

Chapter 2

The Evolution of Perovskite Solar Cells Structures

2.1 Perovskite Solar Cells with Liquid Electrolyte

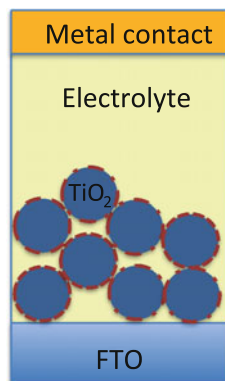
Organo-metal lead halide perovskite was first used in solar cells in 2009 by Miyasaka et al. [1] $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{Br}, \text{I}$) was applied as a sensitizer in a Dye Sensitized Solar Cell (DSSC) with liquid electrolyte. The conductive glass was coated with TiO_2 NPs and the perovskite was deposited on top the TiO_2 NPs, the cell structure is depicted in Fig. 2.1. PCE of 3.1 % was demonstrated for $\text{X} = \text{Br}$ and 3.8 % for $\text{X} = \text{I}$ [1], with spectral response covering the whole visible region till 800 nm. Park et al. [2] reported in 2011 PCE of 6.5 % employing similar structure in which 2–3 nm sensitized nanoparticles of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite was deposited in a one-step solution process on top 3.6 μm thick TiO_2 NPs with iodide/iodine-based redox electrolyte. They have showed that perovskite exhibited better absorption than the standard N719 dye sensitizer, but the ionic crystal perovskite dissolved in the polar electrolyte, resulting in rapid degradation of performance [2].

The effect of TiO_2 film thickness was investigated in sensitized $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells [3] studying the charge transport, recombination, and PV performance using iodide-based electrolyte. It was found that $\text{CH}_3\text{NH}_3\text{PbI}_3$ is relatively stable in a nonpolar solvent with low iodide concentration. However, polar electrolyte or higher iodide concentration of nonpolar electrolyte achieved higher cell performances, but result in degradation or bleaching of the perovskite.

2.2 Perovskite Solar Cells with Solid-State Hole Conductor

Replacing the liquid electrolyte with a solid-hole conductor material (HTM) solved the immediate instability problem of the perovskite-based solar cells and increased their efficiencies. Park and Gratzel [4] reported in 2012 of a solid-state stable

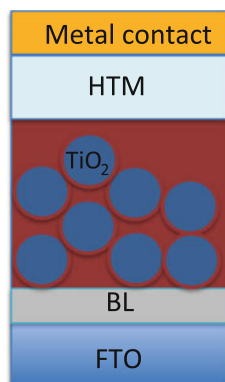
Fig. 2.1 Structure of liquid-sensitized perovskite solar cell. The *brown* color indicates the perovskite



perovskite solar cell. They deposited $\text{CH}_3\text{NH}_3\text{PbI}_3$ onto a mesoporous TiO_2 film and introduced a spiro-MeOTAD (2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene), HTM. When dissolved in an organic solvent, spiro-MeOTAD percolates the TiO_2 NPs, leaving only solute molecules after solvent evaporation (Fig 2.2). The replacement of the liquid electrolyte with spiro-MeOTAD not only improved the stability of the solar cell, but also boosted its efficiency to 9.7 % [4].

Snaith et al. [5] reported a PCE of 10.9 % with high V_{oc} of 0.98 V, in which mixed halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ coated mesoporous Al_2O_3 film rather TiO_2 film with spiro-MeOTAD as HTM. It was shown that the mesoporous Al_2O_3 served only as a scaffold for the perovskite and not as an electron acceptor as in the case of mesoporous TiO_2 , due to the higher valence band of Al_2O_3 . As a result, the electrons must remain in the perovskite, and transferred through the perovskite to the compact TiO_2 then to the FTO electrode. They were able to demonstrate that perovskite is able to transport both electrons and holes between cell terminals, besides of being used as a sensitizer [5]. Their cell structured named “meso-superstructured solar cell” (MSSC), because of the existence meso-structure and the absence of electron injection to meso-structure.

Fig. 2.2 Structure of solid-sensitized perovskite solar cell. BL-blocking layer; HTM-hole transport material

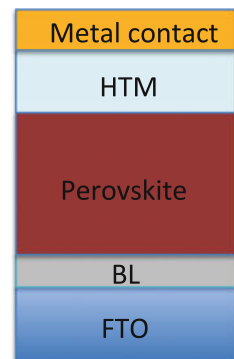


Few months later further progress was reported. The two-step deposition process was reported when the perovskite layer was prepared by spin-coating PbI_2 solution onto the electrode coated with the TiO_2 scaffold and then dip the electrode into the cation iodide solution (such as $\text{CH}_3\text{NH}_3\text{I}$ solution). Better coverage and few hundred-nanometer perovskite over layer were achieved by this deposition technique. As a result PCE of 15 % was reported using this deposition technique.

2.3 Perovskite Solar Cells in Planar Configuration

Due to the superior properties of the perovskite, it was shown that the perovskite could function as light harvester in planar configuration. The initial planar perovskite solar cell was fabricated by Snaith et al. [5], where $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ was deposited through a solution process on top of FTO conductive glass coated with compact TiO_2 (BL), the cell structure is depicted in Fig. 2.3. In the beginning Low PCE of 1.8 % was achieved, due to the need of homogenous high surface coverage. Snaith and coworkers [6] then optimized the film formation of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite by controlling the atmosphere, and annealing temperature and achieved PCE of 11.4 % with J_{sc} of 20.3 mA/cm^2 and V_{oc} of 0.89 V. The use of vapor-deposition technique [7] for the perovskite has improved the PCE of the planar configuration to 15.4 % with V_{oc} of 1.07 V. These findings showed that perovskite could be used in a simple architecture solar cell without the need of mesoporous n-type semiconductor. Kelly and colleague [8] improved the PCE to 15.7 % by deposition MAPbI_3 in a two-step deposition on top of compact ZnO instead of compact TiO_2 . Yang's groups [9] demonstrated further increase in PCE to 19.3 % by modifying the commonly planar configuration.

Fig. 2.3 Structure of planar solid-state perovskite solar cell



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<http://www.springer.com/978-3-319-32989-5>

Hole Conductor Free Perovskite-based Solar Cells

Etgar, L.

2016, VIII, 59 p. 39 illus., 37 illus. in color., Softcover

ISBN: 978-3-319-32989-5