RECENT ADVANCES OF METAL-ORGANIC FRAMEWORKS IN PEROVSKITE SOLAR CELL

Abstract

Among the third generation photovoltaic devices, organic-inorganic hybrid perovskite solar cells (PSCs) are the most significant scaffold due to its skyrocketing increase in the photo conversion efficiency from 3.8% to 25.7% within a decade. The metal organic frameworks (MOFs) scaffolds are porous materials in which metal ions connected with organic ligands through coordination bond thereby creating a three-dimensional network structure. The prominent characteristics of metal-organic frameworks (MOFs) are high porosity, tunable pore size, ultra high surface area, crystalline with rigid and flexible frameworks. It is observed that incorporation of metal-organic frameworks (MOFs) in the different layers of perovskite solar cells improved the device efficiency and improved stability.

Keywords: Metal-organic frameworks (MOFs, Perovskite solar cell (PSC), Power conversion efficiency (PCE), HTL, ETL, Interfacial layer.

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I. INTRODUCTION

The main challenge lies ahead to mankind is energy crisis. We cannot imagine a day without consumption of electricity. As per the approximate, earth uses only small amount 1.8 x 10^{14} k $Ws^{-1}$of solar energy out of 3.8 x 10^{23} k $Ws^{-1}$of solar energy that strikes the earth. The amount of solar energy that strikes the earth per day is sufficient for the energy consumption of the present world for 27 years [1-3]. This fact indicates the greater importance of renewable energy resource solar energy. Due to increase in the environmental risk by combustion of fossil fuel pressurized to search for renewable, green and sustainable energy resources [4-5]. The global energy demand can be meet through renewable energy resources which are most promising energy resources due to their endless free availability and specially there is no effect of these on the environment, climate and human health [6-7]. One of the prominent, promising renewable energy source is solar energy. The solar energy is the indispensable energy among all the renewable energies such as wind, tidal due to its unique characteristics such as tremendous abundance naturally, resource-free, pollution -free and economically viable [8-10]. But we cannot use solar energy directly until it is converted into the useable energy. The device which converts the readily available solar energy into useable electrical energy is called solar cell [11]. So far three generations of solar cells have been evolved. Monocrystalline and polycrystalline silicon cells are first generation solar cells. The second generation involves the construction of thin films and copper indium gallium selenide (CIGS) is one of the extensively studied solar cells. Among the third generation solar cells Perovskite solar cells (PSCs) has garnered the attention of scientific community due to its unique characteristics such as carrier mobility, tunable bandgap, ability of ambipolar charge transporting, low-cost fabrication, ability of wide range light absorption [12-13].

Since the discovery of PSC in 2009 with power conversion efficiency 3.8% has skyrocketing increase in PCE of 25.7% in 2023 but still the key obstacle for the commercialization of Perovskite solar cells (PSCs) is the less stability as it decomposes easily due to sensitivity of perovskites towards oxygen and moisture. PSCs are potential promising candidates to design efficient, stable and low cost photovoltaic techniques [14-15].

The general structure of perovskite is ABX_3, where A is a site contains organic or inorganic cation (Ex. Methylamine, formamidinium, calcium, cesium etc.), B is a site contains bivalent metal cations such as Tin, lead, titanium etc., X is a site contains contains an halide like (Cl^- Br^- I^- etc.,). The basic model of perovskite solar cell comprised of perovskite layer which serves as light absorber, Conductive layer (FTO or ITO), Hole transport layer (HTL made up of spiro-MeoTAD), Electron transport layer (ETL made up of TiO_2) and metal electrode. These PSCs are mainly classified into n-i-p and p-i-n configurations [16-18]. The power conversion efficiency of PSCs are in comparable with that of commercialized silicon based solar cells. However, the lack of long-term stability is the hindrance for its commercialization. If the stability of PSC is improved then PSC will dominate in the market of photovoltaic. So, for the commercialization of PSCs, researchers should focus their attention in increasing the efficiency, low-cost fabrication and stability. Diverse structural modifications and several fabrication processes have been employed to increase the stability. Researchers have tried the incorporation of Metal Organic Frameworks (MOFs) at interfacial layer, ETL and HTL to improve the PCE and stability.

Basically, metal-organic frameworks (MOFs) are porous materials in which metal ions connected with organic ligands through coordination bond thereby creating a three-dimensional network structure. The prominent characteristics of metal-organic frameworks (MOFs) are high porosity, tunable pore size, ultra high surface area, crystalline with rigid and flexible frameworks [19-20]. Since the discovery of metal-organic frameworks (MOFs) in 1990, they have been studied extensively in various fields such as biomedicine, catalysis, sensors, chiral separation, gas storage , opto-electronics etc [21-25]. However, application of metal-organic frameworks (MOFs) and their derivatives in the field of photovoltaic devices found less in the literature. Till date, the usage of metal-organic frameworks (MOFs) in solar cell technology at its toddler stage. The incorporation of metal-organic frameworks (MOFs) in the solar cells first reported in 2007 as an active material in dye sensitized solar cells (DSSCs). Since then MOF-sensitized solar cells were reported in the literature 2016 & 2017 [26-28]. It is observed that incorporation of metal-organic frameworks (MOFs) in the different layers of perovskite solar cells improved the device efficiency and improved stability. In general the porous scaffold metal-organic frameworks (MOFs) enhance the crystallinity of perovskite layer by regulating its growth [29].

This review mainly focused on the major developments that driven in the PSCs by the utilization of metal-organic frameworks (MOFs) are summarized as follows, (a) MOFs as Hole transport layer (b) MOFs as Electron transport layer (c) MOFs as Interfacial layer.

1. **MOFs as Hole transport layer:** The primary responsibility of HTL is (i) extraction of holes created in perovskite and tranfet them to the metal electrode, (ii) to stop the transfer of electrons to the cathode there by blocking the recombination of electron-hole pair and (iii) to increase the stability by preventing moisture absorption into perovskite layer. The very common used HTL in normal n-i-p PSCs is 9,9^{l}-spirobifluorine (spiro-OMeTAD). But, it has low conductivity and low mobility which limits its use. The major challenges that would be improved in HTL is stability and conductivity. An ideal HTL would have excellent thermal stability, strong hole mobility, low electron affinity, hydrophobic, low-cost and easy fabrication. In this section, we presented the recent adavances on MOFs where the stability and conductivities of spiro-OMeTAD were investigated [30].

   To improve the conductivity of spiro-OMeTAD, the additives such as tetra-tert-butyllpyridine (TBP) and lithium bis((trifluoromethanesulfonyl)imide (Li-TFSI) which oxidizes spiro-OMeTAD so that an enhance in the Power conversion efficiency of PSCs. But the stability of these still remains a challenge. Li et al. [31] introduced In2 which is Indium based MOF into the spiro-OMeTAD due to the excellent conductivity of indium. Addition of In2 into spiro-OMeTAD improved the UV-visible absorption from 320 nm to 540 nm. It is observed that of spiro-OMeTAD doped with In2 enhanced the PCE from 12.8% to 15.8% and increased in other PSC properties J_{SC},V_{OC} and Fill Factor. Md Ariful Islam et al. [32] synthesized NiO_x NPs by introducing different ligands. The NiO_x NPs with terepthalic acid (TPA) derived MOF was identified as best hole transport layer for PSCs. They reported the band gap of 3.25 eV for the fabricated thin film with NiO_x NPs. Also calculated the hole mobility , carrier concentration and resistivity as 4..7 x 10^{14} Ohm cm, 6.8 x 10^{14} cm^{-3} and 2.0 cm^2 V^{-1} respectively. The incorporation of different ligands resulted in MOFs of different optical, structural and surface morphological characteristics. Jiupeng cao et al. [33] synthesized two dimensional metal-organic frameworks which is found to be an ideal HTL for Pb-Sn perovskite solar cell. The reported PSE is 22% which indicates that these 2D-MOFs can be served as promising potential hole transport materials for high efficiency PSCs. Ruonan Wang et al. [34]

prepared dopant free HTL $N_3(HITP)_2$ and achieved PCE of 10.3% due to high mobility and capacity to extract holes strongly.

2. **MOFs as Electron transport layer:** The basic role of electron transport layer in PSCs is to transport electrons to the back contact metal electrode. The energy levels of ETL should be in good alignment with the energy levels of other layers in PSC. The ideal ETL should have strong thermal stability, good mobility, low-temperature processibility and easy fabrication. The criteria for efficient charge extraction is that, the conduction band of ETL should be lower than perovskite's conduction band and valence band of ETL should be greater than that of perovskite's valence band. The poor alignment of energy levels of ETL with perovskite observer will leads to recombination of electron-holes there by impacting the device's series and shunt resistance. Hence, the ETL should be chosen in such a way that it should have high carrier mobility and good aligned energy levels with the perovskite observer and hence by blocking the holes at the interface between perovskite and ETL. The most commonly used ETL is TiO_2 for PSCs due to its excellent structural stability and low cost. TiO_2 has a large band gap of 3.3 eV which allows the excitation and injection of electrons by making inefficient ETL. To resolve this issue, some researchers proposed a method of doping the semiconductors with metals to reduce the band gap.

   Nguyen et al. [35] synthesized 1 wt% Co-dopped TiO_2, metal organic framework by thermal decomposition. When Co-dopped TiO_2 used as an electron transport layer in PSC, it is observed that optimal PCE is 15.75% which is greater than that of PSC with commercial $TiO_{2(}$ PCE is 14.42 %) due to the reduced band gap of 2.38 eV.

   Ya-Nan Zhang et al.[36] synthesized MOFs-derived Zinc Oxide and incorporated as electron transport layer (ETO) in contrast to conventional ZnO nanoparticles . It is observed that these MOFs served as more efficient electron extraction, less electron-hole recombination, decrease in trapped state density there by enhancement in the fill factor lead to the increase in PCE of 18.1%

   Bin Rang etal. [37] Prepared Na doped TiO_2 using MIL-125 (Ti) MOF as a precursor. Incorporation of Na-TiO_2 between electron transport layer and perovskite layer as interfacial layer resulted in enhancement in the PCE 20.49% from PCE 17.2% of traditional device. This is due to increase in the interface contact between the layers which enhanced conductivity, electron extraction and decreased trap state density.

   Shaozu sun et al. [38] synthesized carbon nanotube composite MOF (Ni)/CNT by solvothermal method. Application of MOF (Ni)/CNT have boosted the capacitive performance due to the good electrical conductivity, stability offered by nanotube structure of CNT and enough electrolyte storage space offered by corrugated-layered-structure of MOF (Ni).

3. **MOFs as Interfacial Layer:** Main role of interfacial layer improves the photovoltaic performance by enhancing the charge collection, decreasing the trapping state and recombination. Controlling grain boundary and grain size of PSC is very crucial to attain more efficiency. Application of MOFs as interfacial layer in PSCs is a important tools due to their tunable band gap to increase the PCE of PSCs.

Wei et al. [39] first coated ZIF-8 between mesoporous mp-TiO_2 and perovskite layer as interfacial layer which improved the crystallinity and grain size of the perovskite layer. The PCE of mp-TiO_2 /ZIF-8 coated PSC increased to 16.99% which is higher than the PCE (14.75%) by mp-TiO_2 PSC. The improvement in the PCE is due to the suppression of electron-hole recombination by ZIF-8 interlayer coated between mp-TiO_2 and perovskite. Liu et al. [40] synthesized novel Pb-containing metal organic framework by postmetalation of MOF-525 as a interlayer between perovskite and TiO_2 compact layer, which facilitated the crystal growth with quality crystal grain size in the perovskite layer. As a consequence of good quality crystals of perovskite, made easy charge separation between perovskite and ETL by inhibiting the defect sites at the grain boundary. Hence, Pb-based MOF coated PSC exhibited champion PCE of 20.87 % than that of the pristine PSC (PCE: 16.85%). Lee et al. [41] studied the effect of two types of Zr-MOF with UiO-66 and MOF-808 at the interface. As a result, modified PSCs with UiO-66 and MOF-808 increased power conversion efficiency of 17.01% & 16.55% from PCE of control device 15.79%. The effect of introduction of MOFs facilitated the crystallization and enlarged the grain size of prepared film.

II. CONCLUSION

The recent growth in the application of MOFs in perovskite solar cells has been reviewed and discussed the progress. Even though power conversion efficiency of PSCs are in comparable with that of commercialized silicon based solar cells but the lack of long-term stability is the hindrance for its commercialization. Diverse structural modifications and several fabrication processes have been employed to increase the stability. Researchers have tried the incorporation of Metal Organic Frameworks (MOFs) at interfacial layer, ETL and HTL to improve the PCE and stability. It is observed that incorporation of metal-organic frameworks (MOFs) in the different layers such as ETL, HTL and Interfacial layer of perovskite solar cells improved the device efficiency and improved PCE, stability due to the prominent indispensible characteristics of metal-organic frameworks (MOFs) such as high porosity, tunable pore size, ultra high surface area, crystalline with rigid and flexible frameworks. However, mechanism for the improvement of PCE and stability not exactly confirmed. Finally, MOFs are most attracting scaffolds for PSCs due to their facile tunable bandgap by changing the components.

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