

Advances in Low Temperature Fabrication Strategies on Charge Carrier Transport Layers in Perovskite Solar Cells

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Abstract: Perovskite solar cells have garnered extensive attention and profound scrutiny from the global scientific community, attributed to their progressively enhancing photoelectric conversion efficiency, the expedient and efficient solution-based fabrication process, their distinctive lightweight and wearable attributes, and the promise of utilizing cost-effective materials. Over recent years, the efficiency of perovskite solar cells has surpassed the benchmark of 26.7%, while innovations in low-temperature synthesis techniques for crafting high-quality perovskite thin films were still calling efforts, coupled with relentless endeavors to refine the interface and electrode material designs. Simultaneously, the stability of these cells has garnered considerable industry focus. This paper delves into the latest advancements in the low-temperature preparation of perovskite solar cells, offering an insightful examination of pioneering methodologies and technical strategies for achieving low-temperature fabrication of each pivotal layer—specifically the carrier transport functional layers, while exploring a spectrum of enhancement strategies aimed at augmenting their performance further. These endeavors establish a robust foundation for their expanded applications in the foreseeable future.

Keywords: Perovskite Solar Cells, Low Temperature Fabrication, Charge Carrier Transport layers, Interfacial Engineering

1. Introduction

Among the diverse array of photovoltaic materials, perovskite solar cells (PSCs) have attracted considerable attention owing to their exceptional photoelectric properties. The pivotal breakthrough occurred in 2009 when Japanese researchers successfully developed the first stable and efficient perovskite solar cell, which catalyzed a surge of interest and research in this field. As it stands, the efficiency of PSC devices has progressed remarkably, achieving a notable maximum of 26.1%. [1] The evolution of PSCs is advancing at an extraordinary pace, spurred by their remarkable and rapidly improving power conversion efficiency (PCE). Their numerous advantages—including high PCE, the feasibility of solution processing, tunable band gaps, and inherent flexibility—position PSCs as a focal point within energy research. The advent of flexible PSCs (f-PSCs), characterized by their high power-to-weight ratios, holds immense potential as power sources for mobile energy systems, space energy applications, and portable functional devices, among others.

Hybrid organic-inorganic perovskites (HOIP), particularly those of the organometal halide variety featuring an AMX₃ structure, constitute a primary category of innovative photovoltaic materials. In

this structure, "A" signifies an organic cation such as methylammonium (CH_3NH_3^+ or MA) or formamidinium ($\text{NH}_2\text{CH}=\text{NH}_2$ or FA), "M" denotes a divalent metal cation, and "X" represents a monovalent anion, typically a halogen like F, Cl, Br, or I. These materials are particularly advantageous for optoelectronic applications and for the fabrication of devices at low temperatures. Within the realm of HOIPs, lead-organic iodide perovskites exhibit superior practical properties compared to their counterparts. Prominent examples of these compounds include methylammonium lead iodide $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3), methylammonium lead bromide $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (MAPbBr_3), formamidinium lead iodide $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ (FAPbI_3), as well as chloride-doped MAPbI_3 ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$), which feature a mix of triiodides. These materials have demonstrated substantial electronic and photovoltaic capabilities and, more recently, have revealed ferroelectric, pyroelectric, and ferroelastic characteristics, particularly within the tetragonal phase of MAPbI_3 .

The fundamental architecture of perovskite solar cells (PSCs) consists of an electron transport layer (ETL) and a hole transport layer (HTL). Typically, within the PSC structure, the anode is formed from fluorine-doped tin oxide (FTO) glass, while the cathode is composed of a metallic material. PSCs are generally classified into two categories based on their structural configuration: regular n-i-p and inverted p-i-n configurations. This classification depends on the transport material positioned on the outer side of the perovskite layer that first encounters incident light. The highest reported power conversion efficiencies (PCEs) for single-junction PSCs have been achieved with the regular n-i-p architecture. In contrast, the p-i-n geometry offers several advantages, such as simplified fabrication processes, improved compatibility with charge extraction layers, and the potential for low-temperature processing.

The rapid technological advancements within the electronics sector have heightened the demand for portable electronic devices, flexible display technologies, and wearable electronic textiles. As a result, flexible solar cells have attracted increasing interest due to their favorable attributes, including flexibility, lightweight design, portability, and compatibility with curved surfaces. Nevertheless, the inherent properties of flexible perovskite solar cells render them incapable of withstanding elevated temperatures; hence, their fabrication must occur at lower temperatures, approximately 200°C . This low-temperature processing presents an additional significant advantage, as many high-performance and stable PSCs typically require high-temperature processes during fabrication, which can lead to increased production costs and extended energy payback periods. Low-temperature-processed PSCs are particularly crucial, as they significantly reduce expenses and thus lower barriers to industrial implementation. Furthermore, these processing methods are highly relevant for flexible devices and tandem applications that are integrated with other photovoltaic technologies, especially where thermal budgets are restricted. Therefore, the development of stable PSCs that can be produced under ambient conditions, along with cost-effective fabrication methodologies, is extremely desirable.

2. Low Temperature fabricated Hole Transport Layers

The hole transport layer (HTL) material is a critical functional component for device performance, and achieving low-temperature fabrication is significant in reducing production costs. For example, under mild conditions of 100°C , a HTL film with a crosslinking degree of 99% was successfully fabricated using the characteristic of vinyl polymerization, which does not produce by-products. The charge mobility reached as high as $3.84 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$. This successful case maintained a power conversion efficiency (PCE) of 18.49% even in an environment with 60% relative humidity. The unencapsulated device, stored at room temperature for 30 days, was able to retain 88% of its initial efficiency, fully demonstrating the great potential of this crosslinking HTL strategy in enhancing the stability of perovskite solar cells [2].

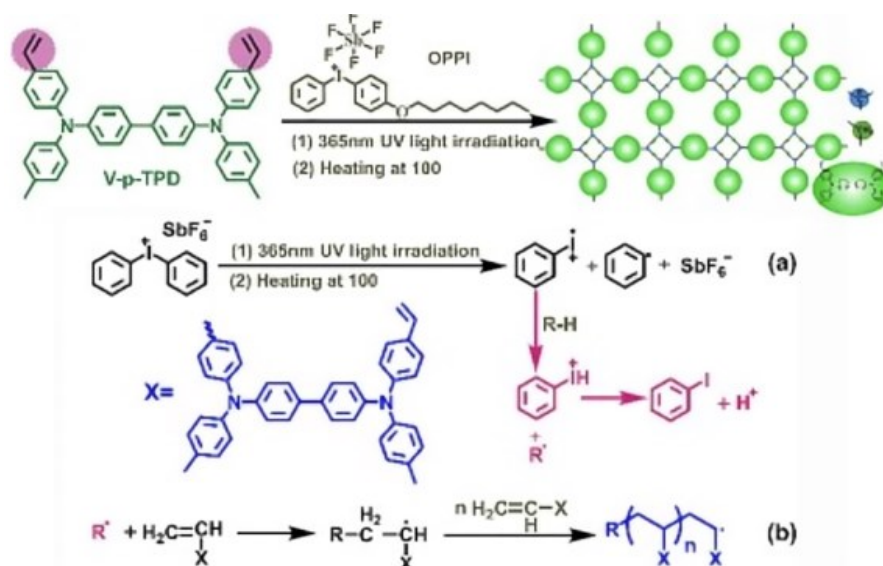


Figure 1: Crosslinked network formed by V-p-TPD polymerization initiated by OPPI: (a) OPPI photolysis and (b) V-p-TPD radical-initiated polymerization mechanism.

Another important type of hole transport layer material is nickel oxide (NiOx) inorganic HTL, which plays a key role in low-temperature preparation processes due to its high conductivity, excellent optical transparency, energy level matching with the perovskite layer. For example, magnetron sputtering can be introduced to prepare NiOx films, which demonstrate excellent crystallinity, flatness, and surface uniformity [3]. To overcome the conductivity limitations of the magnetron sputtering method, co-sputtering technology can be considered, although this technique requires more advanced experimental equipment and may increase production costs. Using Cu-doped NiOx as a target material for magnetron sputtering, efficient doping of the NiOx HTL was successfully achieved [4]. This improvement significantly enhanced the performance of the hole transport layer, effectively increasing the photoelectric conversion efficiency of perovskite solar cells. To further improve the hole transport efficiency of the NiOx HTL, high-crystallinity NiOx films can be fabricated through pulsed laser deposition [5], and by regulating NiOx vacancy defects and doping with Cu⁺ ions, the energy levels and electrical conductivity can be optimized, thereby gradually increasing the power conversion efficiency of perovskite solar cells.

3. Low Temperature Fabricated Electron Transport Layer

Among the many inorganic electron transport layer (ETL) materials, TiO₂ is widely researched and used due to its excellent optoelectronic properties and low manufacturing cost. Anatase-type TiO₂ (a-TiO₂) has been successfully applied to the construction of high-efficiency perovskite solar cells (PSCs) due to its outstanding charge transport characteristics. However, the preparation of a-TiO₂ ETL usually requires high-temperature thermal treatment of around 500°C, which not only increases costs but also limits its application on flexible substrates. Therefore, developing low-temperature deposition techniques for a-TiO₂ ETL has become a hot topic in the PSC field.

To date, various methods have been reported for the low-temperature preparation of a-TiO₂ ETL, including atomic layer deposition (ALD, 200°C), room-temperature sputtering (RT), chemical bath deposition (CBD, 70°C), and other solution-based methods [6]. These methods have effectively reduced the preparation temperature of PSCs. On the other hand, intrinsic defects in a-TiO₂, such as titanium and oxygen vacancies, can act as recombination centers or electron trap states in low-temperature fabricated n-i-p planar PSCs, reducing the cell's performance and stability. To address

this issue, researchers have developed various strategies, such as doping metal elements to replace part of the titanium ions. The Yang team achieved an energy conversion efficiency (PCE) of up to 19.3% by spin-coating a Y-doped TiO₂ nanocrystal solution modified with polyethyleneimine ethoxylate (PEIE) [7]. Liu and colleagues used CBD technology to prepare cobalt- and niobium-doped TiO₂ as a high-quality ETL at 200°C, resulting in PSC efficiencies exceeding 19% [8-9]. Organic components have also been used to passivate internal defects. Tan and colleagues reduced interface recombination and improved interface bonding in low-temperature planar PSCs using chloride-terminated TiO₂ colloidal nanocrystal films [10]. Hu et al. employed a non-hydrolytic method to synthesize amino-functionalized TiO₂ nanoparticles in situ, forming Ti-N chemical bonds between amino (-NH₂) groups and the surface of TiO₂ nanoparticles, producing an effective ETL, and achieving a corresponding PCE of over 21% in PSCs [11]. In addition, researchers have developed other methods, including additive engineering and surface passivation, to reduce defects. Looking ahead, there is reason to believe that the development of simpler and more cost-effective methods for depositing high-quality TiO₂ ETL will further promote the advancement of PSC applications.

Compared to titanium dioxide (TiO₂), tin dioxide (SnO₂) offers a more ideal option for perovskite solar cells (PSCs) in several aspects. SnO₂ has a wider bandgap (3.8 eV), and its conduction band energy level is shifted positively by 300 mV compared to TiO₂, which reduces photocatalytic activity and enhances device stability. The charge mobility of SnO₂ is nearly two orders of magnitude higher than that of TiO₂, while also exhibiting lower trap density [12]. SnO₂ nanocrystals can be synthesized using tin tetrachloride as the tin source through a simple hydrothermal method. These nanocrystals are spin-coated onto a fluorine-doped tin oxide (FTO) substrate and sintered at a relatively low temperature to form the electron transport layer (ETL) for planar PSCs. The concentration of SnO₂, the ratio of the spin-coating solution, and the sintering temperature significantly affect the ETL performance and charge transport characteristics of PSCs. By optimizing the processing conditions (0.15 M SnO₂ solution, 120°C sintering temperature), high-quality SnO₂ ETL with uniform coverage, moderate thickness, low charge recombination, and low resistivity can be successfully prepared [10]. Planar PSCs based on SnO₂ exhibited stable PCE output and minimal hysteresis. These research results provide a low-cost and simple strategy for SnO₂ preparation and pave the way for the replacement of traditional TiO₂ materials in future PSC applications.

Furthermore, UV-sintered Ga-doped SnO₂ electron transport layers can be used to achieve completely annealing-free flexible perovskite quantum dot solar cells. This strategy significantly improved the power conversion efficiency (PCE) of CsPbI₃-PQD solar cells, increasing from 10.39% to 15.06%. Ultimately, an efficiency of 12.70% was achieved on a flexible polymer substrate, which is the highest PCE reported for flexible quantum dot solar cells to date [13]. This also provides a new design approach for the fabrication of high-performance flexible solar cells in the future.

To further enhance the optoelectronic properties of SnO₂ as an electron transport layer and improve its low-temperature deposition capability, tin oxide (SnO₂) combined with aluminum-doped zinc oxide (AZO) has become an ideal choice for the electron transport layer (ETL) in PSCs. However, the high density of surface defects at the ETL-perovskite interface has remained a key factor limiting further improvement of power conversion efficiency (PCE) in planar PSCs. By employing a simple surface treatment method using monoethanolamine (MEA) to passivate the SnO₂/AZO electron transport layer, the interface defects between AZO and the perovskite can be significantly reduced, effectively minimizing carrier recombination [14].

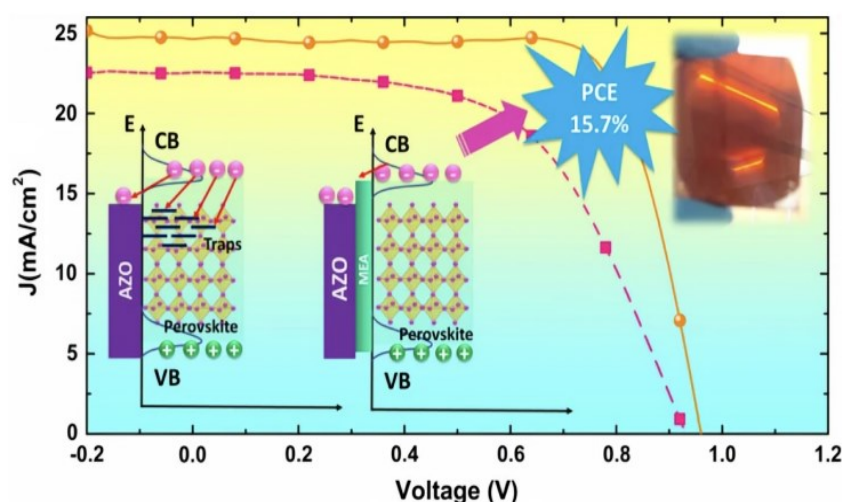


Figure 3: Schematic Diagram of Performance Improvement of Devices with MEA-Modified AZO Electron Transport Layer.

After treatment with monoethanolamine (MEA), the defect states at the AZO/perovskite interface were significantly improved, and the charge carrier transport performance was enhanced, resulting in an increase in the PCE to 15.73%. Additionally, the passivated devices demonstrated excellent stability, maintaining approximately 77% of their initial efficiency after 1,000 hours of storage at room temperature without encapsulation. Therefore, the MEA defect passivation interface engineering strategy provides an effective and innovative approach for improving the quality of the electron transport layer and producing high-efficiency planar perovskite solar cells.

4. Conclusion

The performance improvements in perovskite solar cells in recent years can be described as remarkable, especially in the pursuit of high-efficiency solar cells. Nevertheless, many challenges remain, particularly in developing low-cost, high-efficiency low-temperature preparation processes. These approaches are also applicable to flexible devices and roll-to-roll processing, significantly shortening the fabrication cycle. This paper focuses on low-temperature preparation strategies for carrier transport layers, providing important references for the development of the next generation of transport layers with low-temperature fabrication. It contributes to the development of the next generation of perovskite solar cells with higher conversion efficiency and longer-term stability.

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