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## Introduction – Why Composites-Based Perovskite Solar Cells?

### 1.1 Need to Develop Composites-Based Perovskite Solar Cells

Global electricity demand has continued to increase at a higher rate than the rate of global energy production. Compared to fossil fuels that produce huge amounts of carbon and cause global warming, the development of technologies related to energy conversion and storage for various clean and renewable energy resources such as solar, wind, hydro, and biomass is a big challenge of our time. Among the renewable energy resources, solar energy is the richest and the most eco-friendly energy source on the planet that can supply the growing electricity demand, evaluating that photovoltaic (PV) technology is the most effective and promising technology. The solar PV industry is a vast field with various solar cells divided into several generations.

Silicon-based solar cells, classified as first generation, are the most common type of PV with a market share of 95%. Crystalline silicon solar cells have many benefits, such as high efficiency of more than 20%, nontoxic material, good photoconductivity and stability, resistant to corrosion, long lifetime span of over 25 years, low maintenance, and versatile applications. However, due to the complex processes of manufacturing crystalline silicon and the use of pricey and high quality of silicon, the silicon solar cell panels are quite expensive. By contrast, thin-film solar panels, classified as second generation, are lighter, less expensive, and more flexible than the silicon solar panels, allowing for easier installation in versatile applications.

Among the thin-film solar cells, made with newer and less established materials, are classified as third generation or next generation. The emerging third-generation solar cells include innovative technologies, such as perovskite, dye-sensitized, quantum-dot, organic, and semiconducting compound-based (e.g. CZTS, CZTSe, CIGS, and CdTe) thin-film solar cells. Among the third-generation solar cells, perovskite solar cells (PSCs) have emerged as a promising candidate for the next-generation solar cell industry with an unprecedented rise of power conversion efficiency (PCE) exceeding 26%. It is also worth noting that the best PCEs of tandem cells are 29.1% and 33.9%, respectively, with perovskite tandem cell and perovskite/Si (two terminals) tandem cell [1].

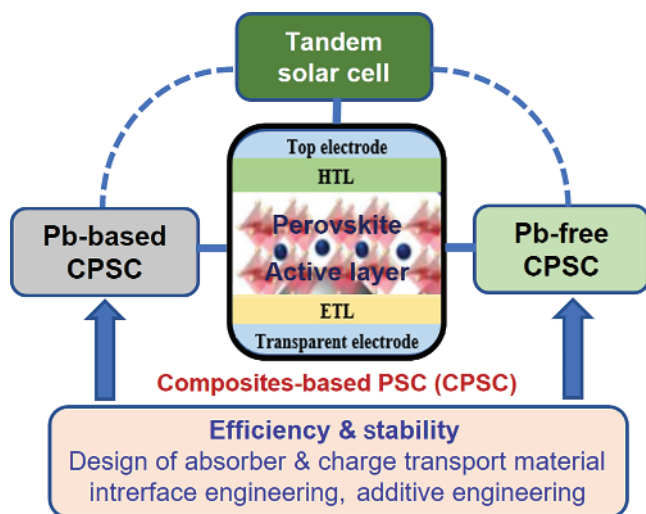
In PSCs, light-harvesting material is the perovskite that has the same crystal structure as the naturally occurring mineral calcium titanium oxide ( $\text{CaTiO}_3$ )

with an  $ABX_3$  crystal structure (see Chapter 2). It is worth noting that perovskites have remarkable characteristics for PV applications, such as direct bandgap, broad light-harvesting ability, high defect tolerance ability, long charge carrier diffusion length, and cost-effective easy fabrication. However, the lack of stability of perovskite materials is a well-known problem that degrades the performance of PSCs. One of the main reasons for instability is that the perovskite materials contain unstable elements due to extra weak interactions, such as van der Waals force and weak hydrogen bonds [2]. Moreover, the stability of perovskite technology depends on its environmental factors, such as humidity, heat accumulation, and continuous irradiation of sunlight [3]. Thus, the degradation of device performance is caused by external and internal factors. The former includes air-, thermal-, and photo-induced instability, and the latter includes intrinsic factors such as ions migration and interfacial recombination attributed to grain boundaries, contact interface, and vacancies.

Solution-processed polycrystalline perovskite thin films present parasitic bulk and interface defects during the crystal growth process. In addition, their bulk and interface trap densities are higher than that of single-crystal perovskites. These bulk and interface defects often cause undesirable deep-level traps: undercoordinated  $Pb^{2+}$  ions, undercoordinated halide ions, metallic lead clusters, and intrinsic point defects (such as ion vacancies and Pb-I antisite defects) [4, 5]. Therefore, defects at the bulk grain boundaries (GBs) and at interfaces of perovskite polycrystalline thin films become major sources to induce shallow trap states and localize charge carriers through nonradiative recombination, which are detrimental to the efficiency and stability of PSCs. To overcome these defects, achieving a high-quality perovskite film and its defect passivation is crucial. Thus, tremendous efforts have been dedicated toward minimizing the perovskite GBs and surface/interface defects by additive engineering to induce the formation of perovskite-based composites.

As the stability issues are mostly related to materials in terms of chemical, optical, and mechanical properties, to resolve the instability problems of PSCs, robust materials that can improve their chemical, electrical, optical, and thermal properties should be developed. The development of perovskite-based composites with composition engineering has been considered an efficient strategy to stabilize the structures of perovskite and further improve their optical and electronic properties. Recently, it has been reported that composite materials are efficient for solving or alleviating the stability issues of PSCs [6–20]. A composite material is a combination of two or more materials having different chemical and physical properties. Compared to traditional materials, composites can improve the properties of base materials and can be applied in many situations. Composite materials have advantages such as design flexibility, specialized chemical and physical properties, and resistance to a wide range of chemicals. Therefore, they may give benefits to solve critical issues related to the efficiency and operational stability of PSCs.

Figure 1.1 illustrates the development strategy of composites-based perovskite solar cells (CPSCs) schematically, in which composite materials can be used for active layer (AL) and charge-transport layers. The incorporation of composite materials can significantly improve the PCE and stability of single-junction solar

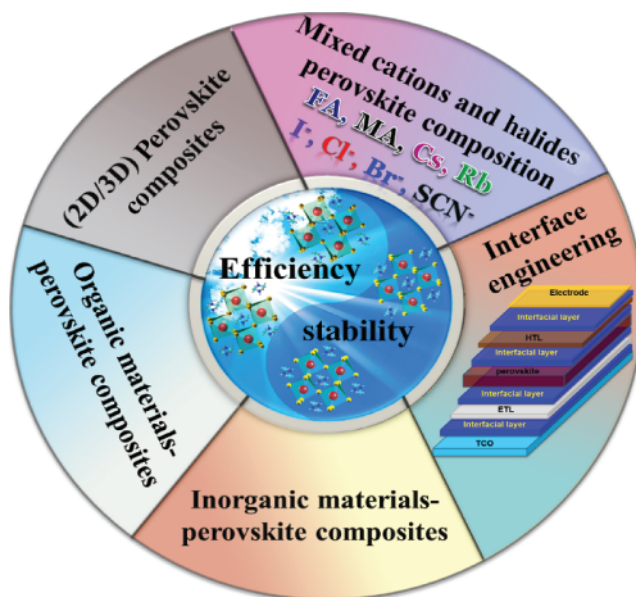


**Figure 1.1** Schematic illustration of the development strategy of composites-based perovskite solar cells.

cells as well as of tandem cells. This strategy is applicable to the development of both Pb-based and Pb-free CPSCs. To enhance the PCE and stability, it is crucial to design optimal light-absorbing and charge-transport materials along with interface engineering and additive engineering.

## 1.2 Fabrication Strategy for Composites-Based Perovskite Solar Cells

In addition to stabilizing the AL with composite-based perovskites, interface engineering plays a crucial role because the interface contacts between the light-absorbing and charge-conducting materials are worthy of further study toward commercialization of PSCs in terms of interfacial energetics, charge transfer, and recombination kinetics, and interfacial degradation [17, 21, 22]. A typical PSC configuration consists of a perovskite film sandwiched between electron-transport layer (ETL) and hole-transport layer (HTL), which can form ETL/perovskite and perovskite/HTL interfaces, respectively. The carrier transport contacts and their interfaces determine device performance, including PCE, long-term stability, and J–V hysteresis. The separated holes and electrons have to transport across the interfaces in the device, but charge loss often occurs because of possible interfacial defects. GBs within the AL separating perovskite grains also induce recombination and provide moisture and oxygen penetration pathways, resulting in J–V hysteresis, device performance loss, and deterioration. Particularly, the interfacial degradation between absorber and contact materials has become a critical intrinsic factor, resulting in poor stability of PSCs. The ETL/AL and AL/HTL contacts may induce interfacial collapse of the perovskite structures because groups



**Figure 1.2** Schematic illustration of an efficient strategy for the fabrication of highly stable and efficient PSCs: inclusion of perovskite-based composites and interface engineering.

of perovskite atoms or interfaces may move or be disordered under real operation conditions such as humidity, air, heat, and UV [17, 23, 24]. Therefore, interfacial engineering is important to improve interfacial contact by interface modifications such as interlayers or multilayers, which form a stabilized interface between active and charge-collecting layers, ultimately improving the device performance and stability. The purpose of interface engineering is to modify perovskite contact and crystal growth, tune energy band alignment for reducing electron or hole transport barrier, lower recombination, enhance charge carriers transfer, and suppress interfacial defects and ions migration.

Figure 1.2 presents an efficient strategy for fabricating highly stable and efficient CPSCs with the inclusion of functional perovskite composite materials and interface engineering. The composite materials include mixed cations and halides perovskite with composition engineering, 2D/3D perovskite composites, organic material-perovskite composites, and inorganic material-perovskite composites. The perovskite-based composites can significantly regulate the optical and electronic properties of perovskites and facilitate the growth of perovskite grains and carriers transport, but they inhibit ion migration and reduce defect formation. Besides, the organic or inorganic materials incorporated in perovskite composites also remarkably enhance stability because of their protective effects and strong chemical interaction and cross-linking behavior. The 2D/3D perovskite composites significantly enhance device stability without sacrificing the considerable performance of PSCs. Furthermore, the organic or inorganic substances contained in perovskite composites significantly improve their stability thanks to their protective

effects and strong chemical interactions and crosslinking with perovskite molecules. In addition, the strategy of interface stabilization can improve interfacial contact, assist the growth of perovskite grains, passivate perovskite film surface, facilitate charge transport, suppress ions migration, and protect perovskite films from water and oxygen molecules. Thus, it can be concluded that the strategy utilizing both perovskite-based composites and interfacial engineering is one of the most efficient ways to achieve high-efficiency and stable perovskite photovoltaics.

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