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MODERN PEROVSKITE SOLAR CELLS: INNOVATIONS IN MATERIALS AND TECHNOLOGIES FOR ENHANCED EFFICIENCY

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Abstract. This review analyzes current research on perovskite solar cells as an alternative to traditional silicon-based solar cells. The paper discusses various types of solar cell architectures, including different combinations of the main layers, materials for electron and hole transport, as well as the anode, cathode, and conductive substrates. Different approaches to improving the stability and efficiency of these cells are examined through the use of new innovative materials for electron and hole transport layers (ETL and HTL), such as organic and inorganic analogs, as well as tandem and heterostructural elements. A review of the performance and limitations of solar cells with various perovskite materials, including hybrid ones, is also provided. A key issue discussed in the paper is the enhancement of the stability of perovskite solar cells, which can degrade significantly under the influence of moisture, ultraviolet light, and heat. The conclusion is drawn that the use of coatings, additives, and innovative materials contributes to the improvement of the stability of high-efficiency perovskite solar cells. The role of

ETL and HTL in enhancing the efficiency and stability of solar cells is also analyzed. The paper emphasizes the importance of research in the field of perovskite solar cells for the development of new efficient, stable cell structures for mass production and commercialization.

Key words: perovskite solar cells, layers, ETL, HTL, $MAPbI_3$, conducting substrate, stability, Spiro-OMeTAD, ultraviolet, absorption coefficient

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ҚАЗІРГІ ЗАМАНҒЫ ПЕРОВСКИТТІ КҮН БАТАРЕЯЛАРЫ: ТИІМДІЛІКТІ АРТТЫРУҒА АРНАЛҒАН МАТЕРИАЛДАР МЕН ТЕХНОЛОГИЯЛАРДАҒЫ ИННОВАЦИЯЛАР

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Аннотация. Бұл шолуда авторлар дәстүрлі кремний негізіндегі күн батареяларына балама ретінде перовскитті күн батареялары бойынша заманауи зерттеулерді жан-жақты талдайды. Күн батареяларының әртүрлі архитектуралары, соның ішінде негізгі функционалды қабаттардың түрлі комбинациялары, электрондық және кемтіктік тасымалдау материалдары, анод, катод және өткізгіш субстраттар қарастырылады. Перовскитті күн батареяларының тиімділігі мен тұрақтылығын арттырудың инновациялық тәсілдері зерттеледі. Атап айтқанда, электрондық және тесіктік тасымалдау қабаттары (ETL және HTL) үшін жаңа материалдарды пайдалану, органикалық және бейорганикалық аналогтарды қолдану, тандемдік және гетероқұрылымды элементтерді енгізу қарастырылады. Сонымен қатар, әртүрлі перовскитті материалдардан, оның ішінде гибридті құрылымдардан жасалған күн батареяларының өнімділігі мен олардың негізгі шектеулері сарапталады. Бұл элементтердің тұрақтылығы ылғал, ультракүлгін сәуле мен температураның әсерінен айтарлықтай төмендеуі мүмкін. Сондықтан, зерттеулер жабындарды, қоспаларды және инновациялық материалдарды қолдану маңызды екенін көрсетеді. Зерттеу барысында ETL және HTL қабаттарының күн батареяларының тиімділігі мен ұзақ мерзімділігіне тигізетін әсері жан-жақты талданады. Перовскитті күн батареяларының негізгі мәселелерін шешу үшін жаңа технологиялар, тұрақтандырғыш қоспалар мен қорғаныс қабаттарын қолдану перспективалы бағыттардың бірі болып саналады. Қорытындылай келе, жоғары тиімді және тұрақты перовскитті күн батареяларын жаппай өндіру мен коммерцияландыру үшін жаңа құрылымдарды әзірлеу қажеттілігі атап өтіледі. Перовскитті күн батареялары технологияларын ілгерілету жаңартылатын энергия көздерін дамытуда маңызды рөл атқарады, жаппай өндіруге, коммерцияландыруға және болашақтың энергия жүйелеріне интеграциялауға жаңа мүмкіндіктер ашады.

Түйін сөздер: перовскитті күн батареялары, қабаттар, ETL, HTL, $MAPbI_3$, өткізгіш субстрат, тұрақтылық, Spiro-OMeTAD, ультракүлгін, сіңіру коэффициенті

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СОВРЕМЕННЫЕ ПЕРОВСКИТНЫЕ СОЛНЕЧНЫЕ ЭЛЕМЕНТЫ: ИННОВАЦИИ В МАТЕРИАЛАХ И ТЕХНОЛОГИЯХ ДЛЯ ПОВЫШЕНИЯ ЭФФЕКТИВНОСТИ

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Аннотация. В данном обзоре рассматриваются современные исследования в области перовскитных солнечных элементов, которые являются перспективной альтернативой традиционным кремниевым фотоэлементам. Особое внимание уделяется различным архитектурам солнечных элементов, включая комбинации основных слоёв, материалов для транспортировки электронов и дырок (ETL и HTL), таких как органические и неорганические аналоги, а также тандемные и гетероструктурные элементы.

Анализируются различные методики повышения стабильности и эффективности перовскитных солнечных элементов, включая применение инновационных органических и неорганических аналогов транспортных слоёв, а также использование тандемных и гетероструктурных решений. В обзоре оцениваются характеристики и ограничения солнечных элементов, созданных на основе различных типов перовскитов, включая гибридные структуры.

Одним из ключевых вопросов является повышение стабильности данных элементов, поскольку они подвержены деградации под воздействием влаги, ультрафиолетового излучения и тепловых факторов. Сделан вывод о важности применения защитных покрытий, функциональных добавок и новых материалов для увеличения стабильности высокоэффективных солнечных элементов.

Рассматривается значительная роль ETL и HTL в улучшении рабочих характеристик солнечных элементов. Подчёркивается необходимость дальнейших исследований для создания надёжных, энергоэффективных солнечных элементов, обеспечивающих высокую производительность. Продвижение технологий перовскитных солнечных элементов играет важную роль в развитии возобновляемых источников энергии, открывая новые возможности для массового производства, коммерциализации и интеграции в энергосистемы будущего.

Ключевые слова: перовскитные солнечные элементы, слои, ETL, HTL, $MAPbI_3$, проводящая подложка, стабильность, Spiro-OMeTAD, ультрафиолет, коэффициент поглощения.

Introduction

The global consumption of electrical energy increases daily, necessitating alternative energy sources to address its shortage. A classical renewable source is solar energy, generated through solar cells. Perovskites, named after the Russian scientist L.A. Perovsky, have a specific formula of ABX_3, where X represents oxygen or a halogen, and A and B are cations. The larger cation (A) occupies a cuboctahedral site surrounded by 12 anions (X), while the smaller cation (B) occupies an octahedral site, sharing it with six cations (Park, 2015).

Due to their remarkable optoelectronic properties, perovskites have emerged as potential materials for solar cells. Currently, three generations of solar cells exist: (1) wafer-based, (2) thin-film-based, and (3) organic-structure-based (Suresh Kumar, 2021). The evolution of photovoltaic materials focuses on reducing cost and toxicity. Various materials have been utilized, including multicrystalline silicon (mc-Si cells), monocrystalline silicon (c-Si cells), copper indium gallium selenide (CIGS), cadmium telluride solar cells, quantum dot-based cells, organic photovoltaics, and perovskite solar cells.

Silicon-based solar cells have dominated so far; however, a new class of perovskite solar cells has become a promising alternative, achieving an efficiency of 22.1%. Perovskites possess an ideal bandgap for light absorption (1.3–1.5 eV), a high absorption coefficient (10^4–10^5 cm^{-1}), energy alignment compatibility with contact materials, excellent charge carrier mobility, and long carrier lifetimes. Furthermore, their ability to be solution-processed at low temperatures significantly reduces production costs. In addition to being cost-effective, perovskite solar cells are highly convenient due to their technological simplicity and ease of roll-to-roll (R2R) processing (Elumalai, et al., 2016)

Organic-inorganic hybrid halide perovskites were first used in photovoltaic cells as sensitizers, replacing dyes in dye-sensitized solar cells (DSSCs). In 2009, they achieved a power conversion efficiency (PCE) of 3.8%. Since then, the efficiency of perovskite solar cells has significantly increased, reaching 22.1% by 2016 and 25.5% by 2020. This progress was accompanied by continual modifications to the materials used in the cell layers.

In 2009, $CH_3NH_3PbI_3$ was the primary material, and platinum was used as the cathode to complete the electrical circuit. By 2016, scientists replaced the core material with doped perovskite $Csx(MA_{0.17}FA_{0.83})_1–x(PbI_{0.83}Br_{0.17})_3$ and substituted the platinum cathode with gold. To improve efficiency, the precursor solution concentration, which was insufficient at 8% for forming a uniform thin film, was increased to 40%, and the liquid electrolyte was replaced with a solid-state analog.

Efforts to enhance the stability of perovskite solar cells and develop lead-free alternatives have been ongoing. However, lead-free perovskite cells have so far achieved only 11% efficiency (Wu T. et al, 2021).

Perovskite solar cells have reached their highest efficiency to date by integrating key features of innovative architectures, advanced chemical compositions, and optimized deposition processes for perovskite materials, alongside newly developed electron and hole transport layers (Seo, et al., 2016).

For the infrastructure of molecular cells the inverted structures with molecular hybrid at the buried interface are used (Liu, et al., 2024). So the steady-state efficiency of 26.54% was reached. When double-side 2D/3D heterojunctions are placed in inverted perovskite solar cells from both sides the power conversion efficiency of 25.6% was achieved too (Azmi, et al., 2024). Another method is described in (Guixiang, et al., 2023), where solar cell improved with using the ordered dipolar structure of β-poly(1,1-difluoroethylene). Thus the perovskite film is able to be controlled from crystallization and energy alignment.

Despite extensive research into advancing perovskite solar cells, significant challenges remain. To make these cells suitable for practical applications, numerous issues must be addressed, including minimizing charge separation, transport, and collection losses. Next table allows to compare new technologies in the field of perovskite solar cells efficiency (Table 1).

Table 1. Modern technologies in the field of perovskite solar cells

Method	Advantages	Limitations
Silicon nanoantennas	- leads to high light concentration (20.5%).	- Requires integration of nanoantennas into existing manufacturing processes.
Tandem cells with perovskite and silicon	- Achieves over 30% efficiency by optimizing perovskite deposition on silicon using phosphonic acid additives.	- Complex production and stability challenges in combining both materials.
Amidinium protective coating	- Enhancing durability, lifespan compared to traditional coatings.	- Further research needed to confirm long-term stability under real-world conditions.
Integration of gold nanograting and photonic crystal	- Increases solar cell efficiency by 35% due to enhanced optical properties.	- Higher production cost due to the use of gold.
Inverted structures with molecular hybrid at the buried interface (Liu S. et al, 2024)	- Steady-state efficiency of 26.54% by improving the molecular infrastructure of the solar cell.	- Complex fabrication and material selection challenges.
Double-side 2D/3D heterojunctions in inverted perovskite solar cells (Azmi R. et al, 2024)	- Reaches 25.6% power conversion efficiency by optimizing the interface from both sides.	- Stability and large-scale manufacturing challenges.
Ordered dipolar structure of β-poly(1,1-difluoroethylene) (Guixiang L. et al, 2023)	- Enhances crystallization control and energy alignment of the perovskite film, improving efficiency.	- Requires precise control over polymer structuring during fabrication.

In this review, we analyze global research and developments related to the structure, architecture, materials, and stability enhancement of perovskite solar cells.

Materials and methods

The foundational technology for perovskite solar cells is solid-state sensitized solar cells, which are based on dye-sensitized solar cells (DSSCs) developed by Grätzel. The key distinction of perovskite solar cells is that the light-harvesting dye is replaced with a perovskite material. Since perovskites exhibit ambipolar properties, they not only absorb light effectively but also require efficient electron and hole transport. To address this, layers such as the ETL (Electron Transport Layer) and HTL (Hole Transport Layer) are utilized.

A solar cell is composed of the following layers: a conductive substrate (such as Fluorine-doped Tin Oxide (FTO), Indium Tin Oxide (ITO), aluminum, nickel, graphene, etc.), an electron transport and light absorption layer (bl-TiO_2 and mp-TiO_2), a perovskite active layer that generates electrons, a hole transport layer (HTL), and a cathode that completes the electrical circuit (e.g., Pt, Au).

There are various solar cell structures based on the layer sequence, such as n-i-p (a) or p-i-n (b), as well as configurations with or without the HTL (c) or ETL (d) (Figure 1).

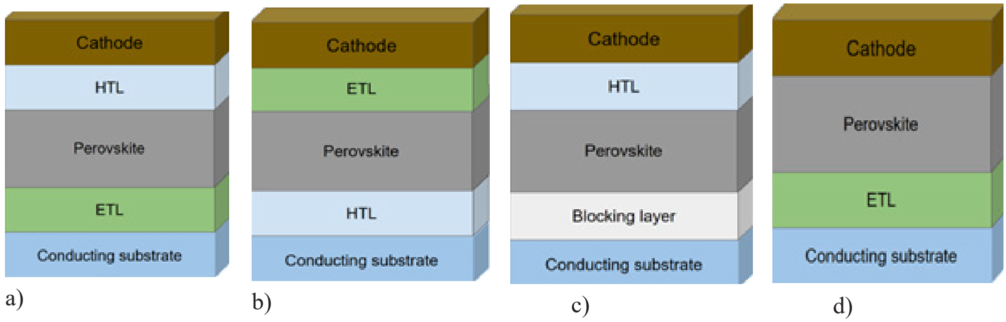

Figure 1. The typical structures of perovskite solar cells

In structures without an HTL, a thin metal layer (cathode) is directly deposited onto the perovskite. Due to the very slow chemical reaction between the perovskite and the metal, the perovskite layer functions as a hole-conducting material.

In structures without an ETL, the perovskite is directly deposited onto the glass substrate, typically FTO or ITO.

The energy structure of the simplest solar cell with both an ETL and HTL is illustrated in the following diagram (Figure 2).

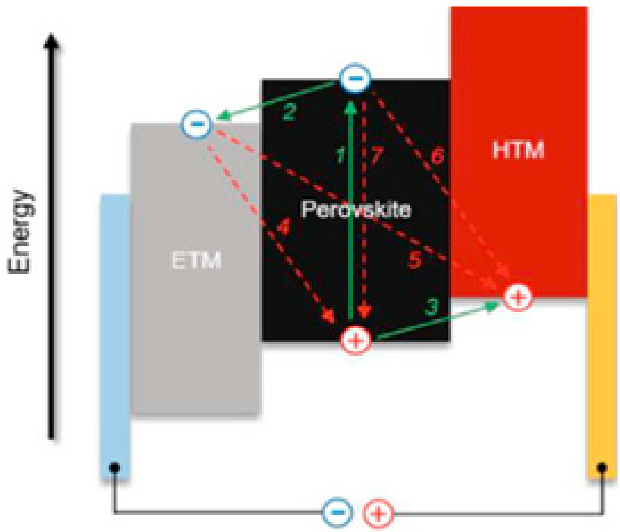

Figure 2. Energy Levels of the Layers in a Simplest Perovskite Solar Cell (Ameen S. et al, 2018)

ETL and HTL materials are selected according to this diagram.

Results and discussion

The base material for perovskite solar cells was the classic lead-containing $CH_3NH_3PbI_3$, which was produced using a two-step deposition method by immersing TiO_2/Al_2O_3 films in a 2-propanol solution of CH_3NH_3I. This resulted in an efficiency of 15%. Later, Ima developed a two-step centrifugation procedure to obtain $CH_3NH_3PbI_3$ cuboids of controlled size, achieving a PCE of 17.0%.

Traditional lead-containing solar films exhibit high efficiency but are highly toxic. To address this, tin-based perovskite films with the general formula $ASnX_3$ were developed. This demonstrated good charge mobility and a high absorption coefficient but faced issues with the oxidation of Sn^{2+} to Sn^{4+}.

One study proposed a method for forming uniaxially oriented perovskite layers with millimeter-sized crystals using methylamine gas for crystallization. By controlling the evaporation rate of methylamine from the liquid intermediate phase, it was possible to reduce supersaturation and decrease nucleation density, which promoted the growth of large grains of $MAPbI_3$. As a result, perovskite layers with grains approximately 1 mm in size were obtained, leading to a low defect density and a high solar cell efficiency (21.36%) (Park, et al., 2015).

A good alternative to the primary perovskite material $CH_3NH_3PbI_3$ ($MAPbI_3$) is $CH_3NH^+(NH_2)PbI_3$ ($FAPbI_3$). This perovskite is also attractive due to its thermal stability and stronger p-type characteristics. Researchers managed to maximize light absorption by using the bandgap of $FAPbI_3$, which is 1.47 eV. They substituted FA cations with 0.03 molar fraction of Cs, achieving stability in the α-phase of $FAPbI_3$ and significantly increasing absorption in the ultraviolet range (Elumalai, et al., 2016).

To stabilize the perovskite phase, a mixed form $(FAPbI_3)_{1-x}(MAPbBr_3)_x$ is more acceptable.

In addition to $MAPbI_3$, $MAPbBr_3$ is also used as a primary perovskite material. Scientists have managed to modify the bandgap by using a mixed perovskite $(MAPbI_3)_{1-x}(MAPbBr_3)_x$, varying it from 1.57 eV to 2.29 eV. Designing the bandgap is a crucial process as it helps prevent significant energy los Prasanna R. ses. Moreover, this mixed structure proved to be highly resistant to perovskite decomposition into its initial precursors due to moisture exposure.

Recently, lead-free perovskite structures, such as $MASnI_3$, have gained the most attention. Unlike $MAPbI_3$, they have an ideal bandgap width (1.3 ~ 1.4 eV), low exciton binding energy (29 meV for $MASnI_3$ and 62 meV for $MAPbI_3$), and high charge carrier mobility (μe (electron mobility) = 2000 $cm^2 V^{-1} s^{-1}$ for $MASnI_3$ and 60 $cm^2 V^{-1} s^{-1}$ for $MAPbI_3$).

The following table presents the main perovskite materials used in solar cells, their efficiency, and advantages (Table 2).

Table 2. The types of perovskites for use in solar cells (Khatoon, et al, 2020, Sharif, et al, 2023)

Type of perovskites	**Formulas**	**Efficiency %**	**Drawbacks**
Meta-lead perovskites	$CH_3NH_3PbI_3$	25,7	Lead toxicity
Meadorresin perovskite	$CH_3NH_3PbI_3$	23	Decreased stability under moisture and ultraviolet radiation exposure
Tin-based perovskite	$CH_3NH_3SnI_3$	13-15	High oxidizing ability
Calcium-based perovskite	$CaTiO_3$, $CaCu_3Ti_4O_{12}$, $CaMnO_3$	15	Mass production and instability
Potassium-based perovskites	$KPbI_3$, $\mathbf{KC_6H_5CH_2I_3}$, $K_4Pb_3I_{12}$, $CsKPbI_3$	20-23	At the research stage

Perovskites with a binary system	$CsPbI_3$, **$CsPbBr_3$,** $MAPbI_3$, $MA_4Pb_3I_{12}$, $CsSnI_3$, $CsSnBr_3$	23	Instability
Hybrid perovskites with organic additives	$CH_3NH_3PbBr_3$, **$C_6H_5C_6H_4NH_3PbI_3$, $CH_3NH_3PbCl_3$**	24-25	Decreased stability under moisture and ultraviolet radiation exposure

In the pursuit of enhancing stability, researchers have also developed tandem structures that incorporate variations of several types of base materials. Tandem structures can be classified into silicon-perovskite and perovskite-perovskite types. The former is utilized to reduce the reflectivity of the device and stabilize the wide bandgap of perovskite materials.

Heterostructures with two or three layers of perovskites are less efficient compared to silicon-based structures but are advantageous for commercialization. This is because the same surface processing technology is applied, while the perovskites within the cell differ in their bandgap widths, for instance, $MAPb_{I3}$ and $MABr_{I3}$ (Elumalai, et al., 2016).

One of the key components of such cells is the electron transport layer (ETL), which plays a critical role in enhancing photovoltaic performance. This layer ensures efficient electron transfer from the perovskite layer to the electrodes, minimizing charge losses and preventing backflow. The choice of material for the ETL is a crucial step in the development of solar cells, as it affects characteristics such as energy level alignment, device stability, and overall efficiency.

In most cases, TiO_2 has been recognized as the primary ETL material due to its excellent ability to transport electrons from the perovskite layer to the electrodes efficiently. Its energy levels are well-aligned with the perovskite bandgap, and it remains transparent for effective solar light absorption. Moreover, the thickness of the TiO_2 film depends on the HTL material since it is proportional to the hole diffusion length and conductivity.

However, the TiO_2 layer was later identified as less stable under UV exposure, significantly reducing solar cell efficiency. As an alternative, $Mg_xZn_{1-x}O$ (MZO) was proposed, demonstrating higher stability and charge mobility compared to titanium oxide.

Additionally, (Park, et al., 2015) showed in their studies that lithium-doped TiO2 could serve as a viable conductive material. Lithium doping reduces the likelihood of defect states and increases the transmittance of the layer. As a result, the efficiency improved to 24.23%, which is 1.97% higher than the undoped counterpart.

Another approach to improving efficiency was the addition of a ferroelectric layer (PbTiO3) between TiO2 and the perovskite to reduce the number of defects and enhance the charge transfer capacity.

Zn_2SnO_4 (ZSO) is a highly promising alternative for ETL due to its reported high Hall mobility of 10–30 $cm^2/(V\cdot s)$, wide bandgap of 3.8 eV, and low refractive index of approximately 2.

Another promising ETL material is (Elumalai, et al., 2016)-Phenyl-C61-butyric acid methyl ester (PCBM).

Recently, tandem solar cells with combinations of multiple layers having different bandgaps for efficient light absorption have gained significant attention in solar cell research. In tandem structures, both the primary layer and ETL or HTL can serve as the tandem component. For instance, in study (Hu, et al., 2020), an efficient electron transport layer was composed of a blocking layer, a mesoporous film, and a fullerene layer (Figure 3, a). The efficiency of such tandem structures can reach up to 30%.

In the work zinc oxide (ZnO) and PCBM were used as tandem components for the electron transport layer (Figure 3, b).

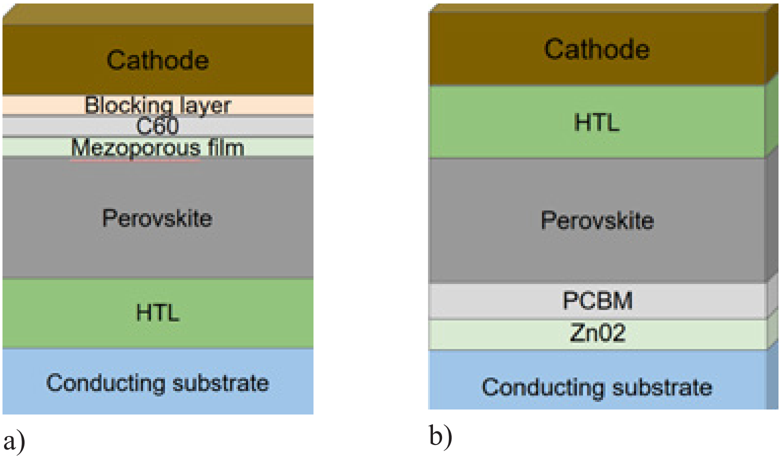

Figure 3. Tandem layers of electron transport

One of the critical layers in the architecture of a solar cell is the hole transport layer (HTL). The HTL plays a pivotal role in enhancing the efficiency, stability, and overall performance of the solar cell by ensuring effective collection and transport of holes while preventing energy losses. Regarding durability, this layer often acts as a moisture adsorbent, protecting the device from degradation.

Initially, liquid electrolytes served as transport materials. Later, Kim et al. developed the first solid-state transport materials with a structure of 2,2′,7,7′-tetrakis (N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene (Spiro-OMeTAD).

The classic HTL materials in perovskite solar cells include Spiro-OMeTAD and its derivatives, such as pp-Spiro-OMeTAD, mp-Spiro-OMeTAD, and op-Spiro-OMeTAD. However, due to its high cost and limited commercial viability, researchers continue to develop more efficient and cost-effective alternatives.

One example is polytriarylamine (PTAA) doped with lithium (Battaglia, et al., 2016). For undoped materials, a derivative of pristine tetrathiafulvalene (TTF-1) achieved an efficiency of 11%, while a graphene-based composite P3HT/graphdiyne reached 14.6% (Hu, et al., 2020).

Inorganic HTL alternatives, such as CuI and CuSCN, have also been identified as promising substitutes for Spiro-OMeTAD.

The use of polymers as HTL materials is justified by their excellent compatibility with the energy band of perovskite, which facilitates efficient hole extraction. Their soft and flexible nature ensures reliable contact with the base material, minimizing energy losses.

Due to the presence of numerous active sites, polymers exhibit strong intergranular interactions. As a result, polymer-based photovoltaic devices demonstrate superior stability and improved power conversion efficiency (PCE).

In study (Tseng, et al., 2020), Cu_2O was used as the hole transport material and SiO_2 as the electron transport material. Typically, the HTL layer must be sufficiently wide to cover the entire surface of the perovskite before being coated with a copper cathode. A thin HTL layer usually has a thickness of 100–300 nm.

Among polymeric materials suitable for mass production, PEDOT: PSS (poly (3,4-ethylenedioxythiophene): polystyrene sulfonate) has proven to be the most accessible. However, despite its affordability, it is less stable compared to Spiro-OMeTAD.

HTL materials and noble metals are often prohibitively expensive for large-scale applications. To address this, researchers have proposed carbon-based architectures without an HTL layer (Tseng, et al., 2020). In these designs, perovskite films were created using a multi-step spin-coating solution process, with a carbon layer directly deposited after the perovskite layer.

For ETL layers, polymers such as polymethyl methacrylate (PMMA), polyethylene oxide (PEO), polyvinylpyrrolidone (PVP), and polyethyleneimine (PEI) have been studied.

Equally important in the solar cell structure are the anode and cathode. Table 2 provides an overview of the materials used for the anode and cathode in perovskite solar cells.

Table 2. Materials of anode and cathode of perovskite solar cell

Architecture	**Anode**	**Cathode**
n-i-p	FTO, ITO	Ag, Au, Al, or ITO
p-i-n	PEDOT:PSS, MoO_x, Au	ITO, Al, Ag

The choice of anode and cathode materials is closely tied to the architecture of the solar cell. For instance, in n-i-p structures, cathode materials may include gold, silver, or aluminum, while conductive substrates typically involve FTO (fluorine-doped tin oxide) or ITO (indium tin oxide). In inverted designs, gold and aluminum can serve as cathode and anode materials, respectively, with ITO as the conductive substrate.

The selection of cathode and anode materials varies due to their specific requirements for energy levels, transparency, and stability. Choosing the appropriate materials is critical for achieving high efficiency and long-term durability in solar cells.

The issues of stability of solar cells.

Despite extensive research into improving solar cell materials, stability issues still require careful attention.

The instability of perovskite solar cells hinders their commercial deployment, as the materials are prone to degradation due to weak bonds between components. This degradation can lead to damage and the leakage of lead, posing risks to both health and the environment.

To address this, researchers have developed lead-absorbing materials to coat the perovskite layer. Among these materials, cation exchange resin (CER) has demonstrated excellent lead ion absorption capabilities.

Perovskite solar cells are highly susceptible to degradation when exposed to two key atmospheric components: O_2 and H_2O. Changes in the chemical composition of perovskite films can result in a color shift from dark brown to yellow.

In the classical perovskite $MAPbI_3$, hydrolysis occurs when the material comes into contact with moisture. This process causes $MAPbI_3$ to decompose into PbI_2 and MAI, with MAI further breaking down into CH_3NH_2(aq) and HI(aq), significantly reducing efficiency.

Wang et al. proposed coating the perovskite with a thin layer of Al_2O_3. Samples with this aluminum oxide layer retained their efficiency, while those without it experienced nearly a 50% efficiency loss.

Another approach to improving stability involves substituting I with Br in $MAPbI_3$. Due to Br's smaller ionic radius compared to iodine, the lattice stability increases, consistent with Goldschmidt's tolerance factor rule.

Park et al. investigated the hydrophobicity of perovskites using an anti-reflective lotus leaf-inspired hierarchical pyramidal array made from polydimethylsiloxane (PDMS).

An alternative method for enhancing stability involves the use of mesoporous Al_2O_3 and TiO_2. When generated electrons interact with air, superoxides form, accelerating the decomposition of $MAPbI_3$. TiO_2 mitigates this process by enabling electron injection, thereby slowing degradation.

A research group led by Yang demonstrated high stability in solar cells where the HTL was NiO_x and the ETL consisted of ZnO nanoparticles.

Perovskites not only degrade under air exposure but also under heat. Thermal degradation occurs both through the decomposition of components and the formation of internal defects. Thermogravimetric analysis revealed that $MAPbI_3$ has poor thermal conductivity, meaning thermal energy can induce defects within the crystal structure, significantly lowering efficiency.

Studies have shown that doped samples, such as $MAPbI_3{-}xBr_x$ and $FAPbI_3$, exhibit greater thermal stability compared to classical $MAPbI_3$ (Park, et al., 2015).

HTLs significantly influence the thermal stability of solar cells, and recently, research has focused on developing solar cells without HTLs. One such HTL material, silolothiophene-linked triphenylamines (Si-MeOTAD), has been found to be more stable than Spiro-OMeTAD and Spiro-MeOTAD.

Researchers have concluded that one of the main ways to enhance the thermal stability of solar cells is through the use of HTL-free designs or by utilizing carbon-based materials for the cathode. These materials conduct heat well and help with efficient thermal dissipation within the device. Graphene is a leading material in this group (Park, et al., 2015).

Another important aspect of solar cell stability is photostability. The ETL material TiO_2 is less stable than Al_2O_3 due to the recombination of electrons from the conduction band of TiO_2 with holes in TiO_2. In contrast, Al_2O_3 has shown long-term stability, lasting 1,000 hours at 40°C. $FAPbI_3$ has demonstrated greater photostability than $MAPbI_3$.

Additive engineering, or the incorporation of molecules, is another method for improving stability. These additive molecules create additional chemical interactions with volatile components, reducing ion migration and preventing irreversible degradation of perovskite films. For example, adding 5-ammoniumvaleric acid (5-AVAI) helps prevent the loss of methylamine and recrystallization of $MAPbI_3$, while adding an organic ionic salt compound $[BMP]^+[BF_4]^-$ aids in stabilizing and suppressing degradation phases, thus improving the longevity of solar cells and preventing iodine and lead leakage.

Using heterostructures between the main layers of a solar cell, particularly between perovskite and the ETL, can significantly enhance structural stability, the ETL was treated with a dicalcium salt of ethylenediaminetetraacetic acid (EDTAK), which greatly reduced defect density in the perovskite layer through interaction with Pb^{2+}. It also shifted the minimum of the SnO_2 conduction band from −3.69 eV to −3.95 eV. The perovskite/Spiro-OMeTAD heterostructure surface was treated with methylammonium iodide, preventing degradation caused by gold penetration into the perovskite layer.

Conclusion

Perovskite solar cells have recently emerged as a promising alternative to traditional silicon cells due to their physical and chemical properties. They possess an ideal bandgap, high absorption coefficient, energy alignment with the contacting material, and high charge carrier mobility. For commercialization, perovskite solar cells offer relatively inexpensive base material alternatives. The combination of anions and cations in the perovskite structure enables the achievement of desired properties, facilitating the design and performance prediction of modern solar cells.

Since the introduction of perovskites as potential materials for solar energy conversion, the architecture, layer combinations, and composition of solar cells have undergone numerous changes to enhance efficiency (<25%), stability, and commercial viability. Solar cells have been explored from classic lead-based perovskites to hybrids with organic additives.

The architecture of the layers, particularly the ETL and HTL, is crucial, as their bandgap must align with that of the perovskite, ensuring high charge carrier mobility and ease of processing. Traditionally used titanium oxide as the ETL and Spiro-OMeTAD as the HTL are highly efficient; however, they have shown sensitivity to moisture and ultraviolet radiation. Therefore, global research in electron and hole transport materials for solar cells has focused on increasing stability, considering both organic and inorganic alternatives, doped materials, heterostructures, tandem structures, base material coatings, and other innovations.

All of these studies contribute to significant advancements and innovations in solar energy conversion, driving progress in the efficiency, stability, and cost-effectiveness of perovskite solar cells.

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