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Perovskite solar cells: Materials, configurations and stability

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ABSTRACT

Perovskite solar cells (PSC) have recently emerged as a strong contender for the next generation of photovoltaic technologies, having received the attention of the photovoltaic community, both scientists and industry. In few years, power conversion efficiency of PSCs reached already 22%. A broad range of architectures and fabrication methods have been proposed, as well as several perovskite compositions and charge selective layers, suggesting that the performance of these devices is still far from being fully optimized. PSCs still exhibiting stability problems and the most efficient absorbers incorporate lead (ca. 13 mg m^{-2}). Moreover, PSCs are sensitive to high temperatures, UV-light, moisture and oxygen: factors that are hindering their commercialization.

The present review frames the last attempts for overcoming these challenges addressing degradation mechanisms and outlining the outstanding achievements. This article also reviews the basic working principles of PSCs, addresses new cell configurations, highlights the need of leak-free encapsulation for long-term stability and environmentally safer devices, and discusses new and lead-free absorbers.

1. Introduction

The accelerated world population growth and post-industrial era bring to attention an unprecedented energy demand, responsible for environment problems, sustainable development concerns as well as economic challenges. At present, fossil fuels are the source for more than 80% of the world primary energy and responsible for most of the greenhouse gas emissions [1]. Technologies that take advantage of renewable energy sources such as sun, wind, biomass, hydraulic and geothermal are being studied and developed. Sunlight has an enormous potential as energy source with an irradiance 1.8×10^{14} kW at earth's surface [2], which can be transform in electricity and heat with minimal environmental impact [3]. Photovoltaic solar cells are one of the most promising technologies for producing electricity from sunlight; in particular, photovoltaic (PV) panels based on silicon technology (c-Si and poly-Si) are widely installed showing normal efficiencies of 15–20% [4,5] with a record-breaking efficiency of 24.4% [6]. However, PV-grade silicon fabrication uses harmful chemicals in a complex purification process [7]. For building integrated photovoltaic (BIPV), silicon-based panels are generally unaesthetic and display significantly lower real efficiencies when used in facades, mostly due to the difficulty in harvesting diffuse light. The third generation of solar cells emerged with dye sensitized solar cells (DSCs); they can be easily adapted to the facades of buildings, display different colors and patterns and with the interesting feature of harvesting efficiently diffuse light. The power conversion efficiency (PCE) of this type of cells reached 14.3% with organic-based dyes and cobalt (III/II) complex redox electrolyte in a lab device [8]. Following these achievements, Kojima et al. [9] presented for the first time in 2009 a DSC using a perovskite as light absorber with 3.8% PCE. The organometal halide perovskite material used, with the generic structure of $CH_3NH_3PbX_3$, soon proved to have an astonishing high-efficiency as light absorber displaying also very high hole and electron conductivities [10–13]. This disruptive finding led to the emergence of a new thin-film photovoltaic family – the perovskite solar cells (PSCs) – presently one of the most investigated families of solar cells. The sudden interest on the PSC is related to the great increase on energy conversion efficiency that this technology experienced in the pasted 7 years, from 3.8% in 2009 to 22.1% in 2016. Moreover, PSCs are easy to produce and display a great potential for BIPV allowing color [14,15] and transparency [16]. Until now, the highest certificated PCE belongs to the Korean Research Institute of Chemical Technology (KRICT) that has reached 22.1% [17]. However, the structure of the perovskite and the architecture of the device is still unknown. The highest PCE reported in a scientific article was presented by Bi et al. that obtained 21% (certified value), using poly(methyl methacrylate) (PMMA) as a template for $(FAI)_{0.81}(PbI_2)_{0.85}(MAPbBr_3)_{0.15}$ perovskite to control the nucleation and crystal growth, thus reducing the pinholes and grain boundaries [18]. Saliba et al. prepared a four cation (rubidium/cesium/methylammoniu/formamidinium) perovskite device with 21.6% PCE, that retained 95% of initial PCE after 500 h at 85 °C under full solar illumination and maximum power point (MPP); poly (triarylamine) (PTAA) was used as hole transport material [19]. This astonishing stability result, was only surpassed this year by Grancini et al. that prepared a 2D/3D perovskite module (10×10 cm^2) with a carbon

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back contact. The module maintained the initial efficiency for more than one year, kept under 1 sun and at short circuit conditions [20].

Although the astonishing power conversion efficiencies reached by now, two major obstacles are still limiting the commercialization of PSC: moisture and oxygen sensitivity responsible for the degradation of the perovskite absorber, and the presence of lead in the composition of the most efficient perovskite absorbers [19,21,22]. These major challenges are boosting the research community to develop effective hermetic encapsulating solutions and to produce efficient lead-free absorbers.

The present article reviews the PSC working principles and the most studied configurations, as well as the role of each layer in the different architectures. Degradation mechanisms due to temperature, oxygen, UV radiation and moisture, the role of deposition methods and hysteresis phenomenon effect in the PSC stability are also reviewed. Finally, it is presented the most recent lead-free materials reported and the innovative sealing processes that can lead to PSC commercialization in few years. This review paper aims to offer an important tool for driving future research.

2. Device operation

"Perovskite" refers to the absorber material of PSC devices, which adopts the crystal structure of ABX_3 [23]. The perovskite family typically used is based on organic-inorganic lead perovskites with the polycrystalline structure $CH_3NH_3PbX_3$, where X is a halide atom (I, Cl, Br or a combination of some of them). This type of materials shows advantageous properties to be used as a PV absorber, namely: 1) strong optical absorption due to s-p anti-bonding coupling; 2) high electron and hole mobilities and diffusion lengths; 3) superior structural defect tolerance and shallow point defects; 4) low surface recombination rate; and 5) favorable grain boundaries since they do not promote the electron-hole recombination [24,25]. In fact, comparing to the most common photovoltaic systems – Table 1 – perovskite semiconductors show tunable band gap, balanced electron/hole transportation, low recombination rate, carrier lifetime over 100 ns and a diffusion length over 1000 nm [26]. The high absorption coefficient of the perovskite nanocrystals makes the perovskite layer within the PSCs to be very thin, in the range of ca. 400 nm.

Perovskite solar cells present a very similar structure to typical DSCs and the most common configuration is composed by five main layers: 1) Transparent conductive oxide (TCO) glass substrate; 2) a semiconductor compact layer (typically called blocking layer); 3) a mesoporous semiconductor film (scaffold); 4) a perovskite absorbing material; 5) a hole transfer material (HTM); and 6) an electrical conductive back contact. The correspondent architecture of this type of devices is sketched in Fig. 1. The blocking layer is normally made of TiO_2, a n-type material that forms a n-i junction selective to the passage of the electrons. The mesoporous layer serves to drive the photoinjected electrons to the blocking layer, however it is not essential in the PSC operation, since there are evidences that the main role is to serve as a scaffold for the perovskite deposition [13]. The perovskite layer is the light absorber material that produces the charge separation driving electrons to the n-i junction and holes to the i-p junction. The hole transport material is a p-type material that forms a i-p junction selective to the holes transport. For an efficient charge extraction, the band alignment of the perovskite with n- and p-type selective materials is very important: the conduction band edge of the electron transport layer must be lower than the perovskite conduction band and the valence band edge of the hole transport layer must be higher than the perovskite valence band – see Fig. 2.

Table 1
Physical properties of most common photovoltaic materials [26,174,175].

	Perovskite	Si	CIGS	GaAs	CdTe
Band gap/eV	1.5 (tunable)	1.1	1.12	1.43	1.5
Absorption coefficient/ cm^{-1}	$10^{4–5}$	10^{3}	$10^{4–5}$	$10^{4–5}$	10^{3}
Carrier mobility/ $cm^2 V^{-1} s^{-1}$	Up to 2000	1500	< 10	8500	10
Carrier concentration/ cm^{-3}	$10^{16–17}$	10^{16}	$10^{15–16}$	10^{17}	$10^{14–15}$
Carrier lifetime	> 100 ns	ms	50–200 ns	< 100 ns	20 ns

In the typical configuration of a PSC device, as the perovskite absorbs light, an electron-hole pair is created – Eq. (1); photogenerated electrons are injected into the mesoporous semiconductor and the holes are driven into the HTM – Eq. (2). The injected electron goes through the external circuit until the back contact, and the hole is transported by a hopping mechanism (electronic conduction) until the same contact. At the interface HTM/back contact the hole and electron recombine regenerating the system – Fig. 2**a)**. The p-n junctions are responsible for the creation of a built-in electric field that allow the charges separation, where electrons move to the mesoporous TiO_2 and holes move to the HTM [27]. Since both materials have different Fermi levels, charges flow until equilibrium is reached; a space-charge region appears at the respective interface and consequent band-bending is observed – Fig. 2**b)**.

$$\text{Perovskite} + h\nu \rightarrow (e^- ... h^+)_{\text{perovskite}} \quad (1)$$

$$(e^+ ... h^+)_{\text{perovskite}} \rightarrow e^-_{cb}(TiO_2) + h^+(\text{HTM}) \quad (2)$$

However, undesired reactions may occur, competing with the extraction of photogenerated charges. The main back reactions are: exciton annihilation by photoluminescence – Eq. (3); non-radiative recombination – Eq. (4) – and recombination of the charge carriers at the interfaces (TiO_2 surface, HTM surface and TiO_2/HTM interface) – Eqs. (5)–(7) – with consequent heat release.

$$(e^- ... h^+)_{\text{perovskite}} \rightarrow h\nu' \quad (3)$$

$$(e^- ... h^+)_{\text{perovskite}} \rightarrow \nabla \quad (4)$$

$$e^-_{cb}(TiO_2) + h^+(\text{perovskite}) \rightarrow \nabla \quad (5)$$

$$h^+(\text{HTM}) + e^-(\text{perovskite}) \rightarrow \quad (6)$$

$$e^-_{cb}(TiO_2) + h^+(\text{HTM}) \nabla \quad (7)$$

3. PSC architectures and materials

In the thin-film solar cells family, the preparation method and the device architecture are key factors for high-efficient light-to-electricity conversion processes. In the case of PSC there are five different configurations: mesoporous-conducting semiconductor scaffold; mesoporous-insulating oxide; planar; HTM-free and inverted. Until now, the best-performing PSCs is not confined to a single architecture [28] depending heavily on the type of perovskite material used. Until the moment of this review, the configurations that originated the highest power conversion efficiencies are mesoporous with 21.6% (certified value of 21.0%) [18] and planar with 20.7% [29]. In the NREL efficiencies plot the most efficient certified cell present 22.1%, however the configuration and the detailed materials used remain unknown.

3.1. Mesoporous conductive semiconductor PSC device

Presently, the most studied architecture of perovskite solar cells is the mesoporous type – Fig. 1. Perovskite $CH_3NH_3PbI_3$ nanocrystals filling the inner porosity of the TiO_2 mesoporous layer were first used to enhance the light absorption in liquid DSCs, resulting in an PCE of 3.8% [9]. In Im et al. [30] proposed a quantum dot (QD) sensitized solar cell using $CH_3NH_3PbI_3$ perovskite reaching the highest efficiency among the reported inorganic QD sensitizers – 6.5%. However, liquid solar cells