

PEROVSKITE BASED SOLAR CELLS- AN INTRODUCTION

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1 Abstract

Energy conversion has been one of the main themes for researchers for the past few decades. Among the various options, employing solar energy and convert it into electricity has been facinating and the device is called soolar cells or photovootaic devices. This device has seen many developments in the last fifty years starting from silicon based solar cells [1]. For various reasons. altermate materials have been considered from cost and processing points of view and in the last decade peroskite based materials (both organic, inorganic and hybrid) have shown promise to give efficiencies almost comparable to silicon based solar cells, but the stability and other aspects have to be improved. The developments in this field is enormous and it is time the current situation is assessed well for possible exploitation of this device in future. In this brief presentation, it has been attempted to trace the history of this remarkable development and also to examine the challenges that have to be considered like lead poison, stability of the materials under various atmospheres and other aspects. It is hoped that thiw write-up will be useful for those who wish to acquaint himself to this field.

2 Introduction

In recent times, there is considerable activity in improving and achieving maximum derivable efficiency from energy conversion devices. This is reflected from the activities on various kinds of batteries and also the anxiety to make viable a fuel cell which was threatening to be a viable device for over 100 years. The main reasons for this fervent activity is the anxiety to make these devices more robust and also make them cost effective solar cells. In the last few decades, research in solar cells have picked up momentum and also to replace silicon based solar cells by other cost effective optional materials. A solar cell, **also known as a photovoltaic cell (PV cell)**, is an electronic device that converts the energy of light (radiation) directly into electricity through the photovoltaic effect. It is a form of photoelectric cell whose electrical characteristics vary when exposed to light. Solar cell as it is known today is a simple amd compact device consisting of light absorbing material, a current collector and counter electrode. Last few years, many methodologies such as solar architecture, solar heating, artificial-photosynthesis, photo-voltaics, photo-catalytic water-splitting, and so on have been established to harness solar-energy. Amongst these alternate possibilities, photovoltaics have gained attention which uses solar-energy and converts sun light into electricity via photovoltaic effect. At this stage it is better a compact design of a typical solar cell is introduced and such a design (schematic) in shown in Fig.1.

Solar cells work by utilizing the photovoltaic effect, which is the process of converting light energy into electricity. When sunlight hits the solar cell, photons are absorbed by the semiconductor material, causing electrons to be elevated in energy. These electrons then flow through the material, creating an electric current. This current can be harnessed and used to power electrical devices or stored in batteries for later use.

There are several different types of solar cells, each with its own unique characteristics and applications. The most common type of solar cell is the crystalline silicon cell, which is made of silicon wafers and is

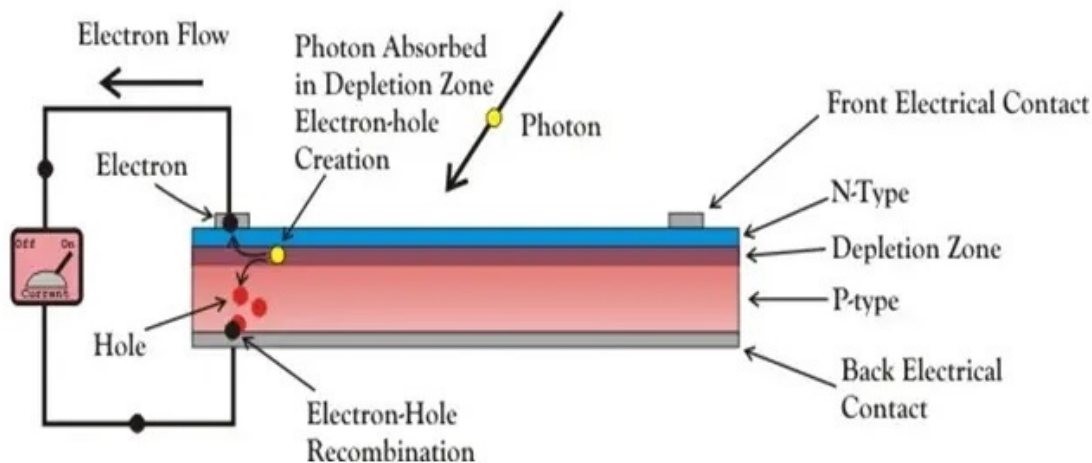


Figure 1: A simplified scheme for the production of Hydrogen

highly efficient at converting sunlight into electricity. Other types of solar cells include thin-film solar cells, which are made of thin layers of semiconductor materials, and organic solar cells, which are made of organic molecules.

Another strategy to improve PV cell efficiency is layering multiple semiconductors to make multi-junction solar cells. These cells are essentially stacks of different semiconductor materials, as opposed to single-junction cells, which have only one semiconductor. Each layer has a different band gap, so they each absorb a different part of the solar spectrum, making greater use of sunlight than single-junction cells. Multi-junction solar cells can reach record efficiency levels because the light that does not get absorbed by the first semiconductor layer is captured by a layer beneath it. While all solar cells with more than one band gap are multi-junction solar cells, a solar cell with exactly two band gaps is called a tandem solar cell. Multi-junction solar cells that combine semiconductors from columns III and V in the periodic table are called multi-junction III-V solar cells. Multi-junction solar cells have demonstrated efficiencies higher than 45%, but they are costly and difficult to manufacture, so they are reserved for space exploration. The military is using III-V solar cells in drones, and researchers are exploring other uses for them where high efficiency is key. Solar cells offer numerous advantages over traditional forms of energy conversion. One of the main advantages of solar cells is that they produce clean, renewable energy without emitting so called harmful greenhouse gases. Solar cells also have low operating costs and require minimal maintenance, making them a cost-effective and sustainable energy solution.

Despite their many advantages, solar cells also have some disadvantages. One of the main drawbacks of solar cells is their high initial cost, which can be a barrier to widespread adoption. Additionally, solar cells are dependent on sunlight, so they may not be as effective in areas with limited sunlight or during cloudy days. Solar cells also require a large amount of space to generate significant amounts of electricity, which can be a challenge in urban areas with limited space.

Silicon is, by far, the most common semiconductor material used in solar cells, representing approximately 95% of the modules sold today. It is also the second most abundant material on Earth (after oxygen) and the most common semiconductor used in computer chips. Crystalline silicon cells are made of silicon atoms connected to one another to form a crystal lattice. This lattice provides an organized structure that makes conversion of light into electricity more efficient.

Solar cells made out of silicon currently provide a combination of high efficiency, low cost, and long lifetime. Modules are expected to last for 25 years or more, still producing more than 80% of their original

power after this time.

A thin-film solar cell is made by depositing one or more thin layers of PV material on a supporting material such as glass, plastic, or metal. There are two main types of thin-film PV semiconductors on the market today: cadmium telluride (CdTe) and copper indium gallium diselenide (CIGS). Both materials can be deposited directly onto either the front or back of the module surface.

CdTe is the second-most common PV material after silicon, and CdTe cells can be made using low-cost manufacturing processes. While this makes them a cost-effective alternative, their efficiencies still are not quite as high as silicon. CIGS cells have optimal properties for a PV material and high efficiencies in the laboratory, but the complexity involved in combining four elements makes the transition from laboratory to manufacturing more challenging. Both CdTe and CIGS require more protection than silicon to enable long-lasting operation outdoors.

Perovskite solar cells are a type of thin-film cell and are named after their characteristic crystal structure. Perovskite cells are built with layers of materials that are printed, coated, or vacuum-deposited onto an underlying support layer, known as the substrate. They are typically easy to assemble and can reach efficiencies similar to crystalline silicon. In the laboratory, perovskite solar cell efficiencies have improved faster than any other PV material, from 3% in 2009 to over 25% in 2020. To be commercially viable, perovskite PV cells have to become stable enough to survive 20 years outdoors, so researchers are working on making them more durable and developing large-scale, low-cost manufacturing techniques.

Organic PV (OPV) cells are composed of carbon-rich (organic) compounds and can be tailored to enhance a specific function of the PV cell, such as band gap, transparency, or color. OPV cells are currently only about half as efficient as crystalline silicon cells and have shorter operating lifetimes, but could be less expensive to manufacture in high volumes. They can also be applied to a variety of supporting materials, such as flexible plastic, making OPV able to serve a wide variety of uses.

Quantum dot solar cells conduct electricity through tiny particles of different semiconductor materials just a few nanometers wide, called quantum dots. Quantum dots provide a new way to process semiconductor materials, but it is difficult to create an electrical connection between them, so they are currently not very efficient. However, they are easy to make into solar cells. They can be deposited onto a substrate using a spin-coat method, a spray, or roll-to-roll printers like the ones used to print newspapers. Quantum dots come in various sizes and their band gap is customizable, enabling them to collect light that's difficult to capture and to be paired with other semiconductors, like perovskites, to optimize the performance of a multi-junction solar cell. Having seen the fundamentals of solar cells, let us turn our attention to perovskite materials and look at the prospects a little closely.

3 Perovskite Solar cells

Photovoltaic performance of the perovskite solar cells is ascribed from their intrinsic properties like high absorption length, ambipolar carrier – transportability and carrier mobility. Especially, organic – inorganic hybrid – perovskite (OHIP) materials are the favorable candidates for establishing efficient and cost – effective solar – cells. In 1990s, Mitzi and coworkers first demonstrated the OHIP material for light emitting diode and transistor applications. The general formula is $(ABX)_3$, where A belongs to organic-cation group like methylammonium, formamidinium B belongs to inorganic cation group like Sn^{2+} , Pb^{4+} and X stands for halide ions such as I, Cl, Br. Further, in comparison with inorganic hybrid perovskites exhibit unique optical and electrical properties. In addition, these OHIP materials consist of an electron-transport layer (ETL) and a hole-transport layer (HTL). When the perovskite – absorber is subjected to light, it in series type and p – type carrier – transporting materials in order to generate free charge carriers. The generated electrons are transported by the ETL to the cathode, while the holes are transported by the HTL to the anode. Accordingly, the hole extraction is in the opposite direction. Finally, recombines with the electron and provides the current. The current generation depends on the energy levels and charge – transfer process of perovskite solar cells are shown in Fig. 2.

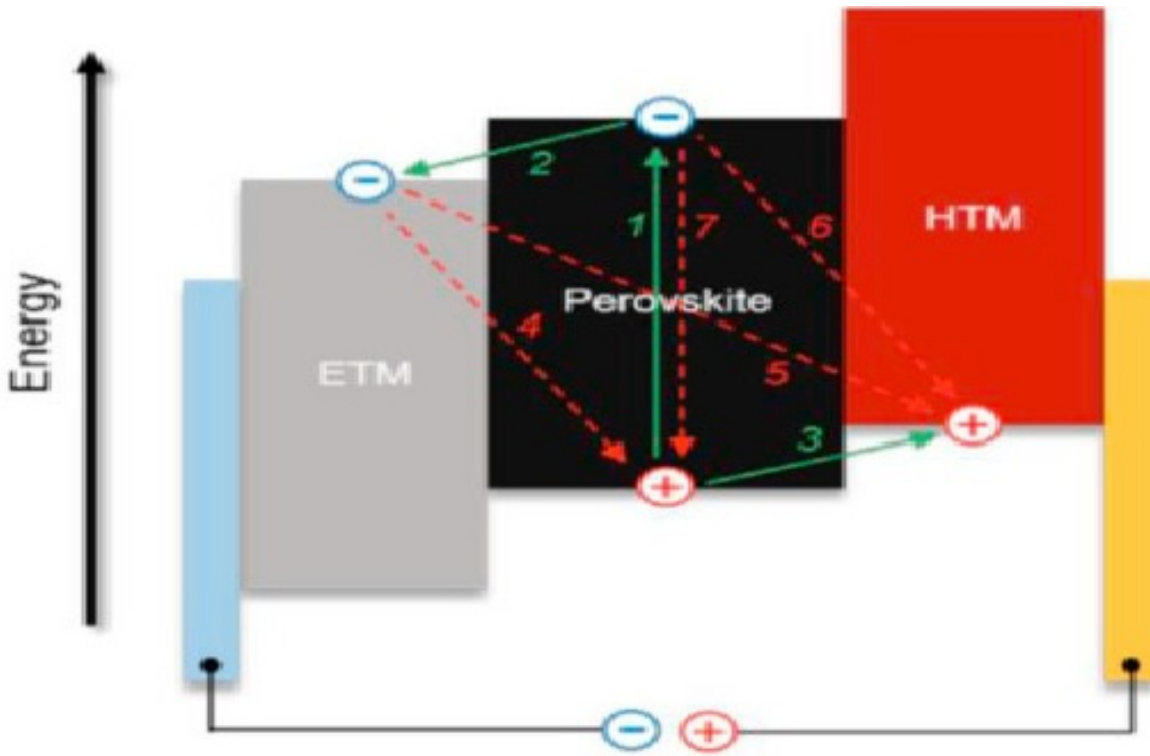


Figure 2: The energy-levels and charge-transfer process of perovskite solar cells

In 2009, Miyasaka and coworkers first demonstrated the perovskite materials in solar cell applications. They used $\text{CH}_3\text{H}_3\text{PbX}_3$ as sensitizer in dye-sensitized solar cell (DSSC) which exhibit the PCE of 3.81%. Subsequent investigations disclosed that the OHIP materials are extremely interesting candidates for solar cell applications. Besides, due to abundant availability of the precursor elements in OHIPs along with the usage of simple preparation techniques like vacuum-deposition, the atmospheric solution-processing, etc., were established. A list of surprising breakthroughs is accomplished within short period of time, with the improvement of the PCE to as high as 23.3%. Furthermore, in the advancement of perovskite solar-cells ETL plays a crucial role. In traditional perovskite solar cells ETL is a colloidal thin-film of SnO_2 , ZnO or their mesoporous systems, which consists large grain-boundaries and weak recombination at interface. Specifically, semiconductor ETL possess natural defects arose due to oxygen vacancies and trap assisted recombination. To overcome these shortcomings various researchers proposed several materials (single crystalline) for ETL in perovskite solar cells. In this view, nano sheet or atom thick of transition metal dichalcogenides such as MoS_2 , WS_2 , TiS_2 can have great potential to serve as ETL material. Because atom-thick and single-crystal nanosheet is virtually defect free. Besides, the thin structure offers rapid transportation of charge carriers to the electrode. Owing to low trap density and high carrier transportation ability, MoS_2 is widely used as ETL. Sometimes it can also be served as HTL due to its ambipolar property. For instance, in 2016, Kim et al. fabricated a perovskite solar cell by using MoS_2 as HTL which exhibit the PCE of 9.53%. Followed by, Das et al. used the MoS_2 thin film as HTL in an inverted p-i-n heterojunction planar perovskite solar cell which shows the PCE of 6.01%. In continuing this, first time Malek et al. demonstrated the preparation of atom-thick MoS_2 -nanosheets directly on indium tin oxide-substrate. They reported that homogeneity of the nanosheet enhances with the substrate temperature and optimum at 473 k. In addition, they observed that the usage of the prepared materials as ETL enhances the performance, stability and interfacial charge transfer capability of the perovskite solar-cell. Further, the PCE of the solar-cell is increased with decrease of the size of the MoS_2 Especially, the 5-atom thick of MoS_2 ETL exhibit short-circuit current-density (J_{sc}) of 16.24 mAcm^{-2} , open circuit-voltage (V_{oc}) of 0.56 V, fill-factor (FF) of 0.37 and PCE of 3.36%. Moreover, the MoS_2 solar cell can retain 90% of its initial PCE after continuous operation for 80 s under the irradiation of sunlight at maximum power point.

In addition, HTL also plays a key role in enhancing the performance of the photovoltaic devices.

Besides, huge efforts have been devoted to improve the conductivity of HTL also to suppress the recombination of charge carriers at HTL and perovskite interface by modifying the HTL through dopants. Amongst various HTMs, 2, 2', 7, 7'-Terakis [N,N-di(4-methoxyphenyl)amino]-9,9-spirobifluorene (spiro-OMeTAD) exhibit some special features such as high solubility, glass transition temperature, etc. Nevertheless, due to insufficient oxidation states raw spiro-OMeTAD shows poor PCE. Usually, high oxidation time is required for attaining good photovoltaic performance in perovskite solar cells. In this regard, in order to step up the oxidation time of spiro-OMeTAD, Kim et al. employed oxygen plasma. But, under plasma the perovskite phase is decomposed to PbI_2 this can be resolved by doping of trivalent (p-dopants) materials which can also enhance the hole-transport properties of spiro-OMeTAD. So far, metal-organic complexes, metal-oxides, organic molecules etc., are effectively active p-dopants. However, low solubility and complex decomposition methods are limiting their applications in perovskite solar cells. Further, cobalt complexes and FeCl_3 can act as efficient p-type dopants which can oxidize spiro-OMeTAD and also generate new holes to enhance the conductivity. Also, acid additives can enhance the oxidation process and shortens the aging time of perovskite solar cells. Recent investigations are focused on designing the HTL by using acid additives and modifying the morphology of spiro-OMeTAD. In continuing this, Guan et al. recently investigated the effect of benzoic-acid on oxidation process of spiro-OMeTAD. They reported that the doping of benzoic acid fastens the oxidation-process and enhances the hole transportation capability of HTL. Moreover, optimization of doping concentration effectively reduces the hysteresis in HTL-based perovskite solar cell. Also exhibits improved PCE of 16.26% under standard AM 1.5G illumination. Furthermore, Yang et al. synthesized a low cost and dopant free fluorinated spiro-OMeTAD-2,7-diamine (2 mF-X59) for solar cell applications. They reported that, the prepared material is sensitive and dopant free which can be applied as HTL into CsPbI_2Br perovskite solar cells. Up next, they modified the surfaces of CsPbI_2Br perovskite and 2 mF-X59 using 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquino-dimethane (F4-TCNQ). The modified and dopant free CsPbI_2Br perovskite solar cells shows the PCE of 14.42% with an impressive VOC of 1.23, which is very high compare to doped ones. Besides, the solar cells based on proposed HTL materials exhibit the extraordinary stability i.e., it shows 94% retention of initial PCE even after aging in air for 30days without encapsulation. So, the prepared dopant free HTL is a prominent candidate for preparing high performance CsPbI_2Br perovskite solar cells. For the first time Zhao et al. demonstrated the preparation of CuSeCN -films for HTL application in p-i-n perovskite solar-cells utilizing the organic amines solvent ($\text{H}_2\text{O}/\text{ETA}/\text{EDA}/\text{DTA}$) mixture with 2:6:1:1 vol ratio for solution-processing. They reported that the prepared HTM-based perovskite solar-cells obtained the PCE of 15.61% at forward-scan whereas at reverse-scan it shows the PCE of 15.97%. Also, CuSeCN -based perovskite solar-cell displays almost negligible hysteresis and excellent long-term stability. Hence, CuSeCN -films have the great potential to serve as an HTM for photovoltaic applications.

Due to high electron mobility, variety of nanostructured morphology and multiple growth methods, ZnO can also be a promising candidate for solar cell applications. As we know that the function of perovskite solar cell is depends on crystalline quality and surface-morphology of the perovskite capping-layer. Besides, the selection of suitable solvent for preparation of ZnO solution can significantly regulate the morphology (i.e., grain size and surface roughness) of the active layer of the perovskite, accordingly the solar cells performance. Recently, with help of cost-effective ultrasonic bath technique, Ahmadi et al. synthesized ZnO nanoparticles by using three different solvents 2-methoxyethanol (2 ME), isopropyl alcohol (IPA) and ethanol to fabricate ETL for perovskite solar-cells. The outcomes of structural, morphological and device performance investigations are evinced that the ZnO layer prepared by using 2 ME as solvent exhibit good characteristics among all the prepared ZnO layers. Moreover, the perovskite solar cell fabricated using methyl ammonium lead iodide (MAPbI_3) as capping perovskite layer and ZnO (2 ME) as ETL shows excellent PCE of 22%. This is due to lowest defect density at ZnO (2 ME)/ MAPbI_3 interface, larger grain sizes and good surface coverage by MAPbI_3 . Hence, the ZnO based solar cells are suitable candidates for solar cell applications. Owing to high transmittance nature, ZnSnO (ZTO) can also be used as ETL in solar-cells. Usually, the oxygen-vacancies present in ZTO plays a vital role in the transportation of charge carriers. Further, the existence of large number of oxygen-vacancies is the major defect in ZTO. To overcome this, Miao et al. demonstrated the effect of oxygen-vacancies in ZTO through fabricating ZTO-based solar-cells with doping of silicon in various doping concentrations. For this purpose, with the help of RF magnetron sputtering technique silicon- ZnSnO (SZTO) amorphous

metal oxide films are prepared by varying the silicon content. Besides, they reported that the x-ray photoluminescence spectra (XPS) analysis confirms the reduction of oxygen-vacancies with respect to silicon concentration. Moreover, the reduction of oxygen vacancies in SZTO causes the improvement in electronic extraction and transfer ability. By using the prepared SZTO as an ETL, they fabricated a perovskite solar cell which exhibits the maximum PCE of 13.4%, JOC of 21.6 mA/cm², VOC of 1.04 V along with FF of 0.67.

Further, TiO₂-based solar cells exhibit good PCE over 20%. Nevertheless, the TiO₂-ETL in n-i-p structured perovskite solar-cell causes instability and fast decay of short-circuit current-density (JSC) under the irradiation of ultraviolet radiation [98]. Many researchers put their efforts to overcome these shortcomings or to protect the perovskite solar cells from UV-light induced degradation through employing an interface layer at TiO₂-ETL and perovskite. Still, the performance of the device is affected owing to TiO₂ in all of the above reported techniques. So, there is a need to fabricate the stable perovskite solar cell with improved performance. In this view, many ETL materials which are stable under ultraviolet (UV) radiation gained much attention [[104], [105], [106]]. Amongst, owing to excellent electron-mobility and deeper conduction-band, Mg_xZn_{1-x}O (MZO) can serve as an effective ETL material in perovskite solar cells which is also stable under ultraviolet irradiation. In continuing this, recently Han et al. demonstrated the MZO-based perovskite solar-cell with outstanding stability under UV-radiation. They reported that, compare to TiO₂, MZO shows superior carrier mobility and conduction mechanism. This property causes the reduction in charge growth at the interface of the MZO and perovskite also enhances the charge transfer between MZO-layer and perovskite. Further, they fabricated MZO-based device, at optimized state the device exhibits large open circuit voltage of 1.11 V along with high efficiency of 19.57%. In addition, even after one year of aging at room temperature, 40–80% relative humidity and 8 h ultraviolet irradiation, the proposed device exhibits 76% of retention of initial JSC whereas under same conditions the TiO₂-based device shows only 12% of initial JSC. Owing to excellent stability under UV-radiation, the fabricated device shows reduced electron trap state density in MZO-ETL. Indeed, zinc-interstitial sites and oxygen-vacancy sites of MZO-ETL strongly opposes the degradation of perovskite-layer under the exposure of UV-radiation. Hence, the proposed MZO-ETL can serve as potential candidate for fabricating stable UV-resistive perovskite solar-cells.

In order to enhance the conductivity of ETL layer, Teimouri et al. demonstrated the effect of lithium (Li) doping on TiO₂. In this connection they prepared Li-doped TiO₂ films by using ultrasonication technique. They reported that, in solution form Li-doped TiO₂ shows improved conductivity and decreased solar power loss. In addition to increased conductivity Li-doped TiO₂ films provides faster electron transport. Besides, to study the effect of various Li-concentrations on efficiency of perovskite solar cells, they modeled the structures by using solar cell capacitance simulator (SCAPS). The perovskite solar cell consisting of an ETL with 0.3 M Li-doped TiO₂ exhibited the PCE of 24.23% which is almost 1.97% larger than the undoped composition. Furthermore, in comparison with the pure TiO₂, doped TiO₂ shows lower trap-density at the interface of the absorber and ETL. All these outcomes are evinced that the Li-doped TiO₂ can also be a prominent candidate to serve as ETL-layer in perovskite solar-cells. With the help of sol-gel synthesis technique, Yang et al. [111] synthesized different compact anatase TiO₂-ETLs (c-TiO₂) by varying the concentration of TiO₂. It is observed that among all the prepared ETLs, the ETL with 2.0 M concentration of TiO₂ shows dominant properties. Besides, the fabricated c-TiO₂ based perovskite solar-cells accomplished a high PCE of 16.11% with FF of 0.656, VOC of 1.1 V and JSC of 22.32 mA/cm². So, c-TiO₂ based perovskite solar-cells show a new direction for preparing low temperature perovskite solar-cells with better efficiency. Fig. 2 shows the schematic representation of c-TiO₂ based perovskite solar cells.

4 Perovskite Based Solar Cells

Solar-cell efficiencies of laboratory-scale devices using perovskite based materials have increased from 3.8% in 2009 to 25.7% in 2021 in single-junction architectures, and, in comparison silicon-based tandem cells, show 29.8%, exceeding the maximum efficiency achieved in single-junction silicon solar cells. Perovskite solar cells have therefore been the fastest-advancing solar technology as since 2016. With the potential of achieving even higher efficiencies and very low production costs, perovskite solar cells have become

commercially attractive. though their stability (short or long term) has to be ensured. The improvement in efficiency of perovskite solar cells is shown in Fig.2.

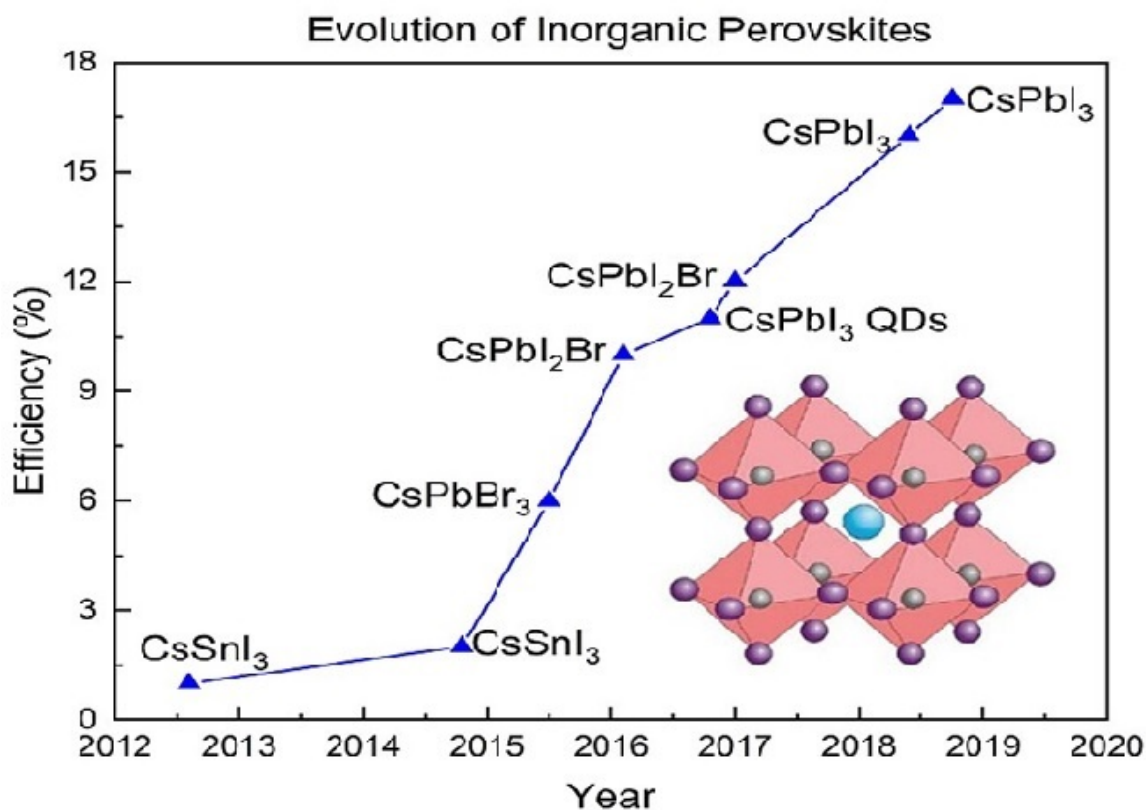


Figure 3: Time line of perovskite based solar cell development

5 History of Perovskite Based solar cells

The utilisation of clean, renewable energy sources has become a prerequisite for the development of human society. Among a variety of new energy technologies, solar power is undoubtedly one of the promising technologies. A solar cell is a device that converts light energy directly into electrical energy via photovoltaic effects or photochemical reactions. In 1839, the French physicist Becquerel discovered the photovoltaic effect for the first time. In 1876, British scientists Adams et al. found that a selenium semiconductor could produce electricity when it was radiated under sunlight. In 1883, Fritts successfully prepared the first semiconductor/metal junction solar cell with a piece of germanium coated with a thin layer of gold although the efficiency was only 1%. In 1954, Pearson et al. from US Bell Labs developed the first piece of crystalline silicon solar cell and achieved a conversion efficiency of 4.5%, thus beginning a new era for the utilisation of solar power. The monocrystalline silicon/polycrystalline silicon solar cells currently employed in industrial applications have achieved a photovoltaic conversion efficiency of more than 20%. However, such silicon-based solar cells are characterised by a high cost, harsh preparation conditions, and serious environmental pollution. Cadmium telluride and copper indium gallium selenium thin-film solar cells have achieved a high efficiency of photovoltaic conversion in the laboratory, but the industrial applications are restricted by the high production cost, environmental pollution, and other problems. In recent years, dye-sensitized solar cells, as the representative of the third-generation solar cells, have achieved a photoelectric conversion efficiency of more than 13% in the laboratory and have developed rapidly due to their significant advantages, including low cost, simple process, and high efficiency. However, dye-sensitized cells still have two disadvantages. Firstly, in order to ensure the full absorption of sunlight's energy, the absorbing layer is thick (>10μm) because it is difficult to achieve complete light absorption using a thinner absorbing layer in the solid-state cells. Secondly, organic dyes cannot avoid the phenomenon of light bleaching. These two problems have prompted researchers to develop excellent all-solid dye materials.

In 2009, Japanese scientists Kojima et al. found that the organic metal halide perovskite was similar to dyes and can absorb sunlight. The perovskite can be applied in the dye-sensitized solar cells with a

liquid electrolyte as a sensitizer to achieve power conversion efficiency (PCE) of 3.8%. In 2012, Kim et al. reported all-solid-state perovskite solar cells with a PCE of 9.7% for the first time. Because of the high efficiency and low cost, perovskite solar cells have attracted extensive attention from researchers worldwide and have developed rapidly in recent years. So far, the highest conversion efficiency has been 22.1% in 2016, which was certified by the National Renewable Energy Laboratory (NREL). Further improvements in the performance of perovskite solar cells are expected to break the bottleneck of conversion efficiency and production cost. As one of the most promising novel photovoltaic cells, perovskite solar cells are of great scientific value and practical significance.

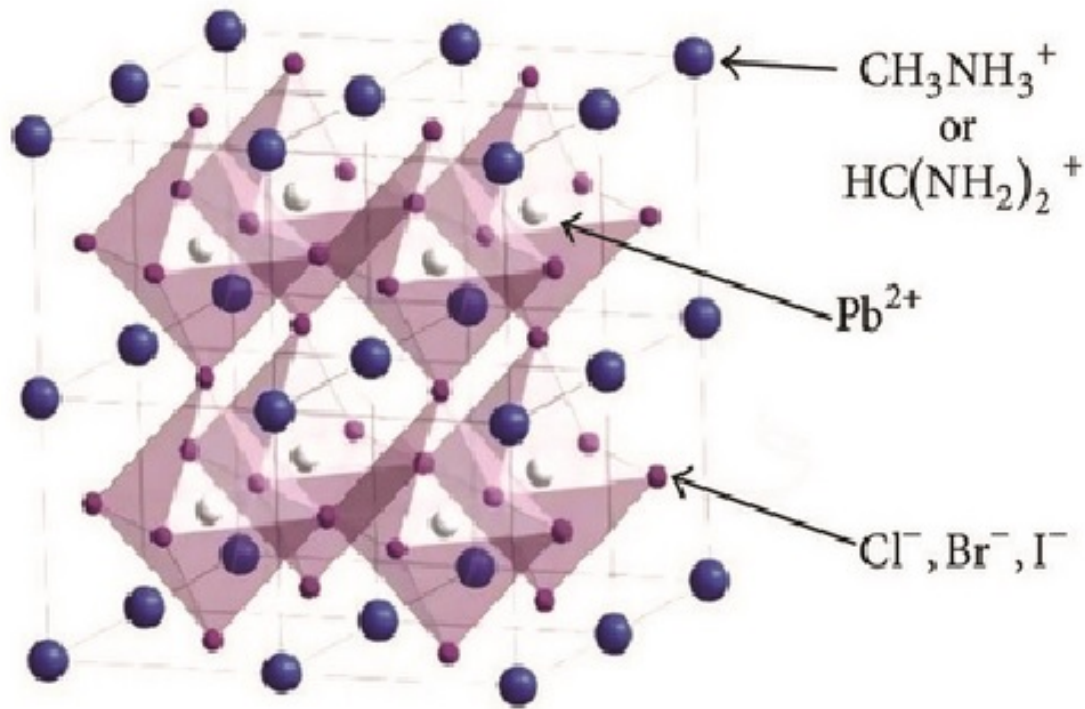


Figure 4: Typical perovskite cubic lattice structure. Reprinted from literature

6 Some Aspects on Materials

The perovskite material is derived from the calcium titanate (CaTiO_3) compound, which has the molecular structure of the type ABX_3 . Perovskite materials have attracted wide attention because of the cubic lattice-nested octahedral layered structures and the unique optical, thermal, and electromagnetic properties vertex of the face-centred cubic lattice, and the metal cation B (Pb^{2+} , Sn^{2+} , etc.) and halogen anion X (Cl, Br, or I, or coexistence of several halogens) occupy the core and apex of the octahedra, respectively. The metal-halogen octahedra are joined together to form a stable three-dimensional network structure. The materials with such a structure have the following four features. Firstly, the materials possess excellent photo-electric properties, lower exciton binding energy, and high optical absorption coefficients (up to 10 cm^{-1}). Secondly, perovskite as the light-absorbing layer can absorb solar energy efficiently. Thirdly, the materials possess a large dielectric constant and electrons and holes can be effectively transmitted and collected. Lastly, electrons and holes can be transmitted simultaneously and the transmission distance is up to 100 nm or more and even more than 1 μm . These features lead to a high open-circuit voltage (V_{oc}) and a short-circuit current density (J_{sc}) if the materials are employed in solar cell devices. During exposure to sunlight the perovskite layer firstly absorbs photons to produce excitons (electron-hole pairs). Due to the difference in the exciton binding energy of the perovskite materials, these excitons can form free carriers (free electrons and holes) to generate a current or can recombine into excitons. Due to the low carrier

recombination probabilities of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃) and other perovskite materials and the higher carrier mobility, the diffusion distance and lifetime of the carrier are long. For example, the carrier diffusion distance is at least 100 nm for MAPbI₃ and longer than 1 μm for MAPbI₃Cl. The longer diffusion distance and lifetime of carriers are the source of the superior performance of perovskite solar cells. Then, these free electrons and holes are collected by an electron transport material (ETM) and a hole transport material (HTM). Electrons are transferred from the perovskite material to TiO₂, which is used for the ETM layers and finally collected by FTO. At the same time, the holes are transferred to the HTM layer and collected by the metal electrode. Finally, the FTO and metal electrode are connected and the photo-current is generated in the outer circuit.

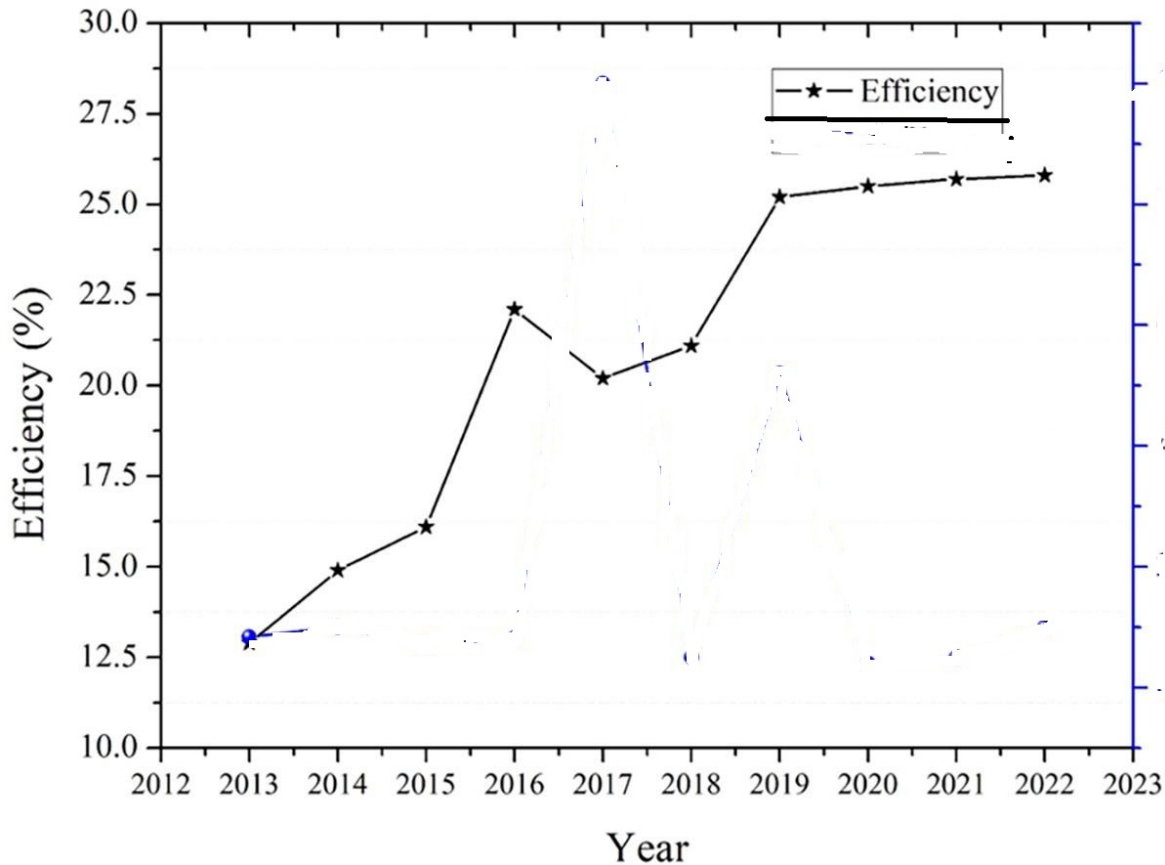


Figure 5: Efficiency improvement of perovskite solar cells in the last decade

7 Aspects which deserve attention

There are various aspects of solar cell that call for attention. In this section let us list the main four aspects which require attention.

1. The stability of the organic lead halide perovskite is greatly affected by external environmental factors (such as humidity, temperature, and ultraviolet radiation), which lead to the low stability of the devices and the great difficulties in encapsulating cells in the later stage. Therefore, the development of a high-stability device composition, including the light-absorbing layer, electron/hole transport layer, and electrode materials, as well as the development of a simple and effective device-packaging method, will be of great significance to promote the practicability of such devices

2. The hole transporting material Spiro-OMeTAD used in perovskite solar cells is expensive (10 times the market price of gold) and its synthesis process is complex. Therefore, it is necessary to design and synthesize new hole transport materials to promote commercial applications of perovskite solar cells.

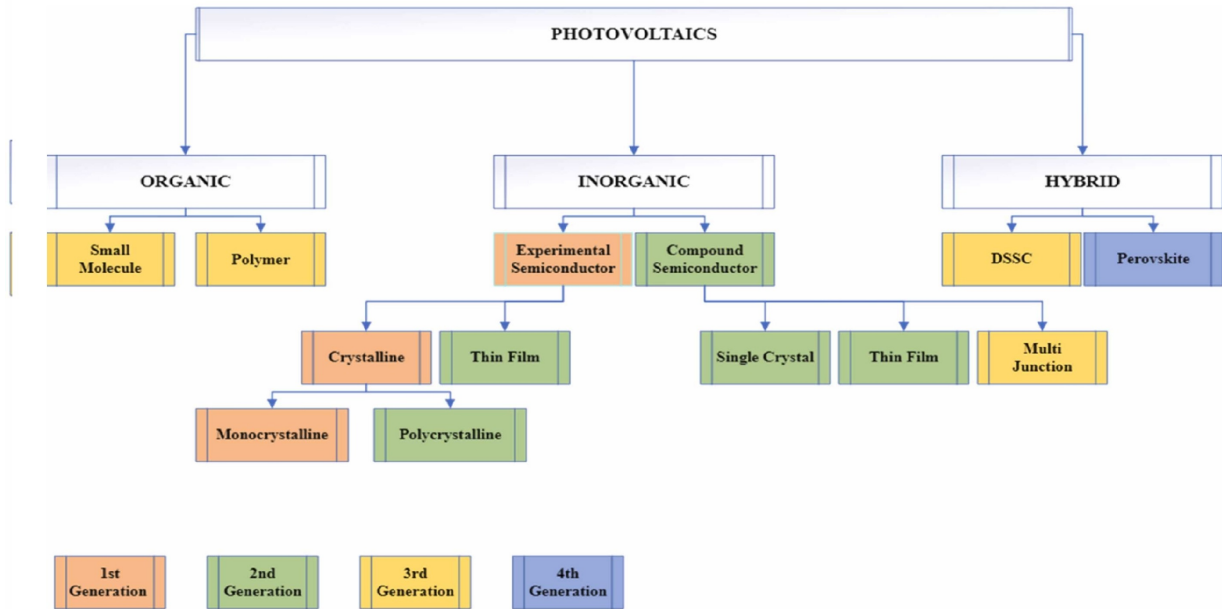


Figure 6: The types of solar cells obtained from perovskite materials

3. It is difficult to deposit a large area of continuous perovskite film with the traditional methods described above and so other methods should be improved to prepare high-quality and large-area perovskite solar cells for commercial production in the future

4. The Pb element employed in perovskite solar cells is highly toxic, which will hinder the industrial promotion and development of perovskite solar cells. Therefore, it is necessary to find a low-toxicity or nontoxic ingredient to replace Pb in the future.

6. There is a lack of deep understanding of the microscopic physics mechanism of perovskite solar cells. Therefore, it is necessary to establish a complete theoretical model to explain the reasons for the increase in the conversion efficiency. Theoretical studies will not only help to further improve the performance of perovskite solar cells but also provide ideas to develop simpler and/or more efficient new materials and structures. In a word, all the above issues need to be addressed before making full application of the perovskite solar cells technology.

8 Structure of Perovskite Materials

The ideal perovskite structure is cubic characterized by A cations positioned at the corners of the unit cell, B cations at the center, and X anions at the face centers. The stability of this cubic structure depends on the coordination of 12 X anions around the A cation and an octahedral arrangement of X anions surrounding the B cation. Deviations from the ideal cubic structure result in various lower symmetries, such as tetragonal, orthorhombic, rhombohedral, or monoclinic forms. There are various text books wherein the structure of perovskites have been dealt with. The stability of perovskite structure is determined by the values of tolerance and octahedral factors. Interested reader can refer to reference [7]. The essential phase transitions (Fig. 5) occur over a range of temperatures, with reversible transformations between tetragonal and cubic symmetry reported between 300 K and 400 K. At lower temperatures, often below 200 K, the material changes from the tetragonal phase to an orthorhombic phase.

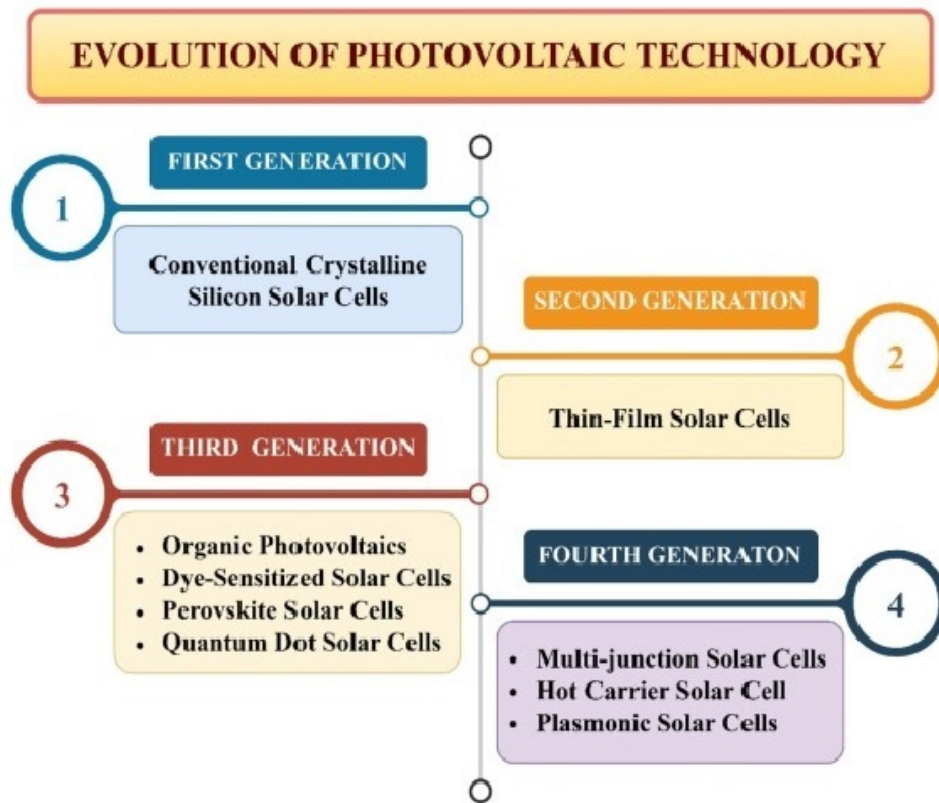


Figure 7: the historical generations of solar cell development

9 Band gap tuning and halide variation

The significant feature of perovskite materials is the ability to tune their band gap which is of importance for the enhancement of such materials for solar cell application.. By altering or tuning the halide content (I, Br, Cl), it has been found to enable tuning the band gap over a wide range (1.5 eV to 2.3 eV) making perovskite materials versatile for various light-absorption requirements. In the case of $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($X = \text{Cl, Br, I}$), the band gap narrows from chlorine to iodide because of difference in electronegativity and ionic radii..

10 Optical absorption and defect tolerance

Perovskites offer exceptional optical absorption, particularly in the visible range. Methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$ or MAPbI_3) is a prime example, with a high optical absorption coefficient due to strong Pb-I orbital interaction. This material's band structure, typified by a well-defined conduction band (CB) and valence band (VB), permits effective light absorption and charge carrier production. As in other materials, the perovskites in this regard do not follow normal semiconductor trends but show inherent fault tolerance. Defects like vacancies; I or Pb^{2+} , normally create shallow trap states rather than deep trap states that would otherwise limit the mobility of charge carriers. Thus, it is possible to have rapid transfer and collection of carriers regardless structural imperfections are present. Consequently, large carrier diffusion lengths, up to 100 m in single crystals, have been observed.

11 Carrier transport, mobility, and recombination

Another significant characteristic of perovskites is their ambipolar carrier mobility, with both electrons and holes having equal effective masses. This results in efficient charge transport and minimum recombination losses. MAPbI₃, in particular, displays long photoluminescence (PL) lifetimes and low recombination rates, further adding to its strong photovoltaic performance. The suppression of electron-hole recombination is due to the high ionic density in the material, which promotes charge screening and lowers recombination via shallow defects.

12 Photovoltaic efficiency and voltage loss

The combination of high optical absorption, defect tolerance, and ambipolar mobility results in perovskites achieving outstanding solar efficiencies. PSCs frequently exhibit high V_{OC} , often exceeding 1.1 V, even under low light conditions. This high V_{OC} , along with a well-balanced charge transfer process, contributes to the outstanding PCE exhibited in perovskite-based solar cells. Despite these advancements, PSCs still suffer from voltage loss due to the presence of defects and trap states, particularly in polycrystalline films, where the trap density can range from 10^{16} cm⁻³. By comparison, single-crystal perovskites have lower trap densities (10^{10} cm⁻³), indicating the opportunity for further optimization in device construction and material processing.

13 Electronic structure and phase transitions

The electronic structure of perovskites is principally dictated by the B cations and X anions, which dictate the material's conduction and valence band properties and positions.. For example, in CH₃NH₃PbI₃, the Pb-I bond angle and lattice constant influence the band gap, which can vary between 1.5 eV and 1.6 eV depending on whether the material is in its cubic or tetragonal phase. Similarly, modifications in the halide composition (e.g., substituting iodide with chloride) impact the band gap, allowing for more control over the material's optoelectronic capabilities. The temperature-dependent phase transitions in perovskites also play a crucial role in their performance.. For instance, the shift from cubic to tetragonal or orthorhombic phases impacts both the optical characteristics and carrier mobility, albeit these changes are frequently reversible with temperature.

14 Working principle of Perovskite Solar Cells

When PSCs were first explored, their behavior was initially believed to mimic that of Dye Sensitized Solar Cells. Early experiments involved PSCs paired with a TiO₂ mesoporous photoanode within liquid electrolyte-based cells, where it was assumed that photoexcited electrons from the perovskite layer would inject into the TiO₂ conduction band and flow through an external circuit, similar to the mechanism observed in DSSCs. This assumption stemmed from a limited understanding of perovskites during the early stages of research. However, while PSCs share certain operational principles with DSSCs and organic solar cells (OSCs), the transport mechanisms in PSCs differ significantly. Instead of relying on an external scaffold, charge carrier transport in PSCs occurs directly within the perovskite film itself, reflecting a distinct underlying physics compared to DSSCs

.. Research revealed that PSCs do not require a semiconducting scaffold such as TiO₂ for efficient electron transport. Instead, electron and hole transport can occur directly within the perovskite film itself, even in planar architectures. This led to a paradigm shift in understanding, where PSCs were realized to behave more like solid-state p-n junction solar cells rather than following the sensitization mechanism seen in DSSCs. This breakthrough allowed researchers to focus on optimizing the perovskite material itself, paving the way for higher PCEs. One intriguing aspect of PSCs is their V_{OC} . Unlike conventional solar cells, where V_{OC} typically shows a clear dependence on the work function difference between the

selective contacts. PSCs exhibit unusual carrier behavior. Despite this, they achieve high V_{OC} and PCEs due to the material's intrinsic properties, such as high optical absorption, long carrier diffusion lengths, and low recombination rates. These attributes highlight the unique physics governing PSC performance, distinguishing them from other solar cell technologies.

15 Concluding Remarks

PSCs have emerged as a promising technology in the field of photovoltaics, demonstrating tremendous breakthroughs in PCE during the past decade. The excellent optoelectronic features of perovskite materials, particularly high absorption coefficients, long carrier diffusion lengths, and fault tolerance, have permitted rapid increases in device performance. Stability concerns, particularly related to moisture sensitivity, thermal degradation, and UV induced degradation, continue to hamper the long-term stability of PSCs. The presence of harmful lead in high-performing electronics increases environmental concerns, encouraging development of lead-free alternatives. Encapsulation techniques, including thin-film deposition and edge sealing, have proven an acceptable potential in enhancing the device stability. The study of both mixed cation and mixed halide perovskites has produced more stable materials with tunable bandgaps. Novel materials like the 2D/3D perovskite composites and using additives offered greater resistance to the environmental factors. PSCs versatility in applications extends beyond the simple solar panel applications.

The preparation methods currently employed need improvement and it can be anticipated that newer device fabrication technologies can expand the field of solar cells beyond the energy envelope.

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