A review of the progress of metal-organic frameworks in perovskite solar cells

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Abstract:

Organic-inorganic hybrid perovskite solar cells (PSCs) have emerged as substantial challenges for future generations of photovoltaic apparatus, largely attributed to their power conversion efficiency (PCE) drastically elevated from below 10% to a staggering 25.7% over the past decade. Owing to characteristics distinct to them like substantial specific surface areas, copious binding locations, adjustable nanostructures, and mutual reinforcement, metal-organic frameworks (MOFs) are commonly utilized as either supplementary components or operational layers for augmenting both the efficiency and durability of PSCs. This paper primarily underlines the recent advancements in implementing MOFs across various operational strata of a PSC. The focal points of this study encompass an examination of the photovoltaic yields, the repercussions, and the advantages of fusing MOF materials into constituents like perovskite absorbers, electron transport, and hole transport layers, in addition to interface layers. The study also extends to an exploration of how MOFs effectively inhibit leakages of Pb^{2+} within halide perovskites and their associated apparatus. This paper concludes by discerning and shedding light on potential research prospects for the deployment of MOFs in PSCs.

Keywords: metal-organic frameworks;perovskite solar cells;electron transport layer;hole transport laye.

1. Introduction

Photovoltaic technology, particularly that which encompasses solar cells, represents a sustainable and eco-friendly approach to energy generation. This technology facilitates the direct conversion of photonic energy from sunlight and other light sources into electrical power. The perovskite solar cells (PSCs) Perovskite solar cells have become the most favorable competitors in the field of next-generation photovoltaics by their unique and excellent photoelectric performance. So far, the efficiency of solar cells has gone from an initial 3.8% to an impressive 25.7%.[1]

The perovskite crystal exhibits ABX3 structure, in which methylammonium (MA^+) or formamidine (FA^+) ions are often used as the A site, while the B site is occupied by metallic ions, such as lead (Pb^{2+}) or tin (Sn^{2+}). Iodide (I^-), bromine (Br^-), or chloride (Cl^-) are generally considered to be in the X position.[2] Metallic electrodes composed of gold (Au), silver (Ag), or copper (Cu) complete the structure. PSC devices exhibit either an N-I-P (normal) or P-I-N (inverted) configuration, with ETL and HTL further delineated into either planar or mesoporous geometries. Under specific power input conditions, the perovskite layer is responsive to solar irradiation, leading to the generation of excitons, or electron-hole pairs. These excitons undergo dissociation and subsequent collection by the ETL and HTL,[3] with potential recombination occurring as well. The transfer of collected charge carriers to the external circuit is mediated by the electrode, culminating in the delivery of electrical power to the load.

The superior functionality of PSCs is principally accredited to the inherent integrity of each distinct operational stratum. The perovskite absorption layer must boast a formidable absorption capability and minimal carrier recombination to proficiently amass photons and transport carriers. Utilization of highly crystallized perovskite could potentially enhance photo-capture efficiency and perovskite grain crystallinity, optimizing charge separation proficiency and curbing the density of defective states spanning all layers. The efficiency of charge extraction in ETL and HTL is predominantly influenced by the interaction occurring between the perovskite absorber and the charge transport layer (CTL).[4] Furthermore, the efficacy of charge transference of carriers in CTL is contingent upon the mobility and stability of CTL, having a consequential impact on the ultimate efficiency of the device. Preceding studies have proposed the implementation of energy level matching strategies to alter the interface layer, thus enhancing charge collection efficiency.

Perovskite Solar Cells (PSCs) are an attractive option for producing efficient and cost-effective photovoltaic technologies. Despite their potential, commercialization efforts are stalled owing to several associated challenges. Notably, the Power Conversion Efficiency (PCE) of PSCs needs to exceed 25.7% to compete with cutting-edge silicon-based solar cells currently leading at 26.7%. This is largely due to inevitable losses during charge carrier transport such as non-radiative recombination and carrier capture within the perovskite layer or the charge transport layer (CTL). Consequently, PSC efficiency remains subpar compared to radiation limit predictions. Moreover, PSCs exhibit compromised durability in extreme conditions as per IEC standard 61215, such as those involving heat treatment at 80℃, 85% relative humidity, and exposure to $1kW/m^{-2}$ sunlight.[5] Moisture in the perovskite layer triggers the invasion of water molecules into the perovskite lattice which subsequently attack the organic components and result in decomposition into PbI2 and volatile organic elements such as MA, HI, NH_3, and I_2. Additionally, illumination engenders the production of light-excited electrons and O_2 molecules that form superoxide (O_2), thereby affecting the organic components and instigating degradation. Exposure to thermal stress further aggravates degradation. Charge transport layers, typified by Spiro OMeTAD or PCBM, may also exhibit signs of deterioration under the aforementioned extreme conditions. Therefore, one must focus on enhancing the endurance of perovskite and CTL layers within the operating environment to extend the lifespan of PSCs over a consecutive twenty-year period for effective commercialization. Further concerns are presented by the potential toxicity of lead and its consequent environmental impact. Lead ions (Pb^{2+}) within PSCs demonstrate lipid solubility, necessitating preventive measures against accidental lead leaching from halide perovskites and their derivatives.[6] Common practices to offset the deleterious consequences of lead in PSC involve the employment of lead-absorbent materials, the application of physical coatings, and the recovery of contaminated lead.

2. Metal-organic frameworks (MOFs)

In recent decades, metal-organic frameworks (MOFs) have developed rapidly, and their heat has not decreased, making them the undisputed "fragrant chicken" in the field of materials. However, conductive MOFs break the almost non-conductive constraints of MOF materials, perfectly combining the structural control of organic materials with the long-range ordering of inorganic materials. Coupled with their unique high electron mobility, conductive MOFs can be described as a collection of thou-

sands of types of PET. Since the first conductive MOF was reported in 2009, this material has quickly caught the attention of top researchers, and significant figures such as Mircea Dinca have also conducted research. However, it was not until 2015 that the conductivity of conductive MOFs reached 1580 S cm^{-1},[7] fully meeting the requirements of various electrical applications. It has indeed sparked a wave of enthusiasm in the field of materials. In just ten years, to be more precise, in just five years, the most popular achievements in conductive MOFs have emerged continuously, and conductive MOFs have ushered in explosive development. They are undoubtedly the rising stars in the materials industry. If you also like to be a pioneer in new fields, conductive MOFs will be a good topic worth exploring. The construction mode of MOFs: Metal ions are connected through organic ligands, which is the main reason for their insufficient conductivity. This article only focuses on MOFs that conduct electricity through electrons and does not include the range of ion conductivity. Introduced the development history, conductive mechanism, construction mode, and application fields of conductive MOFs.

Porous coordination polymers (PCP), MOFs, also known as PCP, have various designable and customizable porous frameworks and pore structures, with large surface area and adjustable functions. It can be said that it is a mixed material of inorganic and organic materials, and its special framework structure has huge application potential in catalysis, batteries, energy storage, and other fields. However, most MOFs are non-conductive, and their extremely low conductivity limits their application in the energy field. In 2009, Professor Hiroshi Kitagawa's research group at Kyoto University in Japan took the lead in conducting MOF research.[8] In 2012, Professor Omar M. Yaghi's research team from the Department of Chemistry at the University of California, Berkeley reported on two-dimensional layered MOF conductivity through π-d conjugation: the conductivity of Cu CAT reached 0.2 S cm^{-1} at room temperature, and conductive MOFs began to be gradually applied in fields such as electrocatalysis, thermoelectric effects, and gas separation.[9] In 2015, researchers of the Institute of Chemistry, Chinese Academy of Sciences reported that the conductive MOF-Cu-BHT reached an ultra-high conductivity of 1580 S cm-1. Since then, the conductive MOF has ushered in a blowout development.[10] In 2018, Professor Bao's research group at Stanford University discovered a class of conductive MOFs with stable performance and simple synthesis methods: Cu HAB and Co HAB, which have excellent performance in capacitors and batteries.[11]

For MOF materials, the increase in carrier concentration can start from the source of carriers, which can be ob-

tained by using high-energy electrons from metal nodes (such as $Cu^{2+}_3d_9$) or ligands with REDOX activity (such as benzoquinoline ligands).[12] The increase in carrier mobility can start from the degree of overlap between orbital space and energy in the MOF, and the increase in orbital overlap can effectively improve the carrier migration ability of the MOF framework; (2) From the perspective of chemical design, the construction of carrier transport channels for conductive MOFs can be divided into two categories: "through space" and "through bonds".

Recent investigations have increasingly focused on the implementation of metal-organic frameworks (MOFs) within the domain of photovoltaic technologies.[13] Indeed, MOFs can be engineered to be compatible with diverse solution-based environments, and their stability can be augmented through the strategic selection of metal ions and organic ligands to strengthen coordination bonds within the framework structure. Consequently, solar cells incorporating MOF components, including organic-inorganic perovskite solar cells (PSCs), dye-sensitized solar cells (DSSCs), and organic photovoltaic cells (OPVs),[14] demonstrate enhanced efficiency and stability owing to the intrinsic physical, optical, and electrical properties of MOFs. The integration of MOFs into solar cell architectures confers several significant benefits: (1) Serving as scaffolds, MOFs offer a high degree of porosity, structural stability, and expansive hosting sites for the inclusion or conjugation of guest species within the framework; (2) MOFs exhibit commendable solvency characteristics, enabling their uniform integration with other precursors via spin-coating methods to fabricate microporous films; (3) The photovoltaic attributes of MOFs are amenable to precise modulation through the manipulation of metal salt and organic ligand compositions. Furthermore, the physical parameters of MOFs, such as particle size, surface area, and pore volume, are amenable to nanoscale adjustments, thus facilitating the enhancement of various functionalities in solar cell devices.

In recent years, the use of MOFs in PSC to improve device efficiency and long-term stability through rational component engineering has attracted widespread attention. Usually, MOFs form microporous scaffolds to regulate the growth of perovskite layers, thereby improving the crystallinity and quality of perovskite.[15] In addition, incorporating MOFs into CTL can improve the band arrangement of PSCs and the conductivity of CTL. Here, we have summarized the latest progress in the application of MOFs in various functional layers of PSC. The main research progress is as follows: 1) MOF as ETL or mixed with ETL; 2) MOF as HTL or mixed with HTL; 3) Mixing MOF and perovskite to form MOF/perovskite hybrid heterojunction; 4) MOFs alleviate Pb leakage. Further ap-

plications of MOF in PSC were discussed.

3. Research on the Application of MOFs

MOFs have been studied not only as components of the perovskite layer in PSCs, but also as potential ETLs, HTLs, or as integrated components within these transport layers. The function of MOFs in the ETL and HTL domains significantly deviates from their use in the perovskite layer, affecting charge separation efficiency, UV region photon capture, and overall device robustness. This section specifically describes and carefully examines the meaning of merging MOFs in the context of ETL.

ETL is crucial for achieving high-performance solar cells as it plays a crucial role in promoting electron conduction and hindering hole conduction. Titanium dioxide (TiO_2) is an n-type semiconductor commonly used in the ETL of PSCs due to its adjustable electronic properties, energy alignment compatible with perovskite structures, inherent optical transparency, and economic feasibility. However, the TiO_2 layer is still plagued by relatively poor conductivity, limited electron mobility, and common defects, including oxygen vacancies and metal gaps at the surface and grain boundaries. This defect hinders effective electron capture and ultimately leads to an increase in the recombination rate of photo-excited charge carriers. To avoid these issues, the research team has used titanium-based metal-organic frameworks (Ti-MOFs) to manufacture porous TiO_2 structures, thereby improving the ETL performance. Hou and his colleagues combined MIL-125 into the framework through a sintering process to synthesize porous-graded TiO_2 nanostructures, resulting in ordered porous-graded TiO_2 (hier-TiO_2). This graded TiO_2 retains some of the organized porosity characteristics of MIL-125 after removing organic ligands, providing a more spacious matrix for perovskite crystallization than traditional compact TiO_2 and nanoparticle TiO_2. It is worth noting that the n-i-p PSC prepared exhibits a significant increase in PCE from 6.4% to 16.6% while enhancing stability under environmental conditions. [16]

In another study, Chen et al. hypothesized the function of zeolite imidazole skeleton 8 (ZIF-8) encapsulated in iodomethane (ZIF-8@FAI) Propose to use it as an intermediate layer between SnO_2 and PbI_2 configurations. ZIF-8@FAI can interact with PbI_2 and form crystal nucleation in perovskite. This process helps to develop perovskite films with enhanced grain size and optimal vertical arrangement. Meanwhile, the nitrogen component of imidazole in ZIF-8 has been identified due to its ability to passivate defects within the perovskite film. Due to these characteristic advantages, the leading experimental unit recorded

a power conversion efficiency (PCE) of 24.08%. [17] Zinc oxide (ZnO) is commonly used as an ETL in perovskite solar cells (PSCs) due to its accessibility and economic advantages. Zhang et al. first introduced MOF-derived zinc oxide (MZnO) as the ETL for PSC.

After 30 days, the residual PCE of aged devices dependent on MZnO was 77% of the initial value. However, according to reports, the PCE of PSC using MOFs as ETL is still not ideal. Future research should mainly focus on the design of MOF materials with excellent electron transfer and energy level arrangement to promote the manufacturing of high-performance perovskite devices. [18]

Ryu and his colleagues utilized nanocrystalline titanium-based metal organic framework (nTi-MOF) particles as ETLs to develop PSCs with n-i-p structures on glass and polyethylene terephthalate (PET) substrates. The film formed by nTi-MOF exhibits excellent transmittance, reaching 97.7% at an optical wavelength of 550nm. In addition, the addition of PCBM significantly improves the conductivity of nTi MOF films. In addition, flexible devices exhibit considerable bending durability and can withstand 700 bending cycles with a radius of 10 mm [19]. To improve the lifespan and operational stability of PSCs, Wu and his team introduced a novel 2D conjugated MOF, ZrL_3, as an ETL at the junction of perovskite and cathode. When ZrL_3 is integrated into the PSC structure composed of indium tin oxide (ITO), phenyl-C61-butyrate methyl ester (PCBM), ETL, and silver (Ag), an increase in efficiency is observed, amplifying it from 18.80% to 20.34%. The improvement in effectiveness is attributed to the improvement in electronic extraction capability, while the seamless integration of ZrL_3 and Ag reduces contact resistance. With the deployment of ZrL_3: bia-C60 as a hybrid ETL, its effectiveness has been further improved to 22.02%, which can be attributed to its excellent plugging ability. In addition, the excellent thermal stability of the 2D ZrL3 layer allows the device to maintain an initial efficiency of over 90% even after 1000 hours of constant light projection at its maximum power point at a temperature of 85℃. In addition, the tendency to degrade lead pollution in perovskite devices is significantly reduced through the formation of water-insoluble solids between ZrL_3 and Pb^{2+}ions. This study indicates that utilizing multifunctional MOFs has the potential to create more stable and environmentally friendly PSCs. [20]

Cao and his colleagues recently published their findings on the deployment of two-dimensional (2D) conjugated MOFs, particularly $Cu_3(HHTT)_2$, as HTL in the tin-lead (Sn Pb) hybrid PSCs. [21] The $Cu_3(HHTT)_2$ ligand has an extended conjugated system that introduces heteroatoms into its structure, promoting strong ligand-to-ligand connections and organized Stacking. These features endow 2D MOFs with superior charge carrier transport characteristics. It is feasible to prepare these 2D MOF films through self-assembly growth techniques that are compatible with widely coated substrate regions. Theoretical studies using density functional theory (DFT) have shown that the presence of C-N groups in MOFs helps to passivate deep anti-site defects, thereby reducing the defect density at the HTL/perovskite boundary. The use of 2D MOF HTL in Sn Pb mixed PSCs resulted in an impressive PCE of 22%. In addition, the PCE of PSCs with an area of 1cm 2 manufactured using this HTL reached 19.86%, which is one of the most commendable achievements of Sn Pb mixed PSCs to date. These results indicate the potential of 2D MOFs as exemplary HTLs for large-scale PSC applications. In addition, MOF derivatives have also shown potential as HTLs in enhancing the stability of PSC. Hazeghi and his colleagues have used MOF-derived core-shells CuO@NiO Nanospheres are used as HTL to construct PSCs with n-i-p configuration. The application of CuO shell on NiO nanospheres reduces the defect state in NiO, thereby alleviating nonradiative interface recombination. Included PSCCuO@NiOHTL Displayed 10.11% PCE and exhibited excellent stability over an extended duration. [22]

The remarkable electron attraction and oxidation ability of POM allows Spiro OMeTAD to directly oxidize under inert conditions. By combining POM with Cu BTC, aggregation and disordered configuration can be prevented, thereby maintaining the oxidation effect. This method promotes controlled oxidation under inert environmental conditions, and compared to the unchanged state, Spiro OMeTAD provides almost twice the hole mobility. Due to improved charge extraction and reduced interface charge recombination, the resulting PSC achieved an efficiency of 21.44%. More importantly, the structural integrity of hybrid power POM@Cu-BTC This framework supports long-term device stability with approximately 90% initial PCE maintained for 30 days after environmental storage. The group subsequently incorporated H3PMo12O40 (POM) into zirconium porphyrin-based MOF-545 to construct a POM-MOF system, which was used as a dopant for Spiro OMeTAD in PSC. The hydrogen bonding formed between POM and Spiro OMeTAD makes it a superior p-type dopant, and due to the improved conductivity and hole mobility, a 21.5% PCE is achieved. In addition, Li and colleagues utilized MOF [In0.5K (3-qlc) Cl1.5 (H_2O) 0.5] 2n (In10) based on quinoline dicarboxylic acid to stimulate Spiro OMeTAD oxidation and improve conductivity. By enhancing charge transfer and minimizing charge recombination, an increase in device efficiency was recorded from 14.1% to 17%. [24]

Subsequent research will integrate various MOFs into spiroOMeTAD to improve efficiency and extend device

durability. Zhou et al. implemented MOF-derived two-dimensional graphite nitrogen-rich porous carbon (NPC) to improve the quality of screw OMeTAD membranes. The significant porosity of NPC promotes the rapid extraction of holes and reduces the recombination of charge carriers, while its inherent hydrophobicity hinders the water-induced degradation of photovoltaic devices.PSCs containing NPCs have demonstrated a PCE of 18.51% and commendable long-term stability. In a related work, Wang et al. explored the use of Li TFSI intrahedral MOFs(Li-TF-SI@NH2-MIL-101)As a dopant to enhance the stability of PSC. The NH_2-MIL-101 framework provides the optimal environment for Li TFSI packaging, thereby protecting it from moisture interactions. In addition, the presence of ammonium groups in MOFs promotes the interaction with $Pb2^+$ions at the boundary of perovskite/HTL, reduces trap states, and inhibits ion migration. The optimized device generated 19.01% PCE with excellent stability, maintaining an initial efficiency of over 85% after 3600 hours of environmental exposure without any protective packaging. In addition, Liu et al. introduced zirconium-based porphyrin MOFs and PCN-224 quantum dots (QDs) into Li-doped spiroOMeTAD matrices to counteract Li^+ion drift. The host-guest coordination between Li^+ions and PCN-224 quantum dots hinders the formation of hygroscopic lithium oxides and inhibits the permeation of Li^+ions into the perovskite domain. This strategic modification resulted in a device that displays 22.51% PCE and has typical operational stability.[25]

In a subsequent study, Zhang et al. incorporated an indium-based anionic metal-organic framework (MOF) FJU-17 containing $(Me2NH_2)$+cations into screw OMeTAD to promote defect passivation in perovskite. The release of (Me_2NH_2)+ions from FJU-17 effectively passivates organic cation vacancies in perovskite materials. At the same time, the anionic structure of FJU-17 plays a role in stabilizing the oxidized form of spiro OMeTAD (spiro OMeTAD$^+$), thereby improving hole mobility. This modification resulted in an increase in the photovoltaic conversion efficiency of PSCs from 18.3% to 20.3%. Recently, Zhang and his colleagues have explored the use of rare earth MOFs, especially Tb FTZB, as additives for snail OMeTAD, to change its electronic properties. The high oxidation state of Tb ions is beneficial for the oxidation of spiro OMeTAD, which improves hole transport within the material. In addition, the nitrogen and oxygen atoms of the tetrazole ligand from Tb FTZB interact with uncoordinated Pb^{2+} ions at the HTL/perovskite interface, providing additional passivation effects. Therefore, the efficiency of photovoltaic devices has increased from 19.44% to 21.31%.

Porous MOF materials can be used as scaffolds to support the crystal growth of perovskite layers. In addition, the organic ligands in MOFs coordinate with Pb^{2+}, I^-, and other components in the perovskite structure, ultimately regulating the crystallization process. This section systematically investigates these interactions and their effects on the formation of perovskites, drawing on recent academic research insights.

Chang et al. integrated zirconium-based porphyrin MOF (MOF-525) nanocrystals of different concentrations into perovskite precursor solutions to design MOF-525/perovskite heterojunction films. The nanoscale MOF-525 particles with a size of approximately 140nm exhibit consistent pore geometry, with an average pore size of 1.8nm. The analysis conducted by X-ray photoelectron spectroscopy (XPS) elucidated the preferential accumulation of MOF-525 nanocrystals towards the substrate of composite MOF-525/perovskite films, indicating that the microporous matrix of MOF-525 promotes the systematic organization of perovskite crystals in the early stages of crystallization. The transition of photoluminescence (PL) spectral emission towards shorter wavelengths indicates enhanced crystallization within the perovskite/MOF-525 matrix.[26] The photovoltaic cells manufactured under these optimized conditions showed a significant improvement in PCE, reaching 14.5% while increasing photocurrent. These observations support the conclusion that the microporous structure of MOF-525 acts as a tissue framework to promote the penetration of precursor solutions, resulting in an ordered perovskite thin film structure. Therefore, adding MOF pore structure to perovskite solar cells is crucial for optimizing device performance.

Lee et al. have publicly disclosed efficient inverted p-i-n perovskite solar cells (PSCs) utilizing perovskite/Zr MOF heterojunctions. Two different zirconium-based MOFs, UiO-66 and MOF-808, were doped into the precursor solution of perovskite. Then, the obtained composite film is directly deposited on the nickel oxide hole transport layer (NiOx HTL) to construct the p-i-n structure of PSC. Further analysis was conducted on the mixed MOFs to evaluate their distribution on perovskite grain boundaries and their effectiveness as surface defect passivation layers. The oxygen lone electron pairs of MOFs effectively passivate defects related to excess Pb^{2+} by coordinating with lead (Pb^{2+}) ions. This interaction enhances the photoluminescence (PL) intensity of the mixed film, making it higher than the original perovskite film, ultimately achieving an impressive 18.01% PCE with minimal lag in the perovskite/UiO-66 hybrid battery. In addition, compared with unhybrid PSCs, these MOF-integrated PSCs exhibit significantly improved stability under environmental conditions (relative humidity of 60±5% at room temperature). This enhanced durability may be due to the grain-locking

phenomenon of the defect passivation layer hindering moisture penetration.

In addition to zirconium-based MOFs, Yang and his colleagues have developed an In (III) based MOF. This is achieved through low-temperature reactions, followed by binding to Pb-based PSCs. This three-dimensional MOF $[In_2 (phen)_3Cl_6]\cdot CH_3CN\cdot 2H_2O$ is referred to as In_2 in the following text. Introducing In_2 into the mixture inhibits the production of $PbI_2(DMSO)_2$; On the contrary, it implies a partial transformation from Pb_2+ to Pb_0. The change in ion formation may reduce the risk of damage to device function caused by Pb_0. In addition, the metal and organic chemical formulas known as In_2 have been shown to have a beneficial enhancing effect on the crystallization process, mainly through the increase in particle size and the reduction of trap states, resulting in favorable changes in PSC morphology. Therefore, the power conversion efficiency (PCE) has significantly improved, from 15.4% to 17.2%. In addition, devices using the In2 formula exhibit higher levels of environmental stability at normal room temperature, with a relative humidity (RH) range of 40-45% for 600 hours, attributed to the hydrophobicity of In2. This dichotomy protects MAPbI3 from unnecessary infiltration of moisture. Yang and his team advanced in-based MOFs by creating $[InI_2O (OH)_{16} (H_2O)_5 (BTC)_6]$ n (In BTC), which helps to form heterojunction perovskite layers. The complex interaction between the interconnected micropores and the terminal oxygen sites in this layer revealed compatibility with Pb^{2+},[27] thereby promoting an environment conducive to perovskite crystallization within the range of regular cavities. This interaction results in excellent crystallinity and reduced grain boundary defects in the obtained thin film. Ultimately, the improved PSC of In BTC increases the fill factor (FF) to 0.79 and the PCE to 20.87%, showing significant improvements compared to the original device (FF: 0.76 and PCE: 19.5%, respectively). Even after 12 days of exposure to environmental conditions of 25°C and approximately 65% relative humidity (RH), this process can still preserve 80% of the initial PCE without the need for packaging.

The recent incorporation of zinc-based metal-organic framework ZnL into the perovskite matrix has demonstrated its practicality in enhancing the passivation of perovskite layers. The structural configuration of ZnL includes acid-base pairs in its coordination environment, characterized by the anionic skeleton $[Zn_2(ox)_3]_2N$ and conjugated cationic supramolecular network $[(Me_2N-H_2)_3SO_4]^+$n. Through density functional theory (DFT) calculations, evidence has been provided for the electron transfer of $[(Me_2NH_2)_3SO_4]^+$n species towards surface lead antiposition defects (IPb). In addition, $[Zn_2(ox)_3]_2$ The framework has been proven to have strong electro-static interactions with Pb^{2+}ions, ensuring the perovskite composition and promoting material stability. Due to this modification, the equipment efficiency has increased from 19.75% to 21.15%, and the significant battery life has exceeded 3000 hours. Parallel studies on the self-assembly of Zn-TTB synthesized by Zn^{2+}ions and 1- (triazole-1-yl) -4- (tetrazole-5-methyl) benzene (TTB) have shown that perovskite precursor materials can develop simultaneously with the Zn-TTB framework. This synergistic growth promotes the intermolecular phase of macromolecules through MOF perovskite connectivity interactions, resulting in larger, interconnected perovskite grains with preferred orientation. The device modified with Zn-TTB showed a significant PCE of 23.14%, and after 300 hours of continuous solar irradiation, it maintained 90.1% of the initial PCE even without any form of packaging.

Introducing Stable Polyoxometalate Based Materials into Metal-Organic Frameworks (MOFs) CoW12@MIL-101 (Cr) resulted in the elimination of Pb0 and passivation of Pb^{2+}, showing a significant increase of 21.39% in PCE and excellent stability. In addition, the device has strong integrity after being heated at 85°C in an N_2 environment and exposed to normal conditions (25°C, 40% RH) for 1000 hours, maintaining 85% and 89% of the original PCE, respectively. MOFs have also been absorbed into inorganic CsPbI2Br PSCs, extending their applications beyond organic-inorganic PSCs. Yuan and his team introduced a tri pyridine chromium Cr MOF [Cr (III) TPy2] 2Pb5I16 based on π - conjugated aromatic structure into the Pb I lattice as an a-site cation. This specific perovskite [Cr (III) TPy2]2Pb5I16 allows for the development of coherent heterojunctions, which advantageously affect carrier transport. In addition, Cr MOF effectively prevents the decomposition of perovskite layers caused by humidity.[28]

The prerequisite for the commercial feasibility of photovoltaic products is their non-toxic nature, which requires non-toxic and ecologically benign components. However, the presence of hazardous lead-based components in PSCs poses a significant risk and may disrupt their marketability. Kwak et al. conducted in-depth research on the embryonic toxicity of lead iodide (PbI_2) on two aquatic species, zebrafish, and Japanese lapis lazuli, and further investigated the chemical form of PbI_2 in embryo culture medium. According to the research, compared with the unexposed control group, specimens exposed to the PbI_2 environment showed a significant increase in adverse outcomes, including increased mortality rate, morphological abnormalities, impaired hatching, growth retardation, and various pathologies. These data suggest the sublethal toxicity of Pb^{2+}ions and emphasize the necessity of designing lead adsorption methods and optimizing device structures to reduce PSC lead leakage. In order to address the serious

environmental hazards and health issues associated with lead pollution, there has been increasing interest in strategies aimed at reducing lead outflows in the past few years. In this regard, the development of porous MOFs with customizable pore characteristics and functions has become a focus area of attention, as they have unique and selective adsorption capabilities for dissociated metal ions, making them promising candidates for lead repair scaffolds and have recently received considerable scientific attention.[29] Wu et al. used a two-dimensional conjugated MOF named ZrL_3 as the electroextraction layer (EEL) in PSCs. Zirconium ions partially interact with carboxylates in a specific manner, forming a dense array of thiol functional groups near the zirconium oxygen cluster. This arrangement endows MOFs with spatial steric hindrance capability. Subsequently, the electronic extraction and hole-blocking performance of related devices were significantly improved. Due to these modifications, the PSC (referred to as M-PSC) combined with ZrL_3: bis-C60 ETL achieved a PCE of 22.02%. This performance exceeds that of the control device designated as r-PSC, which exhibits 21.32% PCE. It is worth noting that due to its disulfide cross-linking network, ZrL_3 exhibits proficient ability in chelating heavy metal ions, which reduces the leaching of Pb^{2+} and enhances the operational durability of PSC. In order to accurately evaluate the leakage of Pb^{2+} in degraded PSCs, PSCs were immersed in deionized water and an experimental model was established to simulate rainwater discharge. The filtrate of the r-PSC sample exhibited significantly higher Pb^{2+} concentration than its M-PSC counterpart, as demonstrated by Pb^{2+} detection measurements. In addition, the lead concentration was accurately quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES). The average Pb^{2+} concentration of M-PSC samples significantly decreased, from 38.4 ppm to 7.6 ppm compared to R-PSC.[30] This indicates that the chelating interaction between thiol-modified ZrL_3 and Pb^{2+}ions can effectively suppress lead leakage, thereby reducing potential environmental and health hazards associated with PSC deployment.

4. Conclusion

Creating efficient synthesis routes is a key area for the future development of MOF materials. Currently, the creation of MOFs utilizes expensive, rare, and toxic metals, which has raised concerns about resource efficiency and global accessibility. Developing new innovative synthesis pathways using more readily available non-toxic elements will greatly enrich the range of available MOFs, potentially paving the way for new applications and reducing the environmental impact of their synthesis. Enhancing

the stability of MOFs under harsh conditions and improving their performance is an urgent area that requires attention. Although MOFs have shown great potential, issues surrounding their stability (especially under humid conditions) and the durability of their structural integrity have hindered their wider adoption and practical use. Therefore, exploring treatment, coating, or other modification methods that can extend the lifespan and durability of MOFs is crucial. Hydrogen and methane gases, due to their high porosity, can be stored in MOFs, providing potential solutions for renewable energy storage. However, these materials currently face challenges in selectivity and adsorption-desorption kinetics in gas separation and storage processes. Priority should be given to improving the gas adsorption capacity, selectivity, and design framework for complex gas mixture separation of MOFs. The successful large-scale production and commercialization of MOFs are greatly hindered by their lack of reproducibility in synthesis and the high cost of required raw materials. Therefore, priority needs to be given to developing cost-effective and scalable production methods. In addition, standardizing the MOF synthesis process will promote consistency, thereby improving scalability. Although MOFs have the potential to completely change various industries, their practical applications are limited. The development of new methods and designs that integrate MOFs into actual equipment will inevitably lead to a surge in applications such as clean energy production, carbon capture and storage, and more efficient industrial processes. MOFs represent a promising class of new materials with enormous potential in reshaping energy, environment, and technology fields. However, ensuring their full potential is the responsibility of the industry and researchers, who are committed to prioritizing the resolution of these optimization challenges. The optimization path of MOFs is both fascinating and challenging, but the potential benefits it brings may far outweigh the obstacles. At present, PSCs are still in the early stages of industrialization. The incorporation of multifunctional MOFs into PSC architecture has been identified as a forward-looking direction for future development. This review provides an analysis of MOF integration within the active layer of PSC, to achieve devices that exhibit both high efficiency and enhanced stability. The use of MOFs as components in PSCs provides various benefits: (i)MOFs have strong physical and chemical stability, wide orderliness, and numerous coordination sites, which can be used as additives to control film growth and improve film quality. They are suitable for perovskite and charge transfer layers; (ii) As an interface modifier, MOFs can passivate defects and optimize the band arrangement at related interfaces; (iii) Can promote charge transfer while suppressing charge

recombination at the interface; (iv) Despite limited research, MOFs have shown the potential to reduce the release of Pb^{2+} from degraded PSCs. In addition, strategic use of MOFs and derivatives in mixed PSCs can significantly improve device performance and environmental robustness through composition and crystal engineering, optimization of device configuration, and enhancement of interface performance.

Future predictions indicate that MOFs will be widely used in PSCs to improve PCE, enhance operational stability, and reduce lead (Pb^{2+}) leakage from perovskite materials. In addition, device engineering is crucial for fully utilizing the potential advantages provided by MOFs.

References

[1] Jung, E. H., Jeon, N. J., Park, E. Y., Moon, C. S., Shin, T. J., Yang, T.-Y., Noh, J. H., & Seo, J. (2019). Efficient, stable and scalable perovskite solar cells using poly(3-hexylthiophene). Nature, 567, 511-515. Retrieved March 20, 2024, from https://doi.org/10.1038/s41586-019-1036-3.

[2] Min, H., Lee, D. Y., Kim, J., Kim, G., Lee, K. S., Kim, J., Paik, M. J., Kim, Y. K., Kim, K. S., Kim, M. G., Shin, T. J., & Seok, S. I. (2021). Perovskite solar cells with atomically coherent interlayers on SnO2 electrodes. Nature, 598, 444-450. Retrieved March 20, 2024, from https://doi.org/10.1038/s41586-021-03964-8

[3] Li, Y., Chen, Z., Yu, B., Tan, S., Cui, Y., Wu, H., Luo, Y., Shi, J., Li, D. & Meng, Q. (2022). Efficient, stable formamidinium-cesium perovskite solar cells and minimodules enabled by crystallization regulation. Joule, 6, 676-689. Retrieved March 20, 2024, from https://doi.org/10.1016/j.joule.2022.02.003

[4] Li, Z., Li, B., Wu, X., Sheppard, S. A., Zhang, S., Gao, D., Long, N. J., & Zhu, Z. (2022). Organometallic-functionalized interfaces for highlyefficient inverted perovskite solar cells. Science, 376, 416-420. Retrieved March 20, 2024, from https://doi.org/10.1126/science.abm8566

[5] Bag, M., Renna, L. A., Adhikari, R. Y., Karak, S., Liu, F., Lahti, P. M., Russell, T. P., Tuominen, M. T., & Venkataraman, D. (2015). Kinetics of ion transport in perovskite active layers and its implications for active layer stability. J. Am. Chem. Soc., 137, 13130-13137. Retrieved March 20, 2024, from https://doi.org/10.1021/jacs.5b08535

[6] Yao, Z., Xu, Z., Zhao, W., Zhang, J., Bian, H., Fang, Y., Yang, Y., & Liu (Frank) S. (2021). Enhanced efficiency of inorganic CsPbI3-xBrx perovskite solar cell via selfregulation of antisite defects. Adv. Energy Mater., 11, 2100403, Retrieved March 20, 2024, from https://doi. org/10.1002/aenm.202100403

[7] Zhou, Q., Duan, J., Du, J., Guo, Q., Zhang, Q., Yang, X., Duan, Y., & Tang, Q. (2021). Tailored lattice "tape" to confine tensile interface for 11.08%-efficiency all-inorganic CsPbBr3 perovskite solar cell with an ultrahigh voltage of 1.702 V. Adv. Sci., 8, 2101418. Retrieved March 20, 2024, from https://doi.org/10.1002/advs.202101418

[8] Kim, D. H., Whitaker, J. B., Li, Z., Hest, M. F. A. M., & Zhu, K. (2018). Outlook and challenges of perovskite solar cells toward terawatt-scale photovoltaic module technology. Joule, 2, 1437-1451. Retrieved March 20, 2024, from https://doi.org/10.1016/j.joule.2018.05.011

[9] Xie, L., Song, P., Shen, L., Lu, J., Liu, K., Lin, K., Feng, W., Tian, C., & Wei, Z., (2020). Revealing the compositional effect on the intrinsic long-term stability of perovskite solar cells. J. Mater. Chem. A., 8, 7653-7658. Retrieved March 20, 2024, from https://doi.org/10.1039/D0TA01668C

[10] Wang, H., Li, S., Liu, X., Shi, Z., Fang, X., & He, J. (2021). Low-dimensional metal halide perovskite photodetectors. Adv. Mater., 33, 2003309. Retrieved March 20, 2024, from https://doi.org/ 10.1002/adma.202003309

[11] Niu, T., Chao, L., Gao, W., Ran, C., Song, L., Chen, Y., Fu, L., & Huang, W. (2021). Ionic liquidsenabled efficient and stable perovskite photovoltaics: progress and challenges. ACS Energy Lett., 6, 1453-1479. Retrieved March 20, 2024, from https://doi.org/10.1021/acsenergylett.0c02696

[12] Cheng, Y., & Ding, L. (2021). Pushing commercialization of perovskite solar cells by improving their intrinsic stability. Energy Environ. Sci., 14, 3233-3255. Retrieved March 20, 2024, from https://doi.org/10.1039/D1EE00493J

[13] Luo, C., Zheng, G., Gao, F., Wang, X., Zhao, Y., Gao, X., & Zhao, Q. (2022). Facet orientation tailoring via 2D-seed-induced growth enables highly efficient and stable perovskite solar cells. Joule, 6, 240-257, Retrieved March 20, 2024, from https://doi.org/10.1016/j.joule.2021.12.006

[14] Zhou, Y., Poli, I., Meggiolaro, D., Angelis, F. D., & Petrozza, A. (2021). Defect activity in metal halide perovskites with wide and narrow bandgap. Nat. Rev. Mater., 6, 986-1002. Retrieved March 20, 2024, from https://doi.org/10.1038/s41578-021-00331-x

[15] Kang, D.-H., Ma, C., & Park, N.-G. (2022). Antiseptic povidone–iodine heals the grain boundary of perovskite solar cells. ACS Appl. Mater. Interfaces, 14, 8984-8991. Retrieved March 20, 2024, from https://doi.org/10.1021/acsami.1c21479

[16] Hou, X., Pan, L., Huang, S., Ou-Yang, W., & Chen, X. (2017) Enhanced efficiency and stability of perovskite solar cells using porous hierarchical TiO2 nanostructures of scattered distribution as scaffold. Electrochim. Acta, 236, 351. Retrieved March 20, 2024, from https://doi.org/10.1016/j.electacta.2017.03.192.

[17] Sheng, W., He, J., Yang, J., Cai, Q., Xiao, S., Zhong, Y., Tan, L., & Chen, Y. (2023) Multifunctional metal-organic frameworks capsules modulate reactivity of lead iodide toward efficient perovskite solar cells with UV resistance. Adv. Mater., 35, 2301852. Retrieved March 20, 2024, from https://doi.org/10.1002/adma.202301852.

[18] Zhang, Y.-N., Li, B., Fu, L., Li, Q., & Yin, L.-W. (2020). MOF-derived ZnO as electron transport layer for improving

light harvesting and electron extraction efficiency in perovskite solar cells. Electrochim. Acta, 330, 135280. Retrieved March 20, 2024, from https://doi.org/10.1016/j.electacta.2019.135280.

[19] Ryu, U., Jee, S., Park, J.-S., Han, I., Lee, J., Park, M., & Choi, K. (2018). Nanocrystalline titanium metal-Organic frameworks for highly efficient and flexible perovskite solar cells. ACS Nano, 12, 4968-4975. Retrieved March 20, 2024, from https://doi.org/10.1021/acsnano.8b02079.

[20] Wu, S., Li, Z., Li, M.-Q., Diao, Y., Lin, F., Liu, T., Zhang, J., Tieu, P., Gao, W., Qi, F., Pan, X., Xu, Z., Zhu, Z., & Jen, K.-Y. A. (2020). 2D metal-organic framework for stable perovskite solar cells with minimized lead leakage. Nat. Nanotechnol., 12, 934. Retrieved March 20, 2024, from https://doi.org/10.1038/s41565-020-0765-7.

[21] Cao, J., Liu, C.-K., Piradi, V., Loi, H.-L., Wang, T., Cheng, H., Zhu, X., & Yan, F., (2022). Ultrathin self-assembly two-dimensional metal-organic framework films as hole transport layers in ideal-bandgap perovskite solar cells. ACS Energy Lett., 7, 3362-3369. Retrieved March 20, 2024, from https://doi.org/10.1021/acsenergylett.2c01714.

[22] Hazeghi, F., Mozaffari, S., & Ghorashi, S. (2020). Metal organic framework-derived core-shell CuO@NiO nanospheres as hole transport material in perovskite solar cell. J. Solid State Chem., 24, 1427. Retrieved March 20, 2024, from https://doi.org/10.1007/s10008-020-04643-w.

[23] Dong, Y., Zhang, J., Yang, Y., Qiu, L., Xia, D., Lin, K., Wang, J., Fan, X., & Fan, R. (2019) Self-assembly of hybrid oxidant POM@Cu-BTC for enhanced efficiency and long-term stability of perovskite solar cells. Angew. Chem., Int. Ed., 58, 17610. Retrieved March 20, 2024, from https://doi.org/10.1002/anie.201909291.

[24] Li, M., Wang, J., Jiang, A., Xia, D., Du, X., Dong, Y., Wang, P., Fan, R., & Yang, Y. (2019). Metal organic framework doped Spiro-OMeTAD with increased conductivity for improving perovskite solar cell performance. Sol. Energy, 188, 380. Retrieved March 20, 2024, from https://doi.org/10.1016/j.solener.2019.05.078.

[25] Zhou, X., Qiu, L., Fan, R., Wang, A., Ye, H., Tian, C., Hao, S., & Yang, Y. (2019). Metal-organic framework-derived N-rich porous carbon as an auxiliary additive of hole transport layers for highly efficient and long-term stable perovskite solar cells. Sol. RRL, 4, 1900380. Retrieved March 20, 2024, from https://doi.org/10.1002/solr.201900380.

[26] Wang, J., Zhang, J., Yang, Y., Dong, Y., Wang, W., Hu, B., Li, J., Cao, W., Lin, K., Xia, D., & Fan, R. (2022). Li-TFSI endohedral Metal-Organic frameworks in stable perovskite solar cells for Anti-Deliquescent and restricting ion migration. Chem. Eng. J., 429, 132481. Retrieved March 20, 2024, from https://doi.org/10.1016/j.cej.2021.132481.

[27] Liu, Y., Liu, T., Guo, X., Hou, M., Yuan, Y., Shi, S., Wang, H., Zhang, R.-Z., Galiotis, C., & Wang, N. (2022) Porphyrinic metal-organic framework quantum dots for stable n-i-p perovskite solar cells. Adv. Funct. Mater., 33, 2210028. Retrieved March 20, 2024, from https://doi.org/10.1002/adfm.202210028.

[28] Zhang, J., Guo, S., Zhu, M., Li, C., Chen, J., Liu, L., Xiang, S., & Zhang, Z. (2021). Simultaneous defect passivation and hole mobility enhancement of perovskite solar cells by incorporating anionic metal-organic framework into hole transport materials. Chem. Eng. J., 408, 127328. Retrieved March 20, 2024, from https://doi.org/10.1016/j.cej.2020.127328.

[29] Zhang, J., Li, J., Yang, Y., Yang, C., Dong, Y., Lin, K., Xia, D., & Fan, R. (2022). Functionalized rare-earth metal cluster-based materials as additives for enhancing the efficiency of perovskite solar cells. ACS Appl. Energy Mater., 5, 13318. Retrieved March 20, 2024, from https://doi.org/10.1021/acsaem.2c01909.

[30] Asghar, M. I., Zhang, J., Wang, H., & Lund, P. D. (2017). Device stability of perovskite solar cells-A review. Renewable and Sustainable Energy Reviews, 77, 131-146. Retrieved March 20, 2024, from https://doi.org/10.1016/j.rser.2017.04.003.