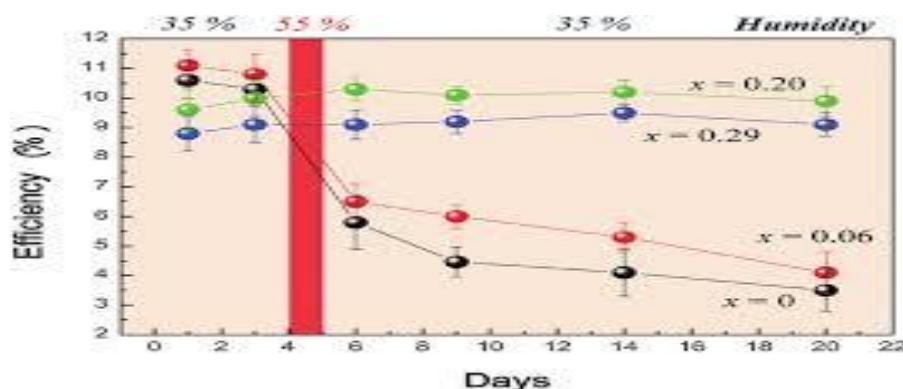


Figure -4 Stability problems of perovskite solar cell under different humid conditions

Beside moisture instability, it has some other constructional issues need to be addressed. Which includes -

- Protective Glass - transparent but not flexible, so it can't be applicable to BIPV type applications.
- ITO/FTO electrode - In and Sn are deficient materials. In is basically used for display purpose and F is harmful for environment and human health.
- TiO₂ layers – Acts as electron transporter but, may exist better electrons transporter materials.
- Holes transporter (HTM): It is not stable in ambient atmosphere

Perovskite-Si Tandem Cell Design

Perovskite cells showing record efficiency beyond 20%, not only efficient but also have a high and tunable bandgap, cheap fabricating techniques makes it suitable for application in tandem devices.

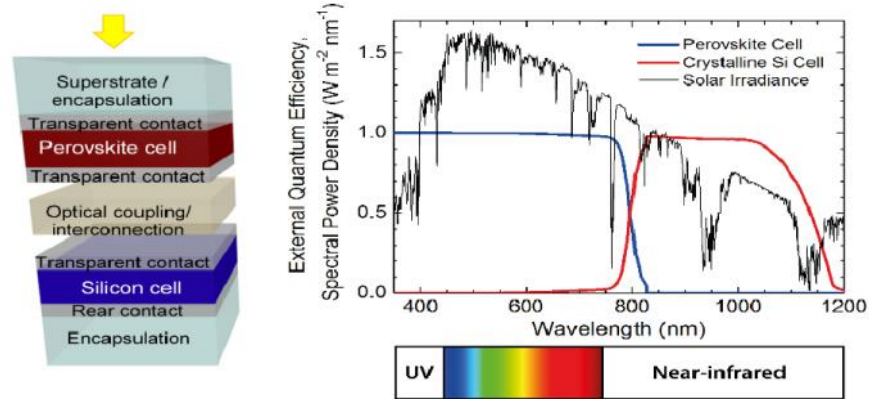


Figure- 5 Perovskite-Si tandem structure and spectral response

As this silicon cell efficiency record is already very close to the practical efficiency limit of this type of solar cells, perovskite/silicon tandem cells with their potential for ultra-high efficiencies at affordable costs represent the most straight forward way to decrease the overall cost of photovoltaic systems and consequently also to reduce the price of electricity for end-users.

CZTS (Copper Zinc Tin Sulfide) Solar Cell

Copper-zinc-tin-sulfur CZTS-based technology uses materials that avoid heavy metals, earth abundant and also at a lower cost. The constituents of this semiconductor material copper(Cu), zinc(Zn), tin(Sn) and sulfur(S), have the advantages of being both abundant in the earth's crust and non-toxic.

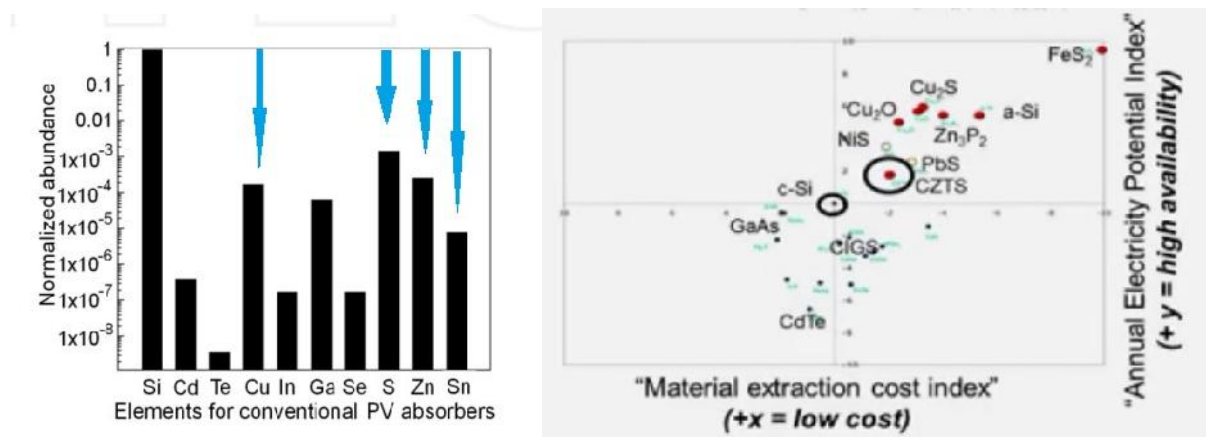


Figure – 6 (a) Normalized abundance of some common PV absorber materials **(b)** Cost Vs Availability curve of the most used solar cell manufacturing materials along with CZTS.

CZTS also has near ideal properties for solar photovoltaics, as it is a very strong absorber and has a band gap of around 1.4eV. IBM has an active research department in this area and recently announced a CZTS based solar cell that had a conversion efficiency of 11.1% and could potentially be printed. [17] This efficiency is lower than the equivalent laboratory records of 19.6% for CIGS and 17.3% for CdTe, however CZTS is at a much earlier stage of development. [18]

Some key factors make the IBM solar cells become a viable alternative to existing "thin film" solar cells. These includes –

Firstly – It uses rather earth abundant, Nontoxic elements as the constituents. It is well known that in case of CdTe based cell, Tellurium are extremely rare, and Cd is toxic. And in case of CIGS, Indium and Gallium are rare and most widely used in displays.

Secondly- An inexpensive ink-based manufacturing process. According to a study done by IBM, thin film solar cells will likely be limited to producing about 0.3 terawatts, but the new cells from IBM could produce an order of magnitude more power. [19]

CZTS has numerous advantages that could lead to its massive use as an abundant, non-toxic, low cost absorber for thin film photovoltaic solar cells –

- it is a compound whose intrinsic point defects lead to p-type semiconductor behavior. Although such intrinsic point defects levels lead to low charge separation, which can be overcome by thanks to the type-II band alignment of the CZTS/CdS interface. Incorporation of CdS buffer layer provide excellent band offset and also improves the efficiency a bit. [20]
- it has a direct bandgap and an absorption coefficient $>10^4 \text{ cm}^{-1}$, which is suitable for thin film photovoltaics applications [21–23];
- Band gap of the CZTS thin film can be modified from 0.94 to 1.6 eV by changing the zinc and tin composition and replacing the selenium (Se) by sulfur (S). CZTS belongs to the Kesterite structure and composed of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) and CZTSSe are the competitors to the CIGS and CdTe based thin film solar cells. This tunability is of particular interest for the manufacturing of absorbers with a band gap between 1.1 and 1.5 eV, which allow theoretical efficiencies higher than 30% [24]
- It includes Zn and Sn which are respectively produced in quantity 20 000 and 500 times bigger than In which is one of the constituents materials of CIGS and moreover Indium is used for display devices. [25]
- As CZTS solar cells use the same structural morphology as CIGS, so the knowledge gathered on back contact, buffer layers and window layer by CIGS scientists can therefore be used and adapted for CZTS solar cells.

Potential research issues for CZTS Solar Cells

There are still numerous hurdles that must be overcome before a truly competitive kesterite technology can be validated [26]:

- Necessary to reach 15% efficiency, on par with CdTe and CIGS technologies.
- Difficulty in growth of pure kesterite phase without secondary phases and stannite structure, which are particularly hard to be detected.
- Optimization of interfaces which is found to be an important factor limiting device performance. As stated CdS interface with CZTS absorber layer shows excellent band offset, but the incorporation of Cd is not welcome everywhere. Because Cd is one of the six

toxic material which hinders both environmental and human health acceptance. There are some other potential interfacial materials like ZnS, In_2Sn_3 , ZnSe, $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ etc., which have their own merits and demerits and performance of the cell largely depends on this.

- The long term stability under heat, light, moisture should be confirmed and compared with its sister competitors like CdTe and CIGS.
- A truly low-cost and high throughput approach needs to be established, without sacrificing on performance, in order to meet a $< \$1\text{Wp}$ price target.
- Overall, the proper fabrication process of CZTS, composition of different elements, Grain boundary, surface quality controlling is yet to be explored.

Dye Sensitized Solar Cell

Dye Sensitized Solar Cells (DSSCs) are placed in the category of third generation photovoltaics (PV) where new trends in the photovoltaic technology are applied. Among the different possibilities of 3rd generation solar cells DSSC have the most promising prospect due to some attractive features, such as, simpler conventional roll-printing manufacturing techniques, semi-flexible and semi-transparent structure, which offers some versatile applicable areas to glass-based systems, especially in Building Integrated PV(BIPV), and most importantly, the materials used are low-cost. The overall efficiency of $\sim 12\%$ (for laboratory small size) placed DSSCs as potential inexpensive alternatives to solid state devices [27].

It is based on a semiconductor formed between a photo-sensitized anode and an electrolyte, a photo electro chemical system. A modern DSSC is composed of a porous layer of titanium dioxide nano particles, covered with a molecular dye that absorbs sunlight. The titanium dioxide which acts like an anode is immersed under an electrolyte solution, above which is a platinum-based catalyst which acts like a cathode.

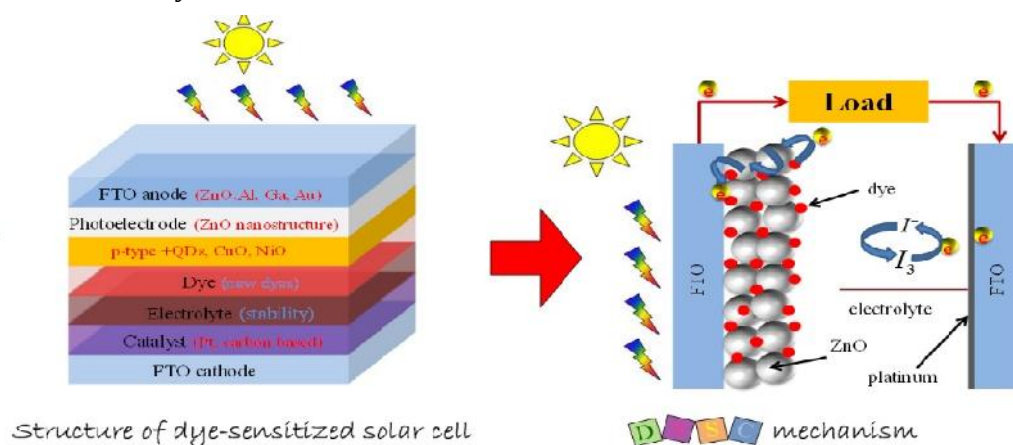


Figure-7DSSC sample structures and working mechanisms

Sunlight passes through the transparent electrode into the dye layer where it can excite electrons that then flow into the titanium dioxide. The electrons flow toward the transparent electrode where they are collected for powering a load. After flowing through the external circuit, they are re-introduced into the cell on a metal electrode on the back, flowing into the

electrolyte. The electrolyte then transports the electrons back to the dye molecules.

There are lots of potential advantages of DSSC, which are -

- DSSCs are attractive as a replacement for existing technologies in "low density" applications like rooftop solar collectors, where the mechanical robustness and light weight of the glass-less collector is a major advantage.
- In quantum efficiency terms, DSSCs are extremely efficient. Due to their "depth" in the nanostructure there is a very high chance that a photon will be absorbed, and the dyes are very effective at converting them to electrons. The quantum efficiency of traditional designs varies, depending on their thickness, but are about the same as the DSSC.
- Differential kinetics of electron transfer from the Dye to TiO_2 provides an extra advantage in case of DSSC. The rate of electron generation from the Dye is very fast and the recombination of the generated electron back to dye is rather very slow process. So as a consequence of this, DSSCs work even in low-light conditions. DSSCs are therefore able to work under cloudy skies and non-direct sunlight, whereas traditional designs would suffer a "cutout" at some lower limit of illumination, when charge carrier mobility is low and recombination becomes a major issue. The cutoff is so low they are even being proposed for indoor use, collecting energy for small devices from the lights in the house. [28]
- Temperature hardness is a very remarkable advantage of the DSSC, which means its performance is remarkably insensitive to temperature change. Thus, raising the temperature from 20 to 60 °C has no effect on the power conversion efficiency. Stability studies have shown the DSSC sustain temperatures of 85 °C without loss of performance.
- A practical advantage, one DSSCs share with most thin-film technologies, is that the cell's mechanical robustness indirectly leads to higher efficiencies in higher temperatures. DSSCs are normally built with only a thin layer of conductive plastic on the front layer, allowing them to radiate away heat much easier, and therefore operate at lower internal temperatures.

Although the DSSC exhibits lots of promises, but there are still some drawbacks of such cells which requires more to explore –

- The major research issue of DSSC design is the use of the liquid electrolyte. This liquid has temperature stability problems. At low temperatures the electrolyte can freeze, ending power production and potentially leading to physical damage. Higher temperatures cause the liquid to expand, making sealing the panels a serious problem.
- In practice it has proven difficult to eliminate a number of expensive materials, notably platinum and ruthenium, and the liquid electrolyte presents a serious challenge to making a cell suitable for use in all weather.
- The dye molecules are quite small (nanometer sized), so in order to capture a reasonable amount of the incoming light the layer of dye molecules needs to be made fairly thick, much thicker than the molecules themselves.
- The instability of the dye solar cell was identified as a main challenge. Its efficiency however, improved during the course of the time by optimizing the porosity, but the

instability remained a problem. [29]

- A third major drawback is that the electrolyte solution contains volatile organic compounds (or VOC's), solvents which must be carefully sealed as they are hazardous to human health and the environment. This, along with the fact that the solvents permeate plastics, has precluded large-scale outdoor application and integration into flexible structure. [30]
- Replacing the liquid electrolyte with a solid has been a major ongoing field of research. Recent experiments using solidified melted salts have shown some promise, but currently suffer from higher degradation during continued operation, and are not flexible. [31]
- Most of the small losses that do exist in DSSC's are due to conduction losses in the TiO_2 and the clear electrode, or optical losses in the front electrode.
- For the future improvement of the conversion efficiency, understanding and control of interfacial effects are essential, as such type of cells have high contact area of the junction.
- It is important to determine the nature of the exposed surface planes of the oxide and the mode of interaction with the dye. [32]
- At this stage the confirmed efficiency obtained with the black dye is 10.4% [33].

Further development will concentrate on the enhancement of the photo response in the near IR region. The goal is to obtain a DYSC having optical features similar to GaAs. A nearly vertical rise of the photocurrent close to the 920 nm absorption threshold would increase the short circuit photocurrent from currently 20.5 to about 28 mA/cm². With the V_{oc} and FF values would raise the overall efficiency to 14.2%. [34]

Quantum Dots Solar Cells

A quantum dot solar cell is a solar cell design that employs quantum dots as the main absorbing material. It attempts to replace bulk materials such as silicon, copper indium gallium selenide (CIGS) or CdTe. Quantum dots have band-gaps that are tunable across a wide range of energy levels by changing the dots' size. In bulk materials the band-gap is fixed by the choice of material(s). This property makes quantum dots attractive for multi-junction solar cells, where a variety of materials are used to improve efficiency by harvesting multiple portions of the solar spectrum. As of 2014 efficiency ranges from 7.0% [35] to 8.7% [36]

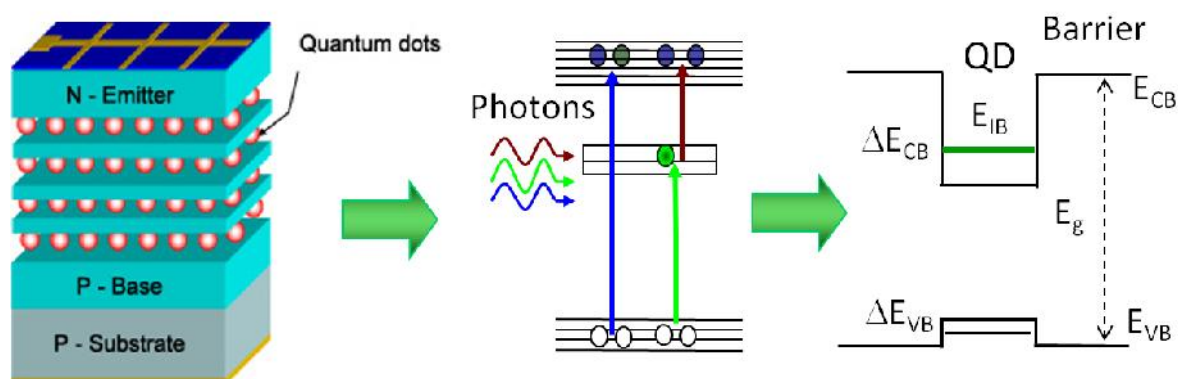


Figure-8 Basic structure of High Efficiency Quantum Dot Solar Cells and its band diagram

Near-infrared PbS quantum dots (QDs) composed of earth-abundant elements [37] have emerged as promising candidates for photovoltaic applications because of a tunable energy bandgap that covers the optimal bandgap range for single and multi-junction solar cells [38] Half of the solar energy reaching the Earth is in the infrared, most in the near infrared region. A quantum dot solar cell makes infrared energy as accessible as any other.

The energy levels are tunable by changing their size, which in turn defines the band-gap. The dots can be grown over a range of sizes, allowing them to express a variety of band-gaps without changing the underlying material or construction techniques.[39] In typical wet chemistry preparations, the tuning is accomplished by varying the synthesis duration or temperature.

Moreover, CQDs offer easy synthesis and preparation. While suspended in a colloidal liquid form they can be easily handled throughout production, with a fumehood as the most complex equipment needed. CQDs are typically synthesized in small batches, but can be mass-produced. The dots can be distributed on a substrate by spin coating, either by hand or in an automated process. Large-scale production could use spray-on or roll-printing systems, dramatically reducing module construction costs.

Although the traditional way to fabricate CQDs is costly MBE technique, but most cost effective techniques are developed later. These use wet chemistry (colloidal quantum dots – CQDs) and subsequent solution processing. Concentrated nanoparticle solutions are stabilized by long hydrocarbon ligands that keep the nano-crystals suspended in solution.

A more recent study uses different ligands for different functions by tuning their relative band alignment to improve the performance to 8.6%.[40] The cells were solution-processed in air at room-temperature and exhibited air-stability for more than 150 days without encapsulation.

There are many potential benefits over the existing solar cell technologies are obtained by using Quantum Dot Cells, which are –

- Using quantum dots as an alternative to molecular dyes was considered from the earliest days of DSSC research. The ability to tune the bandgap allowed the designer to select a wider variety of materials for other portions of the cell. Collaborating groups from the University of Toronto and École Polytechnique Fédérale de Lausanne developed a design based on a rear electrode directly in contact with a film of quantum dots, eliminating the electrolyte and forming a depleted heterojunction. These cells reached 7.0% efficiency, better than the best solid-state DSSC devices, but below those based on liquid electrolytes.[41]
- Cadmium telluride (CdTe) is used for cells that absorb multiple frequencies. A colloidal suspension of these crystals is spin-cast onto a substrate such as a thin glass slide, potted in a conductive polymer. These cells did not use quantum dots, but shared features with them, such as spin-casting and the use of a thin film conductor. At low production scales quantum dots are more expensive than mass-produced nanocrystals, but cadmium and

telluride are rare and highly toxic metals subject to price swings.

- In 2014 a University of Toronto group manufactured and demonstrated a type of CQD n-type cell using PbS with special treatment so that it doesn't bind with oxygen. The cell achieved 8% efficiency, just shy of the current QD efficiency record. Such cells create the possibility of uncoated "spray-on" cells. [42] [43] However, these air-stable n-type CQD were actually fabricated in an oxygen-free environment.

CONCLUSION

A solar cell can be termed as “promising” if the cell can be manufactured by using the cheapest as well as most abundant materials without sacrificing energy-production efficiency. All the solar cell design discussed here have the same goal. Perovskite cells have received tremendous attention in the public, as their research efficiencies recently soared above 20%. They also offer a wide spectrum of low-cost applications. [44-46] Concerns with the price and availability of indium in CIGS and tellurium in CdTe, as well as toxicity of cadmium have been a large motivator to search for alternative thin film solar cell materials, CZTS as it is composed of earth abundant and non-toxic elements, it can outperform CIGS or CdTe based thin film cells. CZTS have increased efficiency to 12.0% in laboratory cells, but more work is needed for their commercialization. [47] Though the DSSC shows a lots of attractive features, it has proven difficult to eliminate a number of expensive materials, notably platinum and ruthenium, and the liquid electrolyte presents a serious challenge to making a cell suitable for use in all weather. Although its conversion efficiency is less than the best thin-film cells, in theory its price/performance ratio should be good enough to allow them to compete with fossil fuel electrical generation by achieving grid parity. [48]

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