Nanomaterial Modified Perovskite Solar Cells: Black Phosphorus, 2D Perovskite Materials, And Quantum Dots.

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Abstract. Perovskite solar cells have gained significant attention due to their high energy conversion efficiency, low cost, and excellent photovoltaic properties. The efficiency and stability of perovskite solar cells can be enhanced by the modification of novel materials which are in the light-absorbing, electron transport, and hole transport layers. Therefore, finding new materials with excellent photovoltaic properties and stable structures is crucial for improving the performances of perovskite solar cells. Black phosphorus, two-dimensional perovskite materials, and quantum dot materials are the research hotspots in recent years, all of which exhibit excellent properties. Using these materials to modify solar cells is an effective way to reinforce the performance of solar cells. This paper introduced these materials briefly. In addition, their applications in the electron transport layer, light-absorbing layer, and hole transport layer of perovskite solar cells were discussed. The impact of utilizing these materials on improving the stability of solar cells were discussed. This work pointed out promising research directions in this field. Exploring novel methods to solve the trap density problem will contribute to further study on this issue. In addition, it is considered that the properties of the hybrid 2D/3D perovskite materials should be explored. Attempting to improve the stability of quantum dot modified solar cells will also be an urgent issue to be addressed in the future.

Keywords: Perovskite solar cells; stability; quantum dot; black phosphorus.

1. Introduction

Perovskite solar cells (PSCs) are recognized for their highly efficient conversion of energy, low cost, flexibility, and excellent photovoltaic properties. Perovskite material exhibits lead iodide octahedron-dominated electronic structure, strong absorption characteristics, and high defect tolerance. In addition, materials with perovskite structures can obtain stable structures with diverse components by doping different elements. PSCs are a novel photovoltaic cell with a theoretical photovoltaic conversion efficiency up to 30.5%. The efficiency of PSCs can be comparable to that of silicon-based solar cells [1,2]. Therefore, PSCs have become an important research direction for solar cells.

The success of PSCs is primarily attributed to the exceptional photoelectric properties of the perovskite absorber. The utilization of novel materials in different layers of PSCs is crucial in developing and optimizing PSCs. For example, black phosphorus has good thermal stability and carrier mobility. It is considered to be an excellent material for passivating interfacial defects and reducing trap density. Two-dimensional (2D) chalcogenides exhibit strong hydrophobicity and low volatility, which helps to mitigate the impact of humidity on the stability of cells. Quantum dots (QDs) have tunable optical properties, stable performance, wide absorption range, and high quantum yield. They can be used to fabricate perovskite layers with excellent photostability or as interfacial materials in perovskite batteries to reduce photo-degradation. This capability enables them to enhance photovoltaic efficiency and stability of PSCs.

Stability enhancement is a current research focus in the progression of PSCs. However, it is also a challenge for their industrialization and large-scale application. This paper provides a brief introduction of the performances and structures of various new nanomaterials. Their applications in improving the stability of PSCs are be highlighted. Besides, the existing problems and challenges are also discussed.

2. New Materials and their Modification of PSCs

2.1. The Role of Black Phosphorus on the Stability of PSCs

Black phosphorus (BP) is a popular candidate for solar cell modification. BP is the most stable phosphorus isomer. The crystal structure of BP consists of multiple layers of wrinkled phosphorus atoms. Within the layers, each phosphorus atom has five valence electrons in its outer orbitals, which are strongly covalently bonded to three neighbouring atoms. The neighbouring layers are ordered by van der Waals interactions to form a structure which is similar to graphite [3].

The atomic structure of BP consists of three covalent bonds. The two single-electron pairs within its structure interact with the mono and divalent cations of the halocarbons. Good electrical contacts could be obtained through electron donor-acceptor interactions [4]. By this means, the stability could be improved. This could enhance the morphology and reduce the trap density of the carbon halide films. It is indicated that the crystallinity of aluminium halide films has been improved through SEM images and X-ray diffraction (XRD) analyses. Besides, surface roughness and the content of lead iodide (PbI_2) were also reduced. SEM images also revealed that the surface of BPQD acts as the nucleation center, facilitating the formation of denser AlGaH thin films compared to samples without BPQD. The intrinsic characterizations of BP make it an appealing material in hydride doped solar cells to improve the electron transport and extraction characterizations of electronic transport layer (ETL).

2.2. The Impact of 2D Perovskite Materials on the Stability of PSCs

2D perovskites are a type of perovskite material with a unique structure and properties. They typically contain large organic cations, providing greater flexibility in adjusting material structures and composition ratios [5]. This makes them promise for use in solar cells. 2D perovskites have been found to exhibit lower volatility and better hydrophobicity compared to traditional three-dimensional (3D) perovskites [6]. These characteristics contribute to the improvement of stability. Besides, 2D perovskites have enormous potential in enhancing the performance and lifespan of PSCs.

The moisture resistance of 2D PSCs is linked to the hydrophobicity of the organic cations in the light-absorbing layer materials. Typically, the organic cations used in 2D perovskites have longer carbon chains and strong hydrophobicity, which enhances the resistance to moisture. It was reported that (PEA)2(MA)n-1PbnI3n+1 maintain 80% of their efficiency after long time of light exposure without encapsulation [7]. After 2,050 hours, they still retain 70% of the efficiency. In contrast, the solar cells in the control group, which were based on the 3D perovskite material MAPbI3, retained less than 40% of their efficiency after a day of light exposure based on the same conditions. Additionally, 2D PSCs exhibit better thermal stability comparing with their 3D counterparts. The thermal stability of the material and the cell is enhanced due to the layered structure of 2D perovskites, which effectively blocks the internal ionic migration and phase transition crystal transformations within the cell.

2D perovskite materials can be spin-coated onto the 3D perovskite absorber layer, creating 2D/3D hybrid PSCs. The upper layer of 2D perovskite blocks water and oxygen and suppresses internal ion migration, resulting in better stability than 3D PSCs [8]. The addition of a 2D perovskite capping layer can effectively inhibit ion migration within the solar cell absorber layer. It was reported that the 3D perovskite was covered with (PEA)2PbI4 2D perovskite, which suppressed internal ion diffusion and migration effectively, thus reinforcing the stability of PSCs.

2.3. The Impact of QDs on the Stability of PSCs

Halide QDs possess unique properties, such as low-temperature synthesis, multiple exon formation, high absorption coefficient, and high carrier mobility. SnO_2 has significant advantages over halocrystals as the ETL of solar cells. These include favorable conduction band energies at the ETL/halocrystal boundary, broader frequency response to UV radiation for improved stability, and higher electron mobility than TiO_2 [9]. The modified QDs exhibit a photoluminescence quantum yield

(PLQY), which remains a high level even after one month. PSCs fabricated with these QDs demonstrated a power conversion efficiency (PCE) of over 12%. It also has good stability, remaining 85% of their initial performance after 3 months of dry storage. The QDs were modified to achieve PLQY of 100%. After one month later, the quantum yield remains nearly 99%.

The stability of the alloyed aluminium hydride material for several months in ambient air demonstrates the feasibility of an alloying strategy to improve the stability of Sn^{2+} ions. Triphenyl phosphite serves as an antioxidant in chromide feedstocks. The $CsSnI_3$ QDs exhibit excellent stability over several months due to the effective scavenging of oxygen by triphenyl phosphite and the prevention of the conversion of Sn^{2+} to Sn^{4+}.

Surface defects can cause moisture and oxygen to penetrate the film, breaking down the perovskite crystals and ultimately leading to bad cell stability. Additionally, intense and prolonged exposure to light causes degradation, migration of FA or MA cations and halide ions, which produce vacancies and interstitial ions in the PSC that act as carrier retention sites. Therefore, to enhance overall stability, it is necessary to produce high quality perovskite films with fewer surface defects and grain boundary trap states. One approach to achieve this is to use various QDs as multifunctional additives to improve the morphology of perovskite films. By this way, their surface defects and the grain boundary trap states could be passivated.

The study revealed that surface defects and trapping conditions could cause damage to the halide crystals and resulte in poor cell stability. Additionally, FA or MA cations are lost with prolonged light degradation. Halide ions also migrated as a result, thus vacancies and voids become carrier traps in PSCs [10]. Therefore, to enhance overall stability, high-quality sulfur-based films with fewer surface and grain boundary defects must be produced. One approach is to use various QDs to improve perovskite film morphology.

A variety of inorganic materials with excellent stability and low cost have been developed, such as NiO, CuSCN and CuI. Cu-based inorganic materials are p-type, non-toxic and exhibit high hole mobility [11]. The use of graphene QDs doped in P3HT films as a hole transport layer can reinforce the long wavelength light scattering of PSCs and thus improve their light absorption efficiency [12]. In addition, excellent hydrophobicity of graphene QDs when doped allows them to improve the stability of PSCs over long periods of time.

Interfacial engineering is an efficient method for improving the performance of PSCs by increasing their efficiency. To achieve this, it is crucial to ensure the efficient transfer of photogenerated charge carriers from the halide layer to the ETL and HTL. The intermediate layer between the halide film and the ETL/HTL plays a vital role in reversing the crystallization direction, slowing down carrier complexation, and facilitating charge release/removal. The intermediate layer acts as an insulating layer to minimize the impact of time, humidity, and heat on stability [13]. QDs can refine the quality of halide films and passivate surface defects. Therefore, QDs are commonly utilized as interlayer modifiers to expedite charge release, diminish photocurrent hysteresis, and enhance device stability.

3. Conclusion

Perovskite is a highly regarded material in the new generation of photovoltaic fields due to its excellent photoelectric properties. Photovoltaic devices based on perovskite materials have achieved efficiencies of over 26%. This article focuses on the role of black phosphorus, 2D perovskite materials, and QDs in improving the stability of PSCs. The BP could improve electrical properties, optical performance of PSCs. In addition, the good compatibility of materials makes them an excellent choice for enhancing battery stability. Previous research has shown that the addition of BPs to PSCs can increase their PCE and enhance device stability. 2D perovskites have better stability due to their layered characteristics. Additionally, the hydrophobic nature of organic cations can prevent the destruction of water and oxygen to the cells, inhibiting ion migration and phase transition within the cells. Thereby it can also improve the stability of PSCs. Besides, PSCs that are a hybrid of 2D and 3D structures, can balance efficiency and stability to a certain extent. This is significant for achieving

high efficiency and stable perovskite photovoltaic devices. Additionally, the use of various quantum dot materials with excellent photoelectric properties were shown to reinforce the efficiency and stability of PSCs. Advanced QDs were shown to be useful as light harvesters, charge carrier transporters, film additives, and interface modifiers. The use of quantum dots has been demonstrated to enhance the crystallinity of halides, decrease surface defects, and improve stability by introducing an intermediate layer between the halide and the ETL/HTL. This reduces the impact of time, humidity, and heat on halide solar cells. In summary, the key to enhancing the stability of PSCs lies in the modification of 2D perovskite materials and QD materials. These materials, when combined with optimized interfacial layers, offer a promising path for stabilizing PSCs systems. Nano-material innovations will contribute to the further application of PSCs.

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