Chapter 11

# Pathways Towards High-Stable, Low-Cost and Efficient Perovskite Solar Cells

Ahmed Mourtada Elseman, Sajid, Dong Wei,
Ahmed Esmail Shalan,
Mohamed Mohamed Rashad and Meicheng Li

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## Abstract

The power conversion efficiencies (PCEs) of perovskite solar cells (PSCs) have been reached the initial value when they emerged as dye sensitized solar cell (DSSC) in 2012. Immediately, the interests were drawn in this field worldwide. The researchers have improved the efficiency of PSCs up-to 22%, which was originally started from its initial value of 3.8%, just in 7 years. The rendering of long-term stabilization and effective cost have special importance for PSCs since the instability issue remained idle in spite of those recently increased efficiency values attained by various research groups. In this way, the better improvements of PSC may increase extraordinary exhibitions as compared to alternate solar cells like organic solar cell (OSC) or DSSC devices. This chapter begins with a general discussion on the requirement for an economical clean energy conversion device. In section 2, fundamental properties of PSC are fit together with their device architecture and working mechanism. In section 3 proceeds with a review on fundamental photovoltaic parameters joined by current-voltage hysteresis. Furthermore, the stability and cost issues will be discussed in Sections 4 and 5. In the end of this chapter, we are discussing the challenges and opportunities based on the chapter content.

**Keywords:** perovskite solar cells, working mechanism, photovoltaic, parameters, stability, low cost

## 1. Introduction

A huge number of researchers have been focused on the inventions in solar cell (SC) worldwide due to the feasible and effective electricity production from available free source of sunlight [1, 2].

There is no doubt that world's main source of energy is petroleum by 40%. The consumption of the petroleum accelerates very quickly due to energy needs of expanding industrial zones. It is relied upon to grow further unless an affordable novel clean energy technology becomes available.

Therefore, the government should take precautions against fuel consumptions by creating an environmental friendliness new energy sources and alternative energy themes. Clean energy is the best way of electricity due to ease of transformation in other energy forms herewith crucial for the human society. Accordingly, the cost of energy consumption have been made by electricity using machinery, for that, this directed the countries to consider the renewable energy transformers [3]. Consequently, numerous scientists from different foundations worldwide grew new sorts of alternative energy conversion devices in order to consolidate their capacity more [4]. The SCs are the most promising devices since solar energy is acknowledged to be almost infinite for human needs.

Nowadays, SCs are used in photovoltaic (PV) panels as new investments and meet the commercial energy requirements. Optimization the efficiency is necessary to satisfy those huge consumption needs. In **Figure 1**, researchers at National Renewable Energy Laboratory (NREL) in Golden, Colorado set the best efficiency for SCs reaching 32.6% under full-sun illumination. Thus, a majority of the investments forced to utilize silicon-based PV panels, which have high conversion rates. Whereas, the problem with expensive production processes that require a huge amount of water which will produce lots of pollutants to the environment.

On the other hand, organic solar cell (OSC) uses environmental friendly production procedures. In another meaning, many new usages of organic materials in electricity production are proposed and applied as favorable alternatives. These novel devices are essentially expected to own the low cost and at the same time high efficiency. In comparison with SCs,

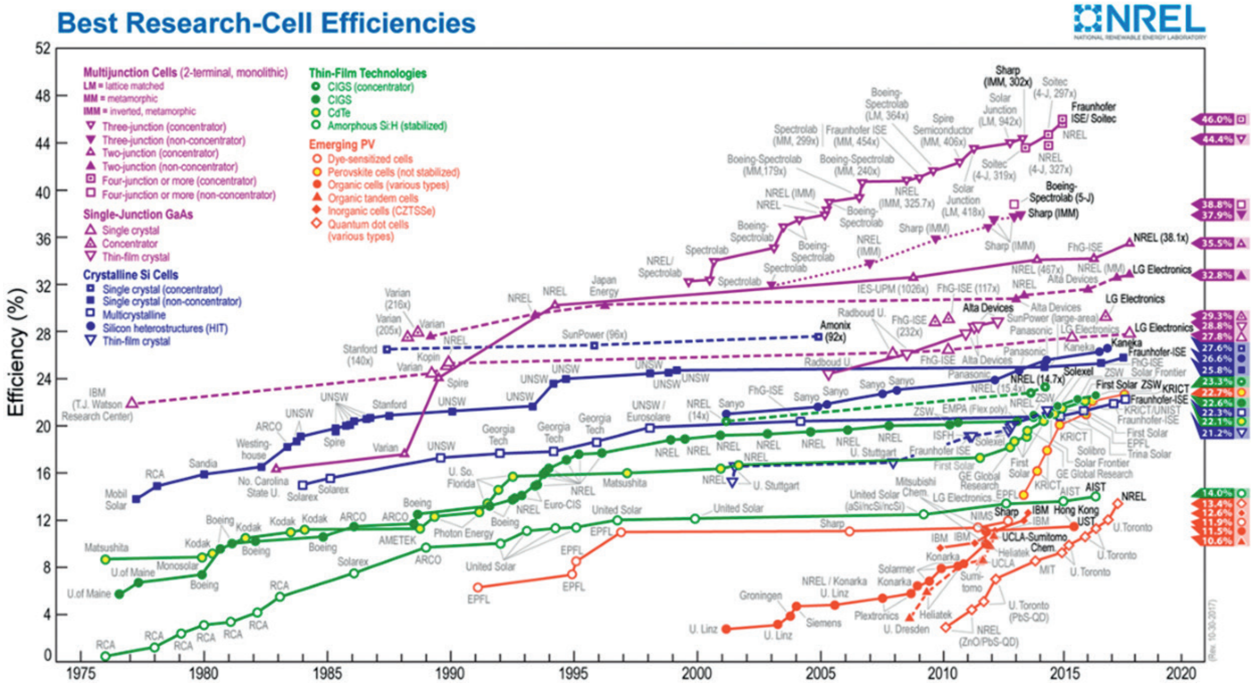

**Figure 1.** Reported timeline of solar cell energy conversion efficiencies (National Renewable Energy Laboratory), reprinted with permission from NREL [5].

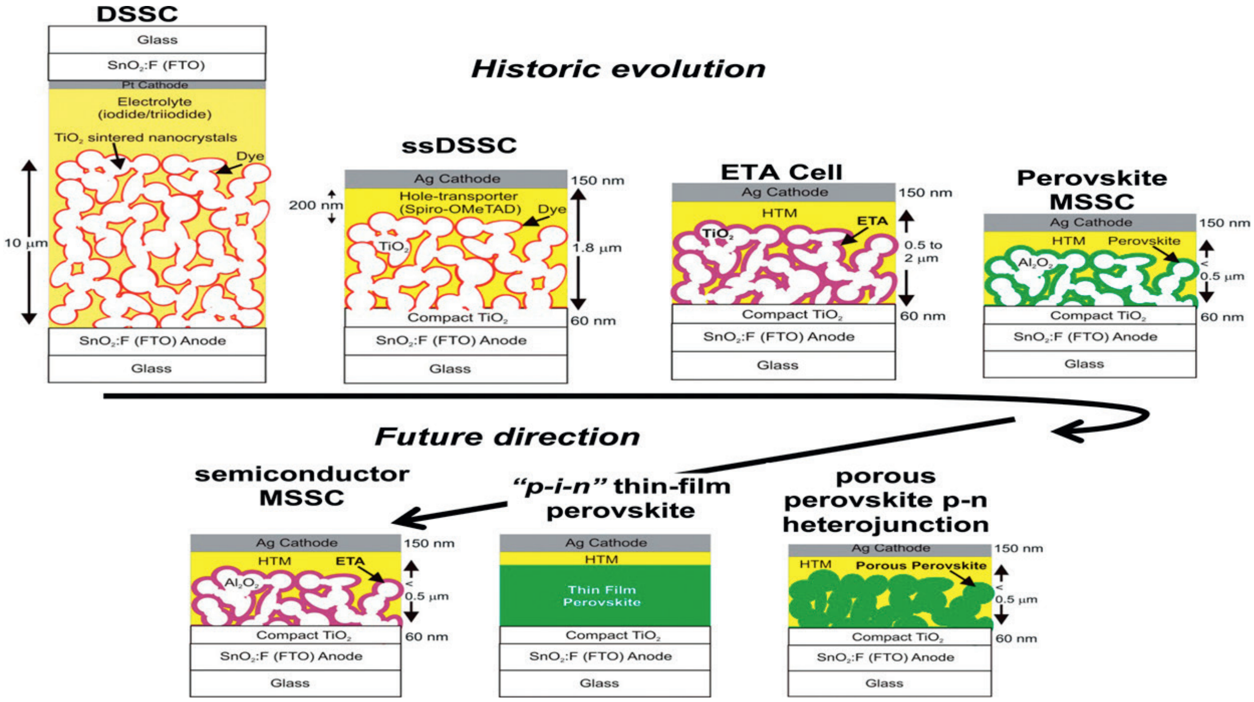

**Figure 2.** Historic evolution of the solar cell technology, starting from the electrolyte-based mesoscopic DSSC, the ssDSSC, the ETA cell to the MSSC perovskite absorber and the n-type TiO$_2$, reprinted with permission from ACS [17].

dye-sensitized solar cells (DSSCs) are commercially available in the market for a decade. However, these types of SCs are suffering from low efficiency, electrolyte degradation, and leaking encapsulation. In turn, to make a cutting-edge for this problem, experiments have been demonstrated a novel SC named perovskite solar cell (PSC) [6–11]. Consequently, this chapter will focus on PSC operational phenomena, device structure, photovoltaic parameters, and stability challenges [12, 13]. In **Figure 2**, the evolution of SC starting from the DSSC based electrolyte-based mesoscopic [14]. Then, ssDSSC where the electrolyte was replaced with an organic p-type whole conductor [15]. After that, the dye was replaced with an ETA semiconductor layer to give the ETA cell [16]. When the ETA was replaced by perovskite absorber and the n-type TiO$_2$ is replaced with a porous insulating scaffold to PSC. The development of the perovskite technology were elucidated as (a) porous perovskite distributed p-n heterojunction solar cells, where the Al$_2$O$_3$ is removed but the perovskite is directly structured to give a porous film subsequently filled in with a charge conductor, (b) thin-film p-i-n perovskite solar cells and the device introduce the structure as intrinsic thin perovskite film sandwiched between p and n type and finally (c) semiconductor MSSCs with solution-processed semiconductor, like SbS can be structured by the porous scaffold to deliver an MSSC.

## 2. Working mechanism and device architectures of PSCs

According to the operating principle of PSCs and the obtained information on the working mechanism, they are still insufficient for now [18, 19]. There are different approaches to figure out a suitable mechanism for the working principles of PSC. The principal mechanism of PSCs like (i) light absorption, (ii) charge separation, (iii) charge transport, and (iv) charge collection are essential to address because they are general SC parameters during conversion of sunlight into electricity.

In this regard, the choice of photon harvesters is the first step for the specification of the physical structure of an SC. Hence, investigation of PV parameters of perovskite has priority during the design engineering. This is optimum in terms of theoretical understanding for energy conversion mechanism [1, 20]. It is known that the structure of organic-inorganic halide exhibits both electron and whole transport properties together. Hence, PSCs can be engineered as *p-n* junction architecture or *p-i-n* junction structure. The two layouts can be described as a p-i-n junction if the light harvester or perovskite is an intrinsic semiconductor, whereas in p-n junction, the light harvester has *n*-type or *p*-type property. This junction is capable to carry electrons or holes to the perovskite harvester [1, 9–11, 21].

The typical structures of PSCs are engineered depending on two structures such as mesoporous and planar. **Figure 3** demonstrates the schematic architecture for both mesoporous and planar type PSCs. The first structure consists of a mesoporous type metal oxide layer like $TiO_2$ or $Al_2O_3$ accompanied by perovskite sensitizer. The second structure contains a perovskite film sandwiched between electron and hole transporting layers. Herein, the photo-generated charge carrier takes place in perovskite which further inject to the $TiO_2$ and finally collect at transparent conductive oxide glass [22–25].

In comparison, the two architectures follow the same charge transport rate. However, the mesoporous PSCs display higher recombination rates [26]. On the other hand, the planar PSCs are suitable for the field of flexible solar cells since they do not need high sintering temperature. The trends of generation and recombination of charge carrier in PSCs are depicted in **Figure 4**. The charge generation rate and charge movement take place from (1) to (3).

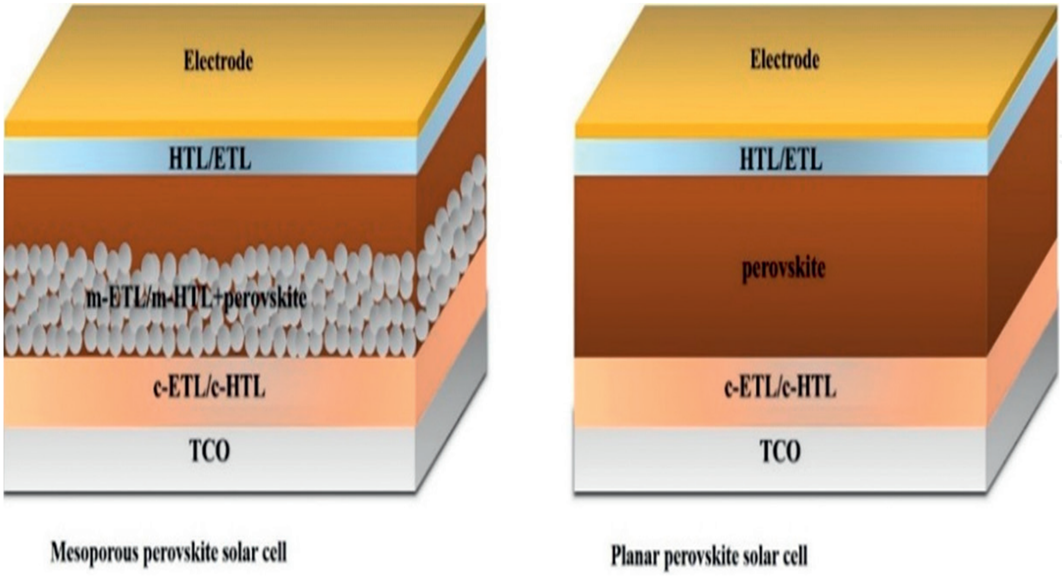

**Figure 3.** Schematic illustration of perovskite solar cells architectures, c-ETL; compact electron transporting layer, c-HTL; compact hole transport layer, m; mesoporous, TCO; transparent conductive oxide.

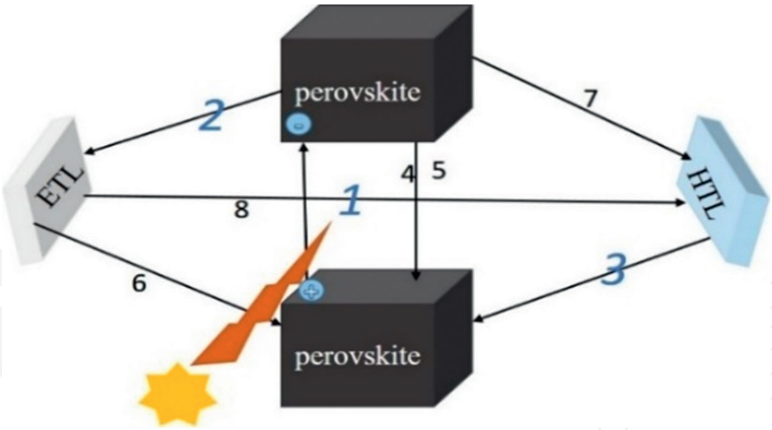

**Figure 4.** Trends of charge generation, charge transportation and recombination.

To manage efficient charge collection, these processes should be much faster than the recombination rate occurred from (4) to (8). This charge carrier and light management will further benefit high power conversion efficiency.

## 3. Paramount photovoltaic parameters of PSCs

### 3.1. Photocurrent density

Analyzing the device architecture of the PSC, it is very important to understand the factors that limit the photocurrents. The devices must minimize parasitic losses while the suitable thickness of photo-absorber such as organic-inorganic trihalide should have a better capability of incident photon harvesting. The enhancement in photocurrent density ($J_{sc}$) from 11 to 21 mA cm$^{-2}$ has been achieved for the PSCs in 2 years [27, 28]. Later on, utilizing 1.6 eV energy band gap of perovskite materials in PSCs a $J_{sc}$ of 22 mA cm$^{-2}$ was obtained [29]. Researches are focused on understanding the photocurrent losses occurring in the PSCs. In this regard, internal quantum efficiency (IQE) has been confirmed as one of the major losses. Additionally, thin films in device stack such as FTO/$TiO_2$/spiro-OMeTAD/Au can cause reflection/transmission losses and parasitic absorption [30]. Crystallinity enhancement has been shown pleasurable to minimize IQE losses. Consequently, yielding photocurrents of 23 mA cm$^{-2}$ [31]. Tuning the energy band gap via Tin (Sn) based perovskites; the photocurrent density has been improved from 25 to 26.9 mA cm$^{-2}$ [32, 33]. However, the unstable Sn-based perovskites are crucial for their quantum efficiencies. This newly emerging field needs further insights to achieve the proposed theoretical photocurrents.

### 3.2. Open-circuit voltage

The enhancement of open-circuit voltage ($V_{oc}$) depends on the tunable energy band gap in PSCs. Thermodynamic limit of $V_{oc}$ relates theoretical efficiency limit. The reciprocity between absorption and emission have been shown avoidable due to the radiative recombination, this returns to the $V_{oc}$ limit of 1.33 V for $CH_3NH_3PbI_3$ (band gap ≈1.6 eV) [34]. The broad absorption edge reduces the maximum $V_{oc}$ with almost no effect on $J_{sc}$. Therefore, a low density of Urbach tail accompanied by a sharp absorption edge is pleasurable for high performance as shown by many perovskite materials [35]. Any further loss is due to non-radiative recombination, which can be quantified by measuring the electroluminescence (EL) yield of the solar cell. Once it was possible to make pinhole-free films, the $V_{oc}$ of PSCs exceeded 1 V [36]. This and the latest realization of solar cells without any charge transport layers [37] made clear that the perovskite itself is the source of the photovoltage generated by a splitting of the quasi-Fermi levels under illumination. Obviously, the charge carrier in the selective layers play a very important role. The surface recombination caused by imperfect charge carrier layers results in a reduce $V_{oc}$. There is no doubt that device engineering with suitable selective layers, optimize film morphology and perovskite composition lead to voltages ≥1.2 V [38]. Further improvement in $V_{oc}$ needs in-depth understanding and reduce recombination rate due to impurities and interfaces.

### 3.3. Fill factor

The fill factor (FF) is connected to $V_{oc}$ via recombination which gives maximum values of state of the art devices up to 82% [39]. There are some factors that affect the additional losses due to charge extraction depending on the electric field, voltage, external series resistances or shunt paths. The high charge mobility and large diffusion lengths in PSCs make it easy to gain high FF in a film of few 100 nm thickness [40]. However, the charge extraction occurs in resistive charge selective layers or recombination in the PSC itself could lead to low FF. In addition, the grain boundaries did not strongly affect $V_{oc}$ and recombination but they can reduce the FF, even resulting in an anticorrelation of the FF and the film thickness. In another indication, grain boundaries constitute an obstacle for charge carrier. Plainly, the devices with p-i-n configuration have been shown the highest values of FF [41]. Increasing the FF further and approaching its theoretical limit of 91% (for $CH_3NH_3PbI_3$), needs to occur along with increasing the $V_{oc}$ and will likely be the subject of future work by the PSCs community [20].

### 3.4. Current-voltage hysteresis

Performance parameters in PSCs cannot be discussed without addressing the hysteresis phenomenon. Scanning the current-voltage (*J-V*) characteristic curve of PSCs with back and forward voltage and vice versa will result in two different traces. This phenomenon makes the exact extraction of PCE from the *J-V* curve ambiguous. After its first reports, it turned into the subject of further examinations, demonstrating that it is a transient phenomenon which strongly depends on the scan rate [42, 43]. Numerous hypothetical and experimental studies elucidate that the PSC itself is responsible for the hysteresis processes that takes place on the timescales of seconds and larger. Further research efforts have demonstrated that the migration of ionic defects like iodine vacancies in the PSC is the most likely underlying process [44]. The documented details and rational results are still lacking and under investigation. Specifically, how articulated the hysteresis is, does rely not only on the slow process itself but also on its effect on photo-generated charge carrier via adjusting the recombination and charge extraction probabilities. However, the hysteresis is a result of complex processes which need thorough understanding of each phenomenon occurring in the whole solar cell.

Collectively, the performance of a PV cell can be determined by measuring the overall PCE from the ratio of maximum $P_{out}$ in W $m^{-2}$ to the input light irradiance ($P_{in}$) as represented in Eq. (1). Under the standard condition, the light intensity of $P_{in}$ is 1000 W $m^{-2}$. The $P_{out}$ of a cell is given by Eq. (2), where $J_{mp}$ and $V_{mp}$ refer to the current density and voltage at the maximum power. The FF is the ratio of $P_{out}$ and the product of the maximum $V_{oc}$ and $J_{sc}$ (Eq. 3). The PCE or $\eta$ relationship of Eq. (1) can be rewritten as Eq. (4), which is used to determine the cell performance.

$$\eta = \frac{P_{out}}{P_{in}} \tag{1}$$

$$P_{out} = V_{mp} \times J_{mp} \tag{2}$$

$$FF = \frac{P_{out}}{V_{OC} J_{SC}} \tag{3}$$

$$\eta = \frac{V_{OC} J_{SC}}{P_{in}} \tag{4}$$

## 4. Stability and cost challenges

Conventional solar cells have been emerged with efficiencies up to 25%. However, there are some shortcomings of these mature solar cells such as high-cost manufacturing, heavyweight, and rigidity. On the other hand, a relatively new PV technology based on PSCs has already achieved more than 22% efficiency. The vast chemical versatility and the low-cost processability of perovskite materials, the PSCs promise to lead the future of photovoltaic technology by offering cheap, lightweight and highly efficient solar cells. However, only highly expensive prototype organic HTMs have been displayed PCE over 20%. Furthermore, by uprightness of their ingredients, these HTMs unfavorably affect the long-term operational stability of the PSCs [45]. In this way, exploring cheap and stable HTMs that deliver similar high efficiencies is in great demand to empower large-scale implementation of PSCs. In the following sections we will discuss some of the promising possibilities with emphasis on inorganic HTMs.

## 5. Possible stable solutions

Regardless of the device architecture, the HTMs is one of the key components to fabricate highly efficient and stable PSCs. Small molecules, polymeric, carbon, and inorganic HTMs are four large families of HTMs used in PSCs. Here in, we will give an outline of the principal advantages/disadvantages for different HTMs, depicting the most recent representative results. There are many p-type semiconductor HTMs, which have been introduced with their corresponding device performance in several recent works [46–49]. Small molecules give the advantage of flexible processing from solution to evaporation joined by compatibility with pre-existing industrial lines designs for large-scale production of organic electronics. Moreover, optoelectronic properties of small molecules have the redox potential and tunable energy band gap which are generally simple to modify in order to adjust the molecular backbone to the particular perovskite [50, 51]. Chemical doping of the small molecule HTMs with Lithium salts, organic Lewis bases and metal–organic oxidants is an effective step to prepare highly efficient PSCs. Increase hole transporting capabilities (conductivity) while maintaining a low charge recombination at the interface with the perovskite is the most evident effect so far observed by doping the HTMs [52].

Carbon HTMs with nanotubes and nanopowder structure have been revealed as stable alternatives to the organics [25, 53, 54]. Carbon nanotubes as HTMs have been used to prepare highly efficient PSCs. However, the disadvantage associated with carbon nanotubes is expensive purification procedure to isolate the right semiconductor tubes. The highest recorded efficiency for a carbon nanotube is 15.5% [55]. On the other hand, carbon nanopowder offers one of the most economical HTM solutions, which is compatible with the large-scale production lines. However highly efficient PSCs prepared with nanopowder HTMs are still lacking. Although, inorganic HTMs have been explored as alternatives for long-term stability [56], but the deposition of inorganic HTMs as top contacts is complicated as the used processing solvents tend to be detrimental to the underlying perovskite layer [57]. Among various inorganic HTMs, copper thiocyanate (CuSCN) stands out as a stable, efficient and cheap candidate ($0.5/gr versus $500/gr for the commonly used spiro-OMeTAD). Recently, researchers at Michael Grätzel's lab have introduced two new concepts that overcome the major shortcomings of CuSCN-based PSCs. First, they developed a simple dynamic solution-based method for depositing highly conformal, 60-nm thick CuSCN layer that allows the fabrication of PSCs with stabilized PCE exceeding 20% [45] as depicted in **Figure 5**. Then, a thin passivation layer with reduced graphene oxide between the CuSCN and back electrode has been introduced to reduce the diffusion of gold contact. The new technique allows the PSCs to record excellent operational stability, retaining over 95% of their initial efficiency while operating at a maximum PCE for 1000 h under full-sun illumination at 60 °C. This exceeds even the stability of organic HTM-based PSCs that are recently dominated the field. These publications also discovered that the instability of the PSC originates from the degradation of CuSCN/gold contact during the solar cell's operation. These findings will pave the way for large-scale commercial deployment of this very promising new PV technology.

## 6. Summary

Effective photon harvesting in perovskite material has already delivered tangible results, contributing to SCs community [7]. The achievements in terms of long-term life-time of PSCs would see an economical photonics for future endeavor. Therefore, the innovation in PSC field engages a large amount of attention in the development of SCs that are reliable, highly efficient at converting sunlight to electricity and inexpensive to manufacture. Additionally, investigating the charge transport properties and improving device engineering methods

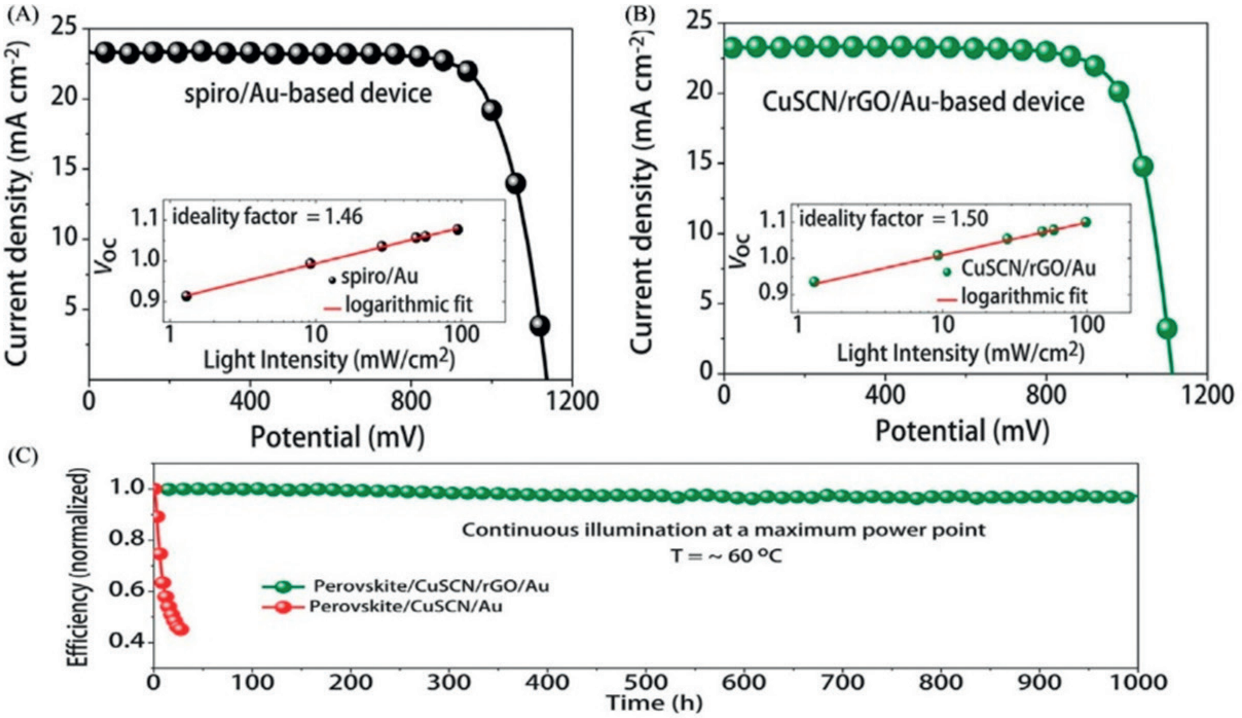

**Figure 5.** PV measurements of PSC based on spiro-OMeTAD and CuSCN HTM. (A) JV curve for the spiro-OMeTAD based device. (B) J-V curve for the CuSCN-based device. (C) Operational stability of an unencapsulated CuSCN-based device with and without a thin layer of reduced graphene oxide (rGO), *reprinted with permission from Science* [58].

are essential. In particular, the modification of used nano-materials has great influence. Moreover, the explanation of the photo-physical mechanism of solid-state SCs also plays an important role. However, the insufficient understanding of the working mechanism of PSCs will need further efforts. Therefore, explanation of the phenomenon on (i) light absorption, (ii) charge separation, (iii) charge transport, and (iv) charge collection are crucial during research to reveal a thorough understanding of PSCs mechanism. In addition, managing these working mechanism further contribute to the PV parameters such as photocurrent density, open-circuit voltage, FF and thus power conversion efficiency of the solar cell.

Furthermore, the HTM layer in the stack of PSC is one of the most important parts in terms of high efficiency and long-term stability. In this regard, PSCs based on inorganic HTMs with the efficiency of 20% has been shown. The incorporation of inorganic HTMs is promising with respect to their improved environmental sustainability. On the other hand, polymeric HTMs are thought to be favorable due to their high charge mobility with unique oxidation potential and preferred morphology [4, 59]. The third kind of HTMs is small molecules. Among these, spiro-OMeTAD has been the most used HTM in PSCs till now [60]; however, the tedious synthesis makes them very expensive. Therefore, commercial viability to PSCs will require us to synthesize and design novel small molecules. It is noteworthy that PSCs emerged rapidly with some uncertain phenomena associated with the device. The continuous investigation on current density and voltage characteristics of the PSCs would provide a good understanding point for the semiconducting behavior [61]. Collectively, improvement in the PSCs efficiency depends on deposition techniques and material composition [62]. In conclusion, solution-processed

PSCs are commercially valuable [63]. Moreover, inorganic HTMs found to be economically viable compared to organic HTMs. The commercialization of PSCs with inorganic HTMs is more flexible for future generated solar cells. It will also benefit the numerous scientists in the field that have been intensively searching for a material that could replace the currently used, prohibitively expensive organic hole-transporters.

## Conflict of interest

The authors declare no conflict of interest.

## Author details

Ahmed Mourtada Elseman[1], Sajid[2], Dong Wei[2], Ahmed Esmail Shalan[1],
Mohamed Mohamed Rashad[1] and Meicheng Li[2]*

*Address all correspondence to: mcli@ncepu.edu.cn

1 Electronic and Magnetic Materials Department, Advanced Materials Division, Central Metallurgical Research and Development Institute (CMRDI), Helwan, Cairo, Egypt

2 State Key Laboratory of Alternate Electrical Power, System with Renewable Energy Sources, School of Renewable Energy, North China Electric Power University, Beijing, China

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