Advancements in solar cells with perovskites

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Perovskites are a nanoparticle semiconductor that have recently taken the photovoltaic industry by storm. Their low cost and relatively easy manufacturing process earns them respect in their field. Additionally, their power conversion efficiency has the potential to overtake that of the common silicon cell. These perovskites can be used in many ways including in solar cells, LEDs, and wearable technology. However, one of their biggest drawbacks is their fragility in water and other environments. Because of the material's thin film, perovskites have a very low structural stability, putting them at a higher risk of decomposing from intense heat, wind, rain, or snow. Ever since their discovery in 2008, different methods such as p-doping, lamination, spray coating, tandem cells, and ligand substitutions have been used as an attempt to increase their stability and functionality.As a result, the PCE of these perovskite cells has increased by over 20% and is estimated to continue climbing even past the Shockley-Queisser limit. Still, there are limits to how ready these cells will be for commercialization. Thus, more research on how to limit the toxicity of the cells continues to be conducted as well as research in how to manufacture them in room temperature conditions. In this literature review, all of the most popular techniques reviewed and discovered by different professionals will be explained and reviewed based on how much they have improved the perovskite cell. The limitations of these cells have also been addressed as well as ways currently being explored to counteract them.

Introduction

Different PSCs

As a species, humans use a very large amount of energy on a daily basis. Even with current attempts to minimize our carbon footprint, our energy usage is still high. In order to reduce society's high energy usage, scientists have explored various materials designed to provide a more sustainable method of using and harvesting energy, and one of the most recent and promising implements are perovskites. As a semiconductor, perovskites show great promise because of their very large power conversion efficiency as well as their low production cost. Compared to their largest competitor, the silicon solar cell, perovskite solar cells (PSC) have a higher absorption potential and are more easily able to convert different wave frequencies of light into energy. When originally discovered in 2009, PSCs had a PCE of only 3.8%. However, due to efforts towards improving the film's quality and stability, which will be discussed further in the review, the PCE has increased by over 22% as of 2022[1].

Perovskites have also attracted the attention of many current researchers because of their hybrid structure combining the flexibility and easier production of organic semiconductors with the high electrical potential of inorganic semiconductors. Perovskites carry the chemical formula of ABX_3 where the A cation is commonly methylammonium (MA) or another monoprotic substance such as rubidium, cesium, or lithium[2,3]. B refers to a diprotic element most commonly being lead or tin both with a 2+ charge. Lastly, X is occupied with halides like iodine, bromine, or chlorine. PSC also generally have an octahedral geometry (Fig. 1) that is identical to that of calcium titanium oxide, but its shape can change based on what components occupy the AB cations of the PSC as well as any outside alterations that have been made[2]. While all perovskites abide by these general criteria, there are many different forms and characteristics that recent researchers have investigated. Some of the most common PSC is the metal halide perovskite, MA lead trihalide ($CH_3NH_3PbX_nY_{3-n}$) as well as MA lead iodine ($CH_3NH_3PbI_3$) due to their PCEs of 25.7%[4]. Both of these cells are thin film meaning that the perovskite is the only photovoltaic cell, but recent studies have found that tandem solar cells can have an overall higher performance and can surpass the PCE of any single cell[5]. In an ideal environment with unlimited amounts of sunlight and infinite tandem junctions, a single photovoltaic cell could reach a PCE of up to 86.8%, but this value is not practically achievable. Commonly, perovskite solar cell PCEs remain below 30%, but when tandem cells are exposed to high concentrations of sunlight, it is expected that they could surpass the Shockley-Queisser limit of 33.7%. To achieve this goal, thin film PSC have been combined with other popular solar cells like crystalline silicon or thin film cells like copper indium gallium selenide (CIGS). Though the overall performance of tandem film cells as well as single cells are both making great headway in their advancements, one of the consistent problems researchers face is how to compensate for their instability in different environments. PSCs, because of their very weak integrity, have a weaker photovoltaic performance when exposed to extreme temperatures or natural occurrences like wind and rain. This research paper will cover many current different methods of preserving perovskites, popular implementations, and personal opinions on the future potential of perovskites and how they can improve even further to become commercialized.

Methods

0.1 Google Scholar data extraction

When conducting my research, I extracted data from a combination of both literature review and original research papers on google scholar. I began by reading as many current papers as I could to gather basic information on how perovskites work and the specifics on how well researchers in the past have used them. I then researched further into what the different perovskite limitations are by looking at different original research papers conducted by experts in the field which addressed how perovskites could be advanced further. Some key factors that I looked for was the perovskites functionality when exposed to intense temperatures or other external conditions such as moisture. Major keywords I used while searching for papers include "perovskites", "water-resistant", "solar cell", and "perovskite doping". Generally, recently published papers held a higher importance in the search for data as they provided better information on the most current innovations in this field.

Results

0.2 P-doping

PSC have been shown to have limited functionality when dealing with different external conditions such as windy and aqueous environments. Due to the fragility of the film, doping is commonly used in order to increase the conductivity capacity of PSCs by injecting another element into the structure of the cell[6]. There are many different types of doping that are respectively used based on the number of valence electrons. P-doping has been used to create empty spaces in silicon crystal lattices by commonly introducing elements with one less electron than what would be required to create a full set of valence electrons in the crystal. Some of the most common dopants for PSCs are B (Boron), Sb (tin)B, or Ga (Gallium)[7,8]. The addition of the dopant allows for the electrons in the cell to move more freely which allows for more photons to be converted into energy. This method of doping is commonly referred to as P-doping because of the overall positive charge of the cell made from the missing electron in the lattice referred to as a hole[8]. In perovskites, though, different dopants can be used to either increase or decrease the bandgap of the cell. In this type of doping, the dopant can replace either the A or B cation depending on the size of the dopant. For instance, small dopants suck as K minimally alter the bandgap of a cell by as little as $0.1eV$, but dopants with large atomic radii like FA enlarge the bandgap from $1.79eV$ to $3.2eV$[7]. Recent studies have reviewed how effective P-doping are on PSC in order to increase their stability. This article specifically focused on a PSC functionality in water and the time it could remain withing that environment and still perform as intended. The results showed that in terms of magnitude, the newly doped perovskite's conductivity increased by five orders as well as its total lifespan increasing by one order[6].

0.3 Lamination

Another common method to improve PSC is a technique called lamination. To minimize decomposition, lamination for perovskites allows for a completely water soluble and stable material[9]. Polar materials have been found to be the most effective when laminating a cell especially towards protection in water. In the laminating technique, the substrate is placed within a vacuumed environment and then fused to another material or another perovskite thin film[10]. This process is completed through hot pressing where the two perovskite and substrate layers are forcibly combined in $194 \deg F$ conditions. Commonly, this encapsulation process is conducted with two independent half stacks of flexible substrates such as the thin plastic polyethylene terephthalate and $CsPbBr_3$ thin films[11]. Additionally, buffers like poly(triarylamine) polymers (PTAA) are commonly used between each stack to increase electrical function. The presence of the buffer is beneficial in laminating as it both provides a physical barrier that limits the perovskite's exposure to environmental conditions as well as increases the contact between the different substrate films. Without the buffer, devices are proved to be almost 7% less efficient at converting solar energy. During the lamination process, immense heat and pressure are applied to the perovskite which recrystallizes the perovskite lattice structure[9,11]. The natural structure of $CsPbBr_3$ is cubic which creates a rough surface of the material, but after lamination, these surfaces smooth over creating a more even surface area for electrical contact and conductivity[9]. This recrystallization improves the overall structure of perovskites which can be used to counteract problems with substrate compatibility and instability. Overall, the addition of fused material provides the cell with a new layer of protection, enabling it to consistently function with a PCE of up to 14.6% even in environmental conditions.

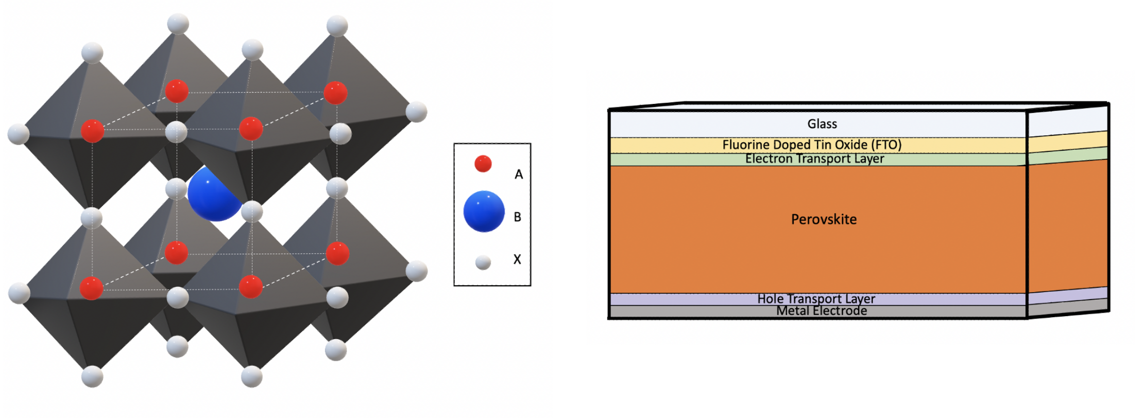

Fig. 1 Diagram of a perovskite's octahedral geometry and ABX3 structure. Figure also depicts a layer-by-layer representation of a thin film PSC.

0.4 Spray coating

Spray coating is a technique highly similar to lamination where the cell is surrounded by a more water-soluble substance. However, the main difference is that spray coating involves applying a new metallic layer, onto the substrate, whereas laminating physically bonds 2 different substrates together[12]. There are many different coating techniques such as blade coating or slot-die coating, but spray coating is by far the most popular and beneficial technique. The method of spray coating consists of applying a thin layer of a polar material, for example, PbI2, onto a perovskite film such as MA lead iodine. The coating process is conducted by using a spray gun to apply an even layer of PBI2 onto the substrate under high temperature conditions of over 100 degrees Celsius. The high temperature environment allows for the interactions between the PbI2 and the substrate to fuse together and create a most stable chemical bond.

Spray coating is one of the easiest and most efficient of the coating techniques because the spray applicator can spray up to 5m per minute. At the time the PCE increased to 11%, but the method has since improved. Currently a continuous spray has been proven to be the most beneficial as a solution, in this case CH3NH3PbI3, was constantly sprayed on the PSC at a temperature of 120 degrees Celsius. The PCE was increased to 18.3% which was a substantial increase from the previous techniques' PCE of 15.5%[12]. Other researchers have also looked into the effectiveness of spray coating and have determined that the temperature has a major role in how effective both the application and performance of the spray coat layer are. When the substrate is sprayed at a higher temperature, the additional layer is found to have much more optimal coverage due to the applied material being able to dry quickly. Additionally, because of the quick dry time, the substrate can be sprayed multiple times which allows for overall more protection to the perovskite film[13].

0.5 Ligand Substitutions

In this method, different bordering sections in a perovskite are replaced by more water soluble, sustainable, or generally stable materials. The process involves removing surface A cations from the typical ABX_3 structure of perovskites. These cations, commonly MA or Cs+, are then replaced with insulating ligands that increase hydrogen bonding. Some of these typical ligands are oleic acid (OA), Oleylamine (OAm), and Oleylammonium Bromide (OAmBr), but there are also recent studies that have tested the effects of materials such as 2- amidinopyrimidine hydrochloride (APC)15. These surfactants are synthetically added into perovskite crystalline structures through a hot injection. This technique involves injecting cold ligand solutions into a boiling hot perovskite solvent. While ligand substitution is one of the newer methods for preserving PSC, it has been proven to be especially beneficial in improving perovskite semiconductor nanocrystals. When a ligand exchange has been properly executed, the imposed ligand will increase solubility as well as provide a barrier of protection from different materials[14,15]. Different studies have been conducted to determine the most beneficial ligand exchange for perovskite LEDs. Perovskites usually have a longer alkyl chain such as capric acid, octylamine[16,17]. In order to continue pushing for longer lifetimes, octylphosphonate acid is being used as a ligand for perovskites that also improves its photoluminescence. Using octylphosphonate as a ligand for the perovskites, the researchers were able to achieve a maximum external quantum efficiency and lumi-

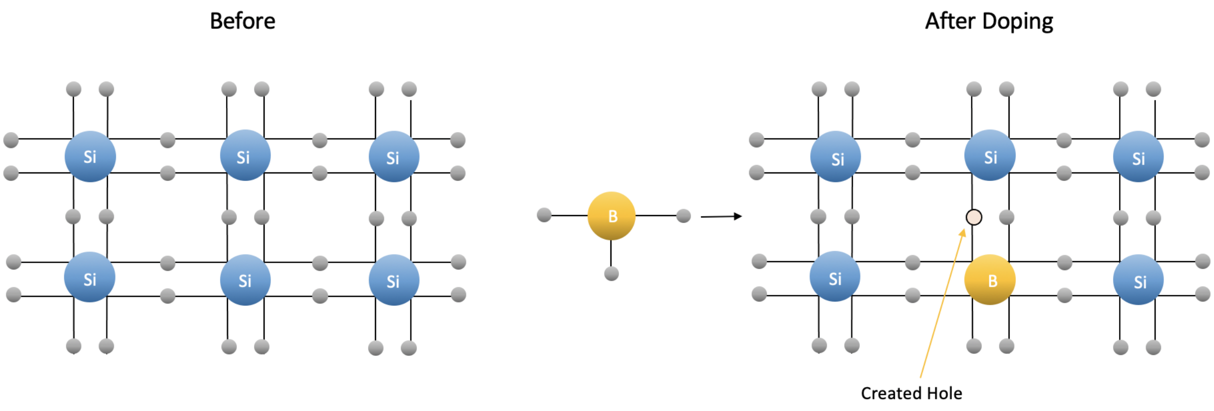

Fig. 2 Representation of p-doping process using the introduction of Boron in a Silicon structure. Shows before and after visuals of a perovskite cell going through this process and shows how the doping of Boron creates a hole in the crystal and creates an overall positive charge.

nescence of $7.74\% cdm_{-2}$ with OPA treatment as opposed to 3.9% and$229 cdm_{-2}$ for untreated perovskites[17]. Additionally, research has shown that by adding APC to a PSC layer, the PCE of the cell increased to 25.17%[14]. In order to continue pushing for commercialization, perovskite cells were synthesized in room temperature which in turn also increased the success rate for the ligand exchange. The ligand exchange was tested on a perovskite cells with bandgaps ranging from $1.7 eV$ to $3.2 eV$, and with the new ligands, the cells were shown to have increased their PCE to over 20%[16].

1 Discussion

1.1 Solar cell implementations

Perovskites have had the most headway in the past couple of years in the solar cell community. They have had great success in this field because of their very large PCE in comparison to over solar cells. Currently, the largest PCE of a PSC has been recorded to be 25.7%. Researchers have declared that they are close to breaking the 35% barrier in the next couple of years which would drastically change the entire industry[3,18]. With this innovation, perovskites would take over the solar cell industry and would quickly be commercialized and accessible to the public. PSC could become even more popular than the silicon solar cells which have been sustainably used ever since their initial discovery in 1954. However, one of the largest downsides of silicon solar cells are their large bandgap. The increased distance between the conduction and valence bands prohibits the solar cell from absorbing many different types of light across the solar spectrum[14]. In order to counteract this limitation, intricate p-doping and post-treatments must be implemented just for them to function properly. Because of this, one of the most important advantages for perovskites over silicon solar cells are their easily synthesized bandgaps. Perovskite bandgaps can be modified anywhere from $1.2 eV$ to $2.3 eV$, allowing them to absorb more types of light with higher quantum efficiency[1].

Because of their structural instability, p-doping, laminating, and spray coating techniques have been implemented to improve perovskites' function. For both p-doping and ligand substitutions, the chemical structure of the perovskite has been altered to incorporate new and more stable materials. Lamination differs in the process, but the end goal stays the same. In lamination, a completely new layer of a material with greater stability is fused to a perovskite substrate to increase durability. Overall, these methods are beneficial in increasing efficiency in perovskites and drastically improve the PCE of PSCs, making them some of the best current techniques for improving and enhancing PSCs. advanced the field of solar cells.

1.2 Other promising applications

PSC can be implemented in many different ways because of their neutrality and their high potential to convert light into energy. Perovskites have already been making their way to becoming one of the most innovative and popular options when producing solar cells. They have made many improvements since their discovery in 1978 and since then have only grown. However, one promising field PSCs can be used in are light emitting diodes (LEDs)[19,20]. Specific flexible perovskite films like metal halide perovskites have the highest potential in the LED field because of their bandgap tunability and natural showcase of color purity[21]. Because of these characteristics, these perovskites have the potential to be implemented in wearable technology, building technology, and other large scale semiconductor applications. Similar to PSCs, these perovskite LEDs can be fabricated through processes like spin coating in order to create a uniform and more stable LED[21]. Perovskites also have the potential to impact the field of photocatalysis. Photocatalysts are materials that use light energy to speed up the rate at which chemical reactions occur. Because of perovskites' high potential to store electricity, the semiconductor has proven to be beneficial as a photocatalysts, and one of the most popular ones is Titania (TiO2). Though this paper dives heavily into perovskites in solar cell applications, the materials' versatility enables it to have many possible implementations outside of solely solar cells, and there are still so many more possible applications yet to be fully explored.

1.3 Limitations for commercialization

One of the largest limitations for perovskites future in commercialization is the materials rapid degradation under working conditions. Currently, Silicon based solar cells dominate the photovoltaic industry. These cells have PCEs of over 30% and have lifetimes of up to 25 years, and even though perovskites have the potential to surpass silicon cells, their fragility and short lifespan of barely a year continue to cause problems[15]. Perovskites are naturally unstable in external conditions such as humidity and wind which cause for the semiconductor to be hard to work with. When exposed to high temperatures and UV light, the chemical bonds in perovskites weaken, causing for their active layer, hole transport layer, and electron transport layer to become less efficient and perform at a slower rate[15]. Additionally, these conditions could cause for ion migration within PSCs to be negatively impacted, for when placed in conditions with immense oxygen or water, the structural stability of the PSC can be altered. This alteration means that holes can be created within the lattice of the PSC and therefore cause for ions and electrons to escape, meaning that the PSC itself will not be able to harvest as much light photons[14,22]. These factors need to be considered and addressed when attempting to make PSCs commercially available, for these conditions will be experienced daily.

1.4 Other Commercial Limitations

Another drawback of perovskites that researchers still need to continue addressing is the sustainability of the cells. Most of the materials composing PSC including lead, and cesium are toxic and excrete substances that can end up harming our environment. New techniques can be developed in the future so that we can mass produce perovskites made out of different materials. Even though massive progress has been made in the perovskite field there are still minor improvements that we can make in order to improve their commerciality in the following couple of years. Another limitation for commercialization is the problem that to develop these thin PSC films, a high temperature is required. In order to make the commercialization process more efficient and cost effective, these materials must be able to be manufactured under lower temperature conditions.

2 Conclusion

Overall, perovskites as solar cells have been critical materials in the photovoltaic industry. Their versatility as well as their high PCE have made them desirable in the eyes of researchers and manufacturers. When dealing with solar cells, tandem perovskite and silicon cells have a higher PCE of over 30% as well as an increased stability. The different stabilizing techniques have all shown improvements in PSC but using a combination of these methods leads to even greater progress. For example, combining doping or using a ligand exchange on a perovskite tandem cell provides even more stability to the cell than solely using one.

With the right time and energy, perovskites could also make large improvements to the LED industry. Their LEDs applications could improve smart technology, handheld devices, homes, and more. The possibilities of perovskites is what truly makes them fascinating. Their adaptable and flexible structures and functions make them able to be modified and applied in many different photovoltaic applications. Arguably one of the most , proving to be one of the promising semiconductors of the time, perovskites continue to evolve and develop, bringing change to the fields of solar cells, LEDs, photocatalyts, and more.

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