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Survey Article

Advances in Perovskite-Based Solar Cells

O.R. Kesinro¹, M.L. Akinyemi¹ and A.O. Boyo²

¹Department of Physics, Covenant University, Ota, Ogun State, Nigeria

²Department of Physics, Lagos State University, Lagos, Nigeria

*Corresponding author: olakesinro02@gmail.com

Abstract. The increase in energy demand due to increase in population and reduction of fossil fuels has led to the search of alternative energy sources. Solar energy, which is an alternative source of energy, has been in the fore front of this research. Various methods of converting solar energy into electricity has been attained by silicon solar cells, thin film solar cells, dye sensitized solar cells and perovskite solar cells. Unlike dye sensitized solar cells, perovskite solar cells based on lead halide perovskite or organic-inorganic halide perovskite have had a significant impact on photovoltaic devices. A power conversion efficiency of approximately 20.1% has been attained by perovskite solar cells compared to organic solar cells. Also, several fabrication techniques, hole and electron transport materials have been developed for high performance. Although, some issues need to be addressed before commercialization is possible. Issues like stability of the cells under moisture and temperature. In this review, fundamental aspects of the perovskite device and recent breakthroughs are illustrated.

Keywords. Hole transport material; Electron transport material; Perovskite; Stability

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1. Introduction

Solar energy is a form of renewable energy, which is an alternative source to traditional resources such as coal. In this regard, developing solar cells is one of the most important approaches to gain electrical energy from the conversion of solar energy with sunlight being the source of energy. The source of energy would be sunlight. Silicon-based solar cells have been used due to their efficient solar to power generation (~30%) particularly crystalline silicon [1]. The cost of silicon based solar cells is relatively high and difficult to utilize in large scale industrial areas. Generally solar cells can be classified as (i) first generation solar cells (mono crystalline and poly crystalline silicon), (ii) second generation solar cells [amorphous silicon (a-Si), microcrystalline silicon, copper indium gallium selenide (CIGS), and cadmium telluride (CdTe)] and (iii) third generation solar cells (polymer solar cells, oligomers, dye synthesized solar cells (DSSCs), and organic/inorganic hybrid perovskite solar cells). The third generation photovoltaic devices, which have been developed based on various dye sensitizers, organic-inorganic materials have reached efficiency up to ~ 15-20% ([2], [3]).

Perovskites are materials used in the fabrication of solar cells and have reached an efficiency of 20% within 5 years, due to substantial improvement of power conversion efficiency (PCE) and low processing cost [4]. Perovskite named after the Russian mineralogist L. A. Perovski has a specific crystal structure with MAX_3 (X = oxygen or halogen). The larger M cation considered as an organic, which is generally methylammonium ($CH_3NH_3^+$) Ethylammonium ($CH_3CH_2NH_3^+$) and Formamium ($NH_2CH=NH_2$) occupies a cubo-octahedral site shared with twelve X anions ([5], [6]). The cation B, Lead (Pb) is universally considered for stabilization efficiency in solar cells. Although Tin (Sn) has similar band gap (1.55 eV) and in the same group as Pb, due to the ease of oxidation and lack of stability, it performs poorly compared to Pb in efficiency.

The most studied perovskite are oxides due to their electrical properties of ferroelectricity or superconductivity. Halide perovskites received little attention until layered organometal halide perovskite were reported to exhibit a semiconductor-to-metal transition with increasing dimensionality [7]. The working principles for perovskite solar cells are different to that of DSSC, they are more like a thin film semiconductor solar cell rather than a device which has a separate sensitizer. The perovskite solar cell is made up of different layers namely Electron Transport Layer (ETL), Hole Transport Layer (HTL) and Electrode.

The first reported perovskite solar cell employing $CH_3NH_3PbI_3$ achieved an efficiency of 3.81% [8], changes to the device geometry and architecture allowed for a rise in device performance for which the highest reported value is 20.1% ([4], [10]).

Unlike silicon solar cells, perovskite solar cells are solution processable with diversity, abundance and large scale manufacturing. Also, they have advantages including mechanical flexibility, light weight, low material consumption, color turning and less toxicity. However, poor stability of perovskite solar cells to temperature and moisture has been its major limitations.

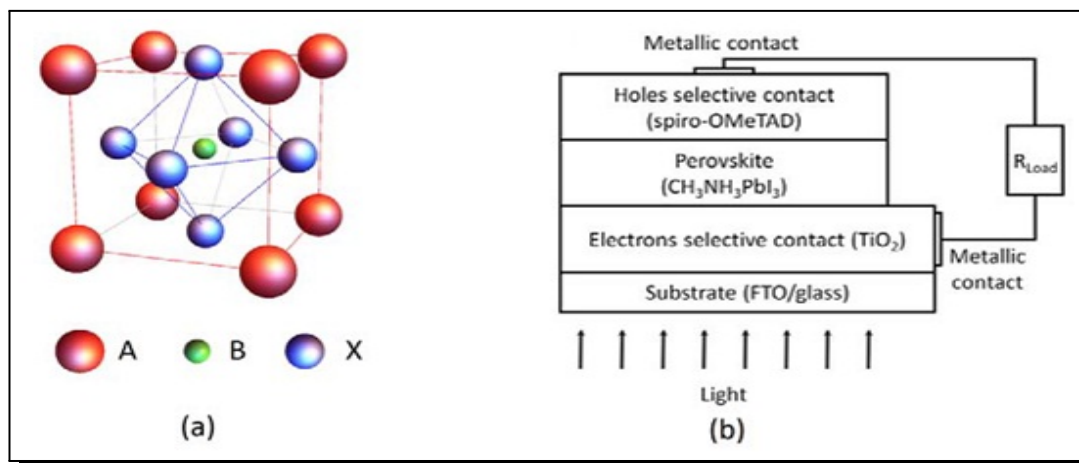


Figure 1. (a) Generic perovskite crystal unit cell structure. (b) Typical structure of PSCs

2. Progress In Organic – Inorganic Halide Perovskite Solar Cells

Reference [11] formed a planar perovskite solar cell by replacing TiO₂ with SnO₂ as the electron selective layer. It was formed by spin coating SnO₂ nanoparticles and sintering at 200°C for 1 hour which is a lower temperature than that required for TiO₂. The perovskite layer was deposited using two step deposition process. A solvent vapor annealing step was included to crystallize the PbI₂ crystallites into the SnO₂/CH₃NH₃PbI₃ interface. A cell efficiency of 13% was achieved. Also, SnO₂ devices that were not encapsulated and stored in ambient conditions, the measured PCE were quite stable for 700 hours. This is significantly more stable than TiO₂ based devices.

Reference [12] made use of chemical engineering to alter the stability of the commonly used CH₃NH₃PbI₃. They included an additive butylphosphonic acid 4-ammonium chloride (4-ABPACl) into a one step spin coating method to modify the CH₃NH₃PbI₃ surface. It was observed that these additive molecules bond to the surface of CH₃NH₃PbI₃, rather than becoming integrated into the perovskite crystal structure. The inclusion of this cross linking additive leads to the formation of improved infiltration into the underlying TiO₂. The improvement gives rise to an increased efficiency higher than 16%, almost double that of the control device. Measuring the device stability at 55% relative humidity within the first week, the control device degraded rapidly indicative of the moisture induced decomposition of the perovskite layer. The 4-ABPACl-modified devices remained relatively constant during the testing period.

Reference [13] described the role of different layers in perovskite solar cells to achieve a PCE of 16%. Vacuum Assisted One- Step solution (VAOS) method was reported for producing high quality perovskite layers. A compact and pin-hole free perovskite layer by accelerating the crystallization process by the VAOS method. The mixed halide perovskite solution was spin coated on the Indium doped tin oxide (ITO) / poly-(2,3-dihydrothieno-1, 4-dioxin)-poly(styrene-sulfonate) (PEDOT: PSS) substrate. C₆₀ layer is used to act as a selective electron extraction

layer on the solar cell. C₆₀ layers with different thickness have been thermally evaporated on top of the perovskite film. For further optimization, lithium fluoride (LiF) was used as an interfacial layer between ETL and metal contact. A PCE of 13.3% was achieved with LiF and 12.6% without LiF.

Reference [14] also developed a simple and robust process to prepare efficient perovskite solar cells. Pinhole free thin films of CH₃NH₃PbI_{3-x}Cl_x were coated on high conductivity PEDOT:PSS. The process utilized PCBM as ETL with a PCE greater than 12%. Different deposition procedures were tested and characterized using scanning electron microscope. Also, the PEDOT:PSS was deposited together with DMSO and zonyl additives. A device architecture of ITO/PEDOT:PSS/perovskite/PCBM/Al was fabricated. Different PCEs were determined by current-voltage characterization by sweeping from negative to positive values and vice versa. The devices showed low leakage currents at reverse bias and good stability when operated under continuous solar illumination. A PCE in the range of 12-12.5% was attained.

Reference [15] used thin film PT instead of PEDOT:PSS film. It was deposited by electrochemical polymerization. The thickness of the PT layer was 5nm, significantly thicker than other HTLs. A PCE of 15.4% was attained for the device which is higher than reference PEDOT:PSS. The stability of the PT/CH₃NH₃PbI₃ device remained stable over a 816 hour test period compared to PEDOT:PSS reference. Zhang et al, 2015 investigated a new structure of CH₃NH₃PbI₂Br and P3HT. Spiro-OMeTAD was replaced with P3HT. The devices using this combination attained a device performance of 6.64%. The stability of such devices was tested for non-encapsulated devices over a test period of 250h, the efficiency remained stable.

Reference [13] showed that the crystallization of the initial PbI₂ layer can be retarded by the use of N,N-dimethylsulfoxide (DMSO) as the solvent instead of N,N-dimethylformamide (DMF), which is typically, used resulting in more controlled particle sizes, more complete conversion and increased reproducibility of film quality. Burschka et al. [7] infiltrated a mesoporous TiO₂ film with solution containing PbI₂ and subsequently converted the film to CH₃NH₃PbI₃ perovskite by exposing it to a solution of MAPI. Devices fabricated using the mesostructured TiO₂ designs achieved a PCE of 15.3%.

Reference [18] demonstrated the use of solution processed Cu-doped NiO_x HTL in the construction of high performance planar heterojunction perovskite (CH₃NH₃PbI₃) solar cells. It was noted that the electrical conductivity and favorable crystallization of the perovskite was due to the Cu-doping. A PCE of up to 15.40% was obtained with decent environmental stability. Also, different HTLs were fabricated and compared with Cu:NiO_x, they included NiO_x and PEDOT:PSS. The different HTLs were spin coated on substrates. Then, perovskite layer was spin coated afterward PCBM and C₆₀-bis surfactant were spin coated sequentially as ETL and cathode interfacial layer respectively. A PCE of up to 15.40%, 11.16% and 8.94% was obtained for Cu:NiO_x, PEDOT:PSS and NiO_x respectively.

3. Methods for Fabricating Perovskite Solar Cells

3.1 Solution Processed Two-Step Method

Two step sequential depositions was first proposed by [18], where PbI_2 was deposited on substrate prior to $\text{CH}_3\text{NH}_3\text{I}$ treatment by either vacuum evaporation or spin coating. The PbI_2 coated substrate will be dipped in $\text{CH}_3\text{NH}_3\text{I}$ solution. Saturated methanol solution of PbI_2 will be used as precursor solution for spin coating process. A similar procedure will be performed, where PbI_2 layer is formed on the mesoporous TiO_2 film by spin coating a PbI_2 solution in *N,N*-dimethylformamide (DMF) at 70°C . The dried PbI_2 film is dipped in a solution of $\text{CH}_3\text{NH}_3\text{I}$ in 2-propanol for 20s. A certified PCE of 14.1% has been achieved using two step method.

3.2 Solution-Processed Single Precursor and anti Solvent Method

One step method was discovered to be better in terms of minimizing the processing step. However, solar cell performance made by simple a one step method is inferior to two step results because of significant difference in morphology of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ [10].

The precursor of $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 will be dissolved in the mixed solution of *N,N*-dimethylsulfoxide (DMSO) and GBL, which will be spin coated on the substrate. Anti-solvent such as toluene will be dripped while spin coating the precursor solution.

3.3 Vacuum Deposition Method

Organo lead halide film was prepared by vacuum deposition process. The vapor process is argued to be better than the solution process in planar heterojunction layout because the former produces a flat and even surface. A sequential layer by layer vapor deposition is produced similar to the two step solution process, where PbCl_2 or PbI_2 will be first deposited by thermal evaporation, which will be followed by vapor deposition of $\text{CH}_3\text{NH}_3\text{I}$. The sequential deposition was developed because of difficulty in monitoring $\text{CH}_3\text{NH}_3\text{I}$ deposition rate in co-deposition process.

4. Conclusion

Perovskite materials are in position to disrupt the present photovoltaic landscape. They will be significant for research and commercialization of solar cells in the next few years. However, few problems need to be minimized with respect to commercialization: (1) Cost effectiveness. (2) stability in moisture and (3) toxicity of Pb atoms. Alternatively, perovskite absorber materials can be coupled with dye sensitized solar cells or silicon solar cells to form higher efficiencies. Also different combination deposition methods can be worked on to determine higher power conversion efficiencies.

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Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

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