Application of Graphene Materials in the Electronic Transport Layer of Perovskite Solar Cells

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Abstract: Perovskite solar cells (PSCs) are a novel type of photovoltaic cells, whose basic structure is composed of perovskite-type compounds. The energy band structure of perovskite materials endows them with excellent light absorption capability and high carrier mobility, enabling efficient conversion of solar energy into electricity. In recent years, the power conversion efficiency (PCE) of PSCs has increased rapidly, with the certified laboratory efficiency reaching up to 26.9%. This paper summarizes various application methods of graphene-based materials as additives in electron transport layers (ETLs) of PSCs, and analyzes the future application potential in this field. Compared with conventional silicon-based solar cells, PSCs feature lower production cost, lighter weight, and broader material selectivity.

Keywords: Perovskite Solar Cells; Carbon Nanomaterials; Graphene; Electron Transport Layer; Thin Films

1. Introduction

Perovskite solar cells possess numerous merits such as excellent light absorption and high carrier mobility, exhibiting substantial advantages over traditional silicon-based solar cells. However, the poor operational stability and short service life of PSCs remain critical bottlenecks restricting their development and large-scale application, making the improvement of perovskite thin film quality and the enhancement of ETL efficiency important breakthroughs for overall device performance. As the light-absorbing layer of PSCs, perovskite is a key component whose quality directly determines the PCE and stability of the devices. The grain morphology, grain size, charge recombination, and defect density are crucial for improving thin film quality. Reducing perovskite thin film defects and regulating crystallization from the precursor stage are essential approaches to obtain high-quality perovskite films and enhance overall photovoltaic performance [1]. Therefore, introducing specific additives during perovskite thin film preparation to control crystal growth and achieve high-quality films is an effective strategy to boost the PCE and stability of PSCs.

Graphene is an ideal material for optimizing the performance of PSCs owing to its atomically thin monolayer structure, superior electrical conductivity, thermal conductivity, and mechanical strength. Its electron mobility can reach up to 200,000 $cm^2/V \cdot s$, far exceeding that of most conductive materials. Meanwhile, its tensile strength is as high as 130 GPa, approximately 200 times that of steel, playing a vital role in improving the mechanical stability and durability of the devices. Additionally, graphene has a specific surface area of 2630 m^2/g, providing abundant reactive sites for composite applications in solar cells and facilitating performance enhancement.

2. Electron Transport Layer of Perovskite Solar Cells

As an emerging photovoltaic technology, the application of perovskite materials in optoelectronic devices has been extensively studied worldwide. Researchers have made remarkable progress in electrode material synthesis, device structure optimization, and stability improvement.

The electron transport layer is an indispensable component of PSCs. Graphene and its derivatives offer advantages of flexibility, electrical conductivity, and optical transparency, attracting widespread attention in the modification of ETLs for PSCs in recent years. The design concepts and innovative directions of graphene composite ETLs can be summarized from extensive research achievements.

3. TiO_2-Based Electron Transport Layers

Li et al. [2] studied the perovskite solar cells prepared by sol-gel method in air as the electron transport layer, and the photoelectric conversion efficiency of the photovoltaic device reached 12.7%, the corresponding short-circuit current density was 14.3mA/cm^2, the open-circuit voltage was 0.83V, and the filling factor was 68.8%, and all the data were better than those of the control group(Table. 1).

Table 1. Performance Parameters of Perovskite Battery Devices with Electron Transport Layers A and B in Samples[2]

Device	JSC/ mA·cm^{-2}	VOC/ V	FF/ %	PCE/ %
Sample A	14.3	0.83	0.688	12.7
Sample B	13.6	0.84	0.505	9.4

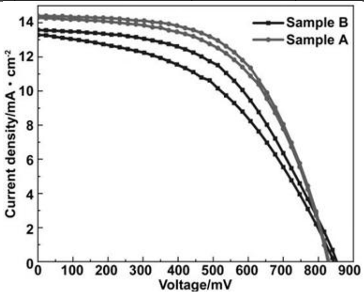

Figure 1. J-V Curves of Perovskite Cells with Electron Transport Layers A and B in Samples[2]

As shown in Fig. 1, TiO_2 electron transport layer is beneficial to improve the performance of perovskite solar cells. However, such methods only significantly improve the photoelectric conversion efficiency, but the problems of improving operational stability and extending battery life have not been solved. Considering the excellent physical and chemical properties of graphene, the specific impact of graphene composites on improving the stability and life of graphene composites can be obtained by comparing and analyzing the performance differences of TiO2 electron transport layers mixed with graphene materials.

3.1 Graphene/TliO₂ Composite Electron Transport Layers

Wang et al. [3] spin-coated ultrasonically dispersed graphene and TiO_2 composite sol onto conductive glass substrates to fabricate a compact layer, in which graphene served as a continuous two-dimensional conductive framework with nano-TiO_2 particles anchored onto graphene nanosheets. The incorporation of graphene reduced charge recombination losses, and the device PCE reached 15.6%. The improved efficiency is mainly attributed to the reduced energy barrier at the material interface induced by graphene, enabling more efficient electron extraction compared with the pure TiO_2 compact layer. Furthermore, the high charge mobility of graphene enhances the electrical conductivity of the composite ETL.

When reduced graphene oxide (RGO)/mesoporous TiO_2 nanocomposite thin films were used as ETLs, the PCE was enhanced by ~18% compared with pure TiO_2 at an RGO volume fraction of only 0.4% [4]. This is because the RGO composite thin film reduces the interfacial resistance between perovskite and mesoporous TiO_2, thereby improving electron collection efficiency.

3.2 Graphene Quantum Dot/TiO_2 Composite Electron Transport Layers

In 2014, Zhu et al .[5] took advantage of the ultra-fast electron extraction speed of graphene quantum dots to insert an ultra-thin graphene quantum dot layer between the electrical transport layer and the perovskite film, which significantly improved the short-circuit current density of the device and increased the photoelectric conversion efficiency from 8.81% to 10.2%.

Fang et al.[6] introduced 7% graphene quantum dots into the perovskite solution and prepared the perovskite film by one-step spin coating, thereby increasing the photoelectric conversion efficiency of the device to 17.6%, which was 8.2% higher than that without the addition of graphene quantum dots. The main reason for this is to reduce the series resistance of the device and promote the transfer of electrons from the perovskite to the electron transport layer.

3.3 Graphene Oxide/TiO_2 Composite Electron Transport Layers

Agresti et al.[7] rotated GO-Li as an electron transport layer to the mesoporous TiO_2 matrix, and the limit current and filling factor of the prepared batteries were significantly increased, mainly because the work function of GO-Li (4.3 eV) matched the conduction band energy level of TiO_2 well, which improved the electron injection of perovskite into TiO_2. In addition, the electron transport layer GO-Li passivated the oxygen hole defect of TiO_2 and improved its stability under long-term sunlight.

Nouri et al.[8] used graphene oxide lithium salt GO-Li as the electron transport layer to construct a low-cost perovskite solar cell with an inverted structure, and added TiO_2 sol to GO-Li to further improve stability. The photoelectric conversion efficiency of graphene composite electron transport layer cells is up to 10.2%, which is higher than that of GO-Li or TiO_2 sol as the electron transport layer alone.

4. Graphene/Non-TiO_2 Composite Electron Transport Layers

Wang et al.[9] used graphene/$SrTiO_3$ nanocomposite thin film as the electron transport layer of perovskite solar cells, and added graphene to improve the light absorption of perovskite, reduce photoelectronic compounding, and achieve a photoelectric conversion efficiency of the device to 10%.

Jiang et al.[10] prepared zinc oxide/graphene oxide nanoparticles by electrochemical method and applied them to perovskite solar cells as an electron transport layer, which has a protective effect on methylamine, lead, and iodine, with a photoelectric conversion efficiency of 9.31% and can be stable for a long time.

Li et al.[11] invented a method for preparing graphene-doped nanooxide coating solution and thin films for the preparation of perovskite solar cell photoabsorbing layer skeleton films, which overcome the shortcomings of existing nano-Al_2O_3 skeleton films that are easy to crack and non-conductive through graphene doping, and are suitable for the industrial preparation of perovskite solar cell electron transport layers.

Zhang Farong et al.[12] invented a method for preparing transparent conductive films co-doped with graphene and aluminum with zinc oxide, which can be applied to the preparation of perovskite solar cell electron transport layers, which can control the flexibility, conductivity, and porosity of graphene composites through coating solution formulations, and overcome the shortcomings of excessive rigidity of mesoporous TiO_2 electron transport layers.

The graphene used in the above studies includes graphene quantum dots, reduced graphene oxide, and vapor phase chemical deposition graphene. The graphene derivatives used include graphene oxide, lithium salt of graphene oxide, and graphene chloride oxide, all of which are aimed at matching the energy level of perovskite materials. The electron transport layer materials used are TiO_2, ZnO, Al_2O_3, $SrTiO_3$, and perovskite photoabsorbing materials themselves, which are mainly aimed at improving the amount of electron injection and electron transport speed.

Graphene and its derivatives are selected to form graphene composite electron transport layers with traditional electron transport layer materials, because there are complex chemical and physical bonds between the two types of materials, and graphene composites can promote the effective transport of electrons through synergistic effects. The design of the electron transport layer should consider three aspects: energy level matching, electron injection and electron transport performance, and the combination of graphene and traditional electron transport materials can innovatively design a variety of new composite materials. Based on the same principle, they can also improve the performance of non-lead perovskite solar cells, and the application of functional graphene composite electron transport layers in perovskite solar cells will be the main innovation direction in the future.

5. Influencing Factors of Photoelectric Performance and Improvement Strategies

Light-absorbing materials are the technical core of perovskite solar cells, and their charge transport layers play an important role in stabilizing and improving the overall performance of perovskite solar cells. The degradation of light-absorbing layer materials occurs at the interface of perovskite solar cells, which is generally believed to be water intrusion, ultraviolet irradiation, temperature rise, and atmospheric environment influences, crystal structure changes, photodegradation, and chemical oxidative decomposition of light-absorbing materials. This leads to the invasion of ions and moisture into the charge transport layer or electrode layer through grain boundaries, resulting in a decrease in the overall performance of perovskite solar cells. An excellent charge transport layer can promote the separation of carriers, passivation to reduce defects on the surface of the perovskite layer, control the degree of carrier recombination, and reduce the adverse effects of the external environment on light-absorbing materials.

Taking the $CsPbX_3$ system as an example, water intrusion is the primary environmental factor leading to the degradation of perovskite phase in solar cells, which is irreversible, and its degradation path is as follows

$$CsPbX_3+H_2O \rightarrow CsX+Pb(OH)X \rightarrow Pb(OH)_2 \rightarrow PbO$$

Moisture intrusion can also cause tiny holes and cracks on the surface of the film, which gradually spread throughout the film over time.

The degradation of oxygen is mainly reflected in photocatalytic oxidation. O_2 molecules can capture photogenerated electrons on the surface of perovskite, generate superoxide radicals, break Pb-X bonds, and form PbO and X_2. The residual Cs ions will combine with the unreacted halogen ions to form CsX, which will lead to the complete decomposition of the perovskite phase[13]. The charge transport layer is one of the core components of solar cells, and the fragility of this part will lead to the deterioration of the overall performance, so avoiding physical or chemical damage is the key goal to improve operational efficiency and stability, and extend the service life.

Functional molecular or nanomaterial layers such as fullerenes and their derivatives, ammonium halide, graphene oxide, and other materials can also be inserted between the perovskite material and the charge transport layer, such as ammonium halide and graphene oxide, as well as interface layers. This method can effectively passivate the suspension bonds on the perovskite surface and block ion migration and side reactions at the interface, achieving defect passivation and energy level adjustment[14]. In addition, more stable inorganic materials can be considered to replace the organic transport layer, but the specific performance changes and whether it will reduce the photoelectric conversion efficiency of cells still need to be explored, and further research is needed to prove a significant association.

Packaging is an effective guarantee to ensure the long-term performance of battery devices in the operating environment. Through the development of new structures, water intrusion and air oxidation can be reduced from the physical aspect, and the performance deterioration caused by the reaction between electrode materials and perovskites can be prevented. The use of highly sealed materials such as glass for encapsulation, edge sealants, and the addition of appropriate desiccants can be effective means and improvement strategies to improve operational stability.

6. Summary and Outlook

As a material with excellent electrical conductivity and mechanical properties, graphene has great potential for application in perovskite solar cells. To improve the performance of graphene to meet the needs of perovskite cells, chemical and physical modification methods can be used. Specific methods include introducing different functional groups to enhance its interaction with perovskite materials, or improving its structural stability and conductivity through physical methods such as heat treatment and vapor deposition. This process will help improve the dispersion and interfacial binding ability of graphene in cells, thereby improving the overall performance of the composite.

When in-depth study of the mechanism of action of graphene composites in perovskite cells, it is necessary to focus on the analysis of its impact on battery performance, and explore how graphene improves the light absorption capacity, carrier mobility and interfacial charge transfer efficiency of perovskite. In addition, the role of graphene in improving the environmental stability of cells is also the mainstream direction, especially under adverse conditions such as high temperature and high humidity. Through systematic theoretical analysis, the key role of graphene composites in combating various harsh environments can be revealed, providing theoretical basis and practical guidance for future research and application.

This review summarizes the applications of graphene materials in perovskite solar cells and their preparation methods, as well as the environmental factors and corresponding mechanisms affecting battery operation, and provides feasible improvement strategies. Through the in-depth exploration of the above research contents, it is hoped that the research of perovskite solar cells can make further progress and expand their application in renewable energy and other fields.

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