



Review of recent developments and persistent challenges in stability of perovskite solar cells



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ARTICLE INFO

Keywords:

Perovskite solar cell
Stability
Degradation
Moisture
Organo-metallic halide

ABSTRACT

An exponential increase in performance and stability of perovskite solar cells (PSCs) has been observed in the last decade, reaching over all power conversion efficiency up to 22.1%. This made them the most promising rival to the third generation silicon-based solar cells. However, there are still several issues to resolve to promote PCS's outdoor applications and commercialization. PSCs showed varying degree of sensitivity towards moisture, oxygen, temperature, and UV illumination, depending on the materials used. Other factors also influencing PSCs performance are the stability of carrier lifetime and current–voltage hysteresis. This review is focused on the parameters directly and indirectly affecting the PCSs stability and performance. Recent in-depth studies on different stability parameters are discussed for better understanding of these issues and possible solutions.

1. Introduction

Perovskite solar cells are made up of mixed organic-inorganic halide, commonly defined as ABX_3 , where A and B are cations, having different sizes (A greater in size than B) and X represents an anion [1]. Common structure of a perovskite crystal is shown in Fig. 1. There are various techniques in which perovskites can be processed, such as spray pyrolysis, dip coating [2], 2-step interdiffusion [3], chemical vapor deposition, ink-jet printing [4], spin coating [5], atomic layer deposition to blade coating deposition [4,6]. Making it one of the most promising photovoltaic (PV) materials. Although these crystals are known for long, but it was only in 2009, when Miyasaka et al. [5] first time used this crystal as a light absorber for a dye-sensitized solar cell. They obtained total power conversion efficiency of 3.8% with their cell [7]. But within few years its efficiency reached to 16.2% [9] in 2013 and 22.1% [10] in 2015. Some key features of the perovskite solar cells (PSCs) includes, high solar absorption, ease of fabrication, higher energy conversion efficiency, superb light harvesting and comparatively lower production cost [8]. These features, outshined most of the currently used thin film solar cells which have been under study for decades. Stability of the perovskite materials and subsequent cell performance become a major concern to the photovoltaic community for

commercialization. Major issues related to stability and performance, like temperature, moisture, oxygen and UV illumination carrier lifetime, and current–voltage hysteresis of this cell are being investigated for better understanding and possible solution.

For contemporary solar cells, the device structure, interfacial modification and related materials play significant role in the light to electricity conversion. Generally, PSCs have two architectures, (i) meso-structured device, and (ii) planar device as shown in Fig. 2. In a meso-structured device, the perovskite is used to sensitize the mesoporous Titania (TiO_2) layer [12]. Whereas, the planar device has comparatively simpler structure and gave better cell performance. Gradual improvement of the perovskite film quality improved the overall cell efficiency [9–13].

2. Stability of the perovskite layer

The stability of perovskite materials is a well-recognized problem [15] and it was observed that, at the device level several degradations arise simultaneously at different interfaces [16]. These degradations can be resulted as a direct consequence of moisture, UV illumination, elevated temperature and exposure to ambient atmosphere. Thus, like other materials made up of organic materials, the following factors can

Abbreviation: PSC, perovskite solar cells; UV, ultraviolet; PV, photovoltaic; MA, methylammonium; XRD, X ray diffraction; RH, Relative humidity; XPS, X-ray photoelectron spectroscopy; Spiro-OMeTAD, $N^2,N^2,N^2,N^2,N^7,N^7,N^7$ -octakis(4-methoxyphenyl) – 9,9'-spirobi[9H-fluorene] – 2,2',7,7'-tetramine; HTL, hole transport layer; Pka, acid dissociation constant; PCE, power conversion efficiency; FA, formamidinium; SWNTs, single walled nanotubes of carbon; HTM, Hole Transporting Material; TTF, Tetrathiafulvalene; TBP, 4-tert-butylpyridine; GA, Guanidinium (CH_6N^+); PCBM, [6,6]-phenyl- C_{60} -butyric acid methyl ester; PEDOT, poly(3,4-ethylenedioxythiophene); LITFSI, Bis(trifluoromethane)sulfonimide lithium salt; TFSL, Trifluoromethanesulfonimide; OPV, organic photovoltaic; ISOS, international summit on organic photovoltaic stability

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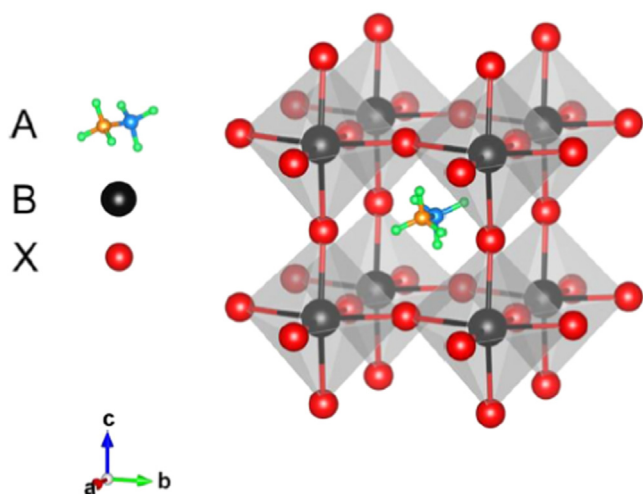


Fig. 1. The crystal structure of PSC. Reprinted from [11].

be identified as the cause of stability problem: intrinsic stability, moisture ingress, oxygen ingress and illumination stimulated decomposition [17]. Hence, these stated factors can cause the following decomposition processes within the material: crystallization instability, photodegradation, oxidation of the organic layer and top electrode instability. Because of the intrinsic degradation caused by thermal stress or illumination, several degradations can start even without the presence of the water or oxygen [18]. The shortcomings associated with the stability arise due to both instability of the charged transported material used and the perovskite material itself [19]. There has also been a great concern that the presence of Titanium oxide under ultra violet illumination can cause adverse effect on the stability of the device. Because of less stability of divalent oxidation state of tin, PSCs that contain tin become unstable in oxygen-presence environment [20]. In presence of moisture, hydrolysis of the perovskite films occurs due to the hygroscopic nature of the organic methylammonium cation [21]. Despite the major issues associated to the stability of the perovskites, there have been several achievements depicting promising stability results [20]. Djurišić et al. [21] reported a 500 h of stability for their PSC in ambient environment without any encapsulation. In another case, Bush et al. [22] obtained 1000 h of stability under dark storage condition and inert atmosphere [22]. But in most cases researchers observed poor stability in ambient condition [23,24]. For instance, it was stated that devices stored in nitrogen or dry air can maintain up to 80% of their initial performance after one day and 20% after six days, whereas those operated in ambient air maintain below 20% after one day [25].

2.1. Effect of moisture

Environmental stability turns to be a key impediment to the commercialization of organic-inorganic PSCs [26]. The PSC is susceptible to

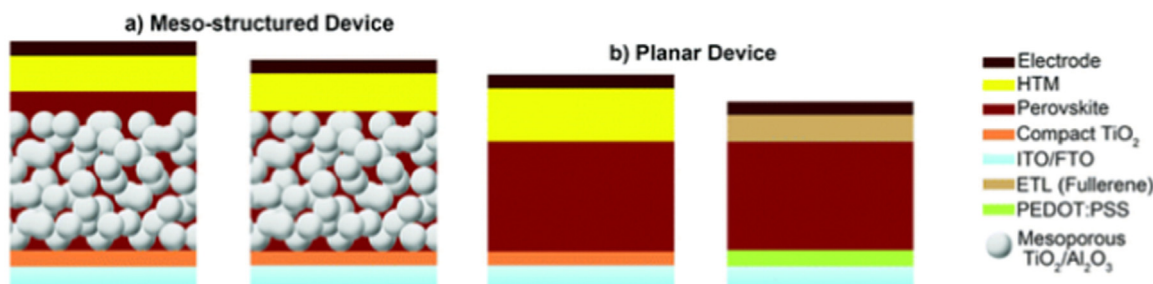


Fig. 2. structure of types of perovskites solar cells. Reprinted from [14].

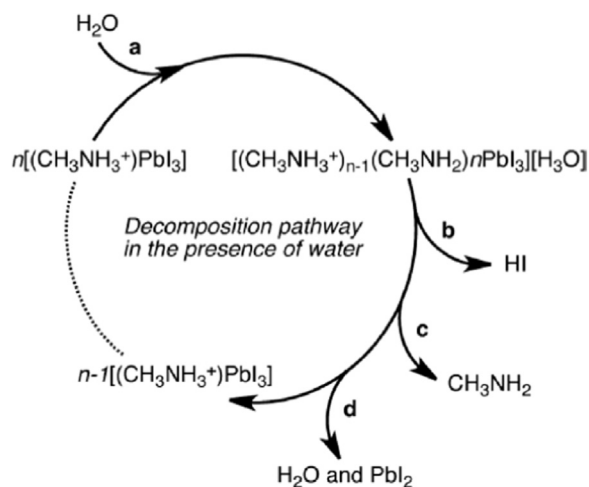


Fig. 3. Suggested pathway for the degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in the presence of H_2O with PbI_2 as the main product. Reprinted from [29].

moisture ingress, corrosion of metal electrodes through interaction with halides in the material and methylammonium iodide ingress [25]. Extensive research work have been carried out to stabilize the perovskites, like, adding encapsulation layer to avoid moisture ingress, using hydrophobic heterojunction contacts and using a pin hole free material oxide layer to stop metal halide reaction [25–27].

Niu and colleagues have excellently reviewed the chemical processes responsible for the perovskite film degradation [25]. They outlined five main causes of degradation in the perovskite film, such as, UV-light, solution processing, thermal effects, oxygen and moisture. Several literatures have reported that water acts as catalyst needed for the irreversible decomposition of the perovskite layer [28]. Frost et al. [29] have schematically displayed the possible moisture catalyzed decomposition process of the methylammonium lead iodide, as shown in Fig. 3.

It appears that MA and hydrogen iodide are soluble in H_2O . One major impediment for the lifetime of photovoltaic cells is the irreversible degradation of the perovskite layer; however, the nature of the by-products has compounded this discrepancy. As observed in Fig. 3, PbI_2 is the main by-product of this reaction and it is insoluble in water [30]. Several eco-toxicological mishaps could arise with this kind of decomposition of the organo lead halide perovskite layers. Yang et al. studied the degradation mechanism by conducting in situ absorbance and grazing incidence XRD measurements [30] in a controlled environment. Experimental setup to control the relative humidity (RH) is schematically presented in Fig. 4(a) and the homemade sample holder is presented in Fig. 4(b). $\text{CH}_3\text{NH}_3\text{PbI}_3$ film was exposed to different RH and absorption was measured. Fig. 4(c) shows the in-situ absorbance results of the perovskite film at 98% RH.

Fig. 4(d) shows the impact of relative humidity on the perovskite film with respect to the time of exposure. It was vividly seen that higher RH values significantly decreased the film absorption. The degradation

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