Recent advances in perovskite-based solar cells

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Organic–inorganic halide perovskites have a significant impact on photovoltaic devices and the solar-to-power conversion efficiency is considerably high (~20.1%) compared to the present existing organic solar cells (OSCs) and dye sensitized solar cells (DSSCs). For the past 3 years, there has been tremendous improvement in photovoltaic efficiency of perovskites, i.e. ~9.7% in 2012 to 20.1% in 2015. Meanwhile, several fabrication approaches, inorganic and organic hole transport materials and device concepts have been developed for high-performing devices. Nevertheless, some issues have to be addressed to commercialize the pervoskite solar cells. Particularly, stability of these cells is not well documented in the literature so far and this is the noteworthy concern. In this review, fundamental aspects of the perovskite device and recent developments are illustrated to provide high-performance perovskite solar cells with durability.

Keywords: Hole transport material, perovskite, photovoltaic efficiency, solar cells.

SOLAR energy is an alternative source to traditional resources such as coal and fossil fuel for the present growing energy demand. In this perspective, developing solar cells is one of the best approaches to convert solar energy into electrical energy based on the photovoltaic effect. Over the years, silicon-based cells have been used for industrial purposes due to their efficient solar-to-power generation (~30%), particularly crystalline silicon[1]. However, the cost of Si-based photovoltaic cells is relatively high and difficult to utilize in large-scale industries. An alternative to silicon solar cells is third-generation excitonic photovoltaic devices, which have been developed based on various dye sensitizers, organic and hybrid (organic–inorganic) materials; and these reach a photovoltaic efficiency up to ~15–20% (refs 2–9). Among those materials, perovskites (organic–inorganic) have reached top position (~20.1%) within ~5 years, due to substantial improvement of power conversion efficiency and low processing costs[10]. As the efficiency of the device increases, the number of publications is also rapidly increasing since 2009 (Figure 1). Significant aspects of perovskites are synthetic feasibility, strong optical absorption, charge recombination rate, and ease of fabrication. Moreover, hybrid perovskites can be pre-pared by simple synthetic methods and are easy to capitalize when compared to the existing excitonic photovoltaic technologies such as dye sensitized solar cells (DSSCs) and organic solar cells (OSCs). Another important aspect is high charge-carrier mobility, which is more useful for developing high-performance solar cell devices. However, toxicity of lead is a major concern which easily degrades on exposure to humidity and ultraviolet (UV) irradiation. Today's research mainly focuses on the commercialization of perovskite solar cells by controlling degradation and toxicity. In this review, we highlight the fundamental aspects of perovskites and recent progress in perovskite-based device fabrication. Still, there exist some issues which need to be resolved in the commercialization of perovskites.

Organic–inorganic halide perovskites: crystal structure, device fabrication and optical band gap

Crystal structure

Perovskites have the common formula ABX_3 where A and B are cations which reside in the corner and the body centre of the pseudo cubic unit cell and X is the anion which occupies the face centre. The crystal structure of perovskite can be alternatively viewed as corner-linked BX_6 octahedral with interstitial A cation. Figure 2 *a* represents the crystal structure of ABX_3. The crystallographic stability and apparent structure can be deduced
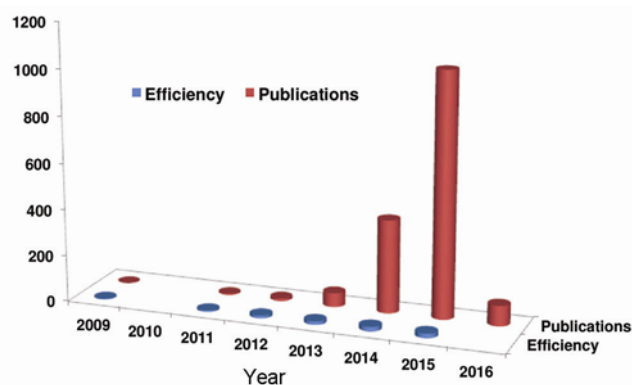

Figure 1. Number of publications on perovskite solar cells and efficiency per year found using the search term 'perovskite solar cells' from *Scopus* (31 January 2016).

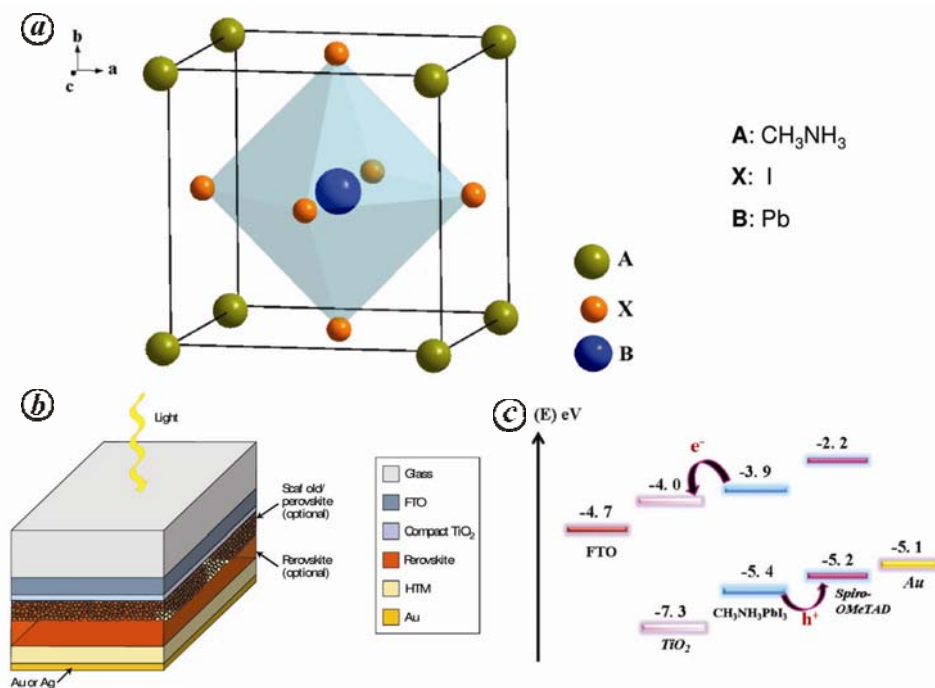*For correspondence. (e-mail: giribabu@iict.res.in)

Figure 2. *a*, Crystal structure of organic–inorganic halide perovskite ABX_3 ($CH_3NH_3PbI_3$). *b*, General device structure of ABX_3 (reprinted with permission from ref. 21). *c*, The corresponding energy levels.

by considering a Goldschmidt tolerance factor t and an octahedral factor μ. Here, t is defined as the ratio of the distance *A–X* to the distance *B–X* in an idealized solid-sphere model ($t = (R_A + R_X)/\{\sqrt{2}(R_B + R_X)\}$, where R_A, R_B and R_X are the ionic radii of the corresponding ions) and μ is defined as the ratio R_B/R_X. For halide perovskites (X = F, Cl, Br, I), t and μ have a narrower range, i.e. 0.89–1.0 and 0.4–0.88 respectively[11].

In case of ABX_3, the larger cation A is considered as a organic, which is generally methylammonium ($CH_3NH_3^+$) with $R_A = 0.18$ nm. Ethylammonium ($CH_3CH_2NH_3^+$; $R_A = 0.23$ nm) and formamidinium ($NH_2CH=NH_2^+$; $R_A = 0.19–0.22$ nm) also provide excellent results. The anion X is a halogen, normally iodine ($R_X = 0.220$ nm). Br and Cl are also used in perovskites as well as mixed halide materials[12–18]. For cation B, Pb is universally considered for stabilization and efficiency in solar cells. Although Sn has similar band gap (1.55 eV) and is in the same group as Pb, due to the ease of oxidation and lack of stability, it performs poorly compared to Pb in case of efficiency[19]. For the last 7 years, methylammonium lead triiodide ($CH_3NH_3PbI_3$) perovskites have been widely using for fabrication of solar cells and show good efficiency (~20.1%), with mixed halides $CH_3NH_3PbI_{3-x}Cl_x$ and $CH_3NH_3PbI_{3-x}Br_x$ also being important.

Device fabrication

Today DSSCs serve as an example for design of organic and inorganic halide perovskite solar cells. Figure 2*b*

shows a schematic illustration of device structure of perovskite. TiO_2 layer (hole-blocking layer) is deposited on fluorine-doped tin oxide (FTO) followed by deposition of mesoporous layer of *n*-type TiO_2 above compact TiO_2 layer by screen-printing/spin-coating technique of TiO_2 paste and annealed further. Likewise, porosity and thickness of TiO_2 are adjusted by solvent concentration and various fillers. In order to prepare perovskite films, various solvents such as γ-butyrolactone (GBL) or *N*,*N*-dimethylformamide (DMF) have been used. Therefore, these films spin-coated on *n*-type mesoporous TiO_2 layer, followed by deposition of hole transporting material (HTM, spiro-OMeTAD) with suitable dopants to enhance conductivity. Lastly, a metal electrode is placed on top of the HTM[20].

Optical bandgap

Reflectance and ultraviolet photoelectron spectroscopy (UPS) measurements utilized to calculate the optical band gap, valence band, conduction band and respected values are estimated at 1.5, 5.4, 3.9 eV. Subsequently, the electronic structure of perovskites is measured theoretically by density functional theory (DFT) without considering spin-orbit coupling effect. Thus, these results match with the experimental results (1.5 eV) which corroborate the excellent photovoltaic properties of halide perovskites. Figure 2*c* shows a schematic illustration of the energy levels of hole transporting material (HTM) and electron transporting material (ETM) well aligned with the perovskite leads high charge separation and transport.
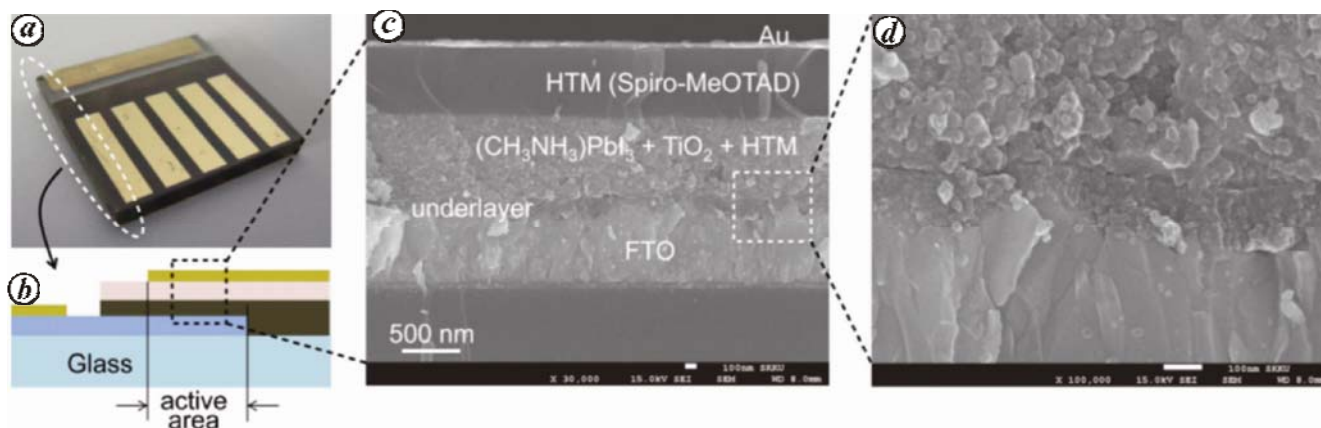
Figure 3. *a*, *b*, Real solid-state and schematic representation of the perovskite device. *c*, *d*, SEM image of the device and high-resolution image of perovskite layer (reprinted with permission from Kim *et al.*[24]).
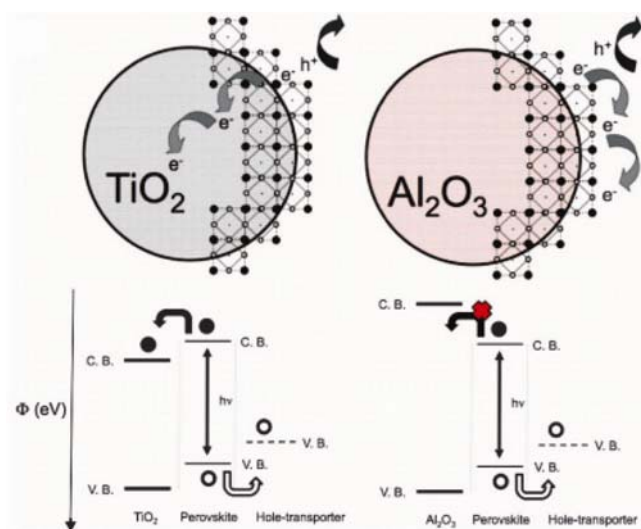

Figure 4. Schematic representation of charge transfer and transport in perovskite-sensitized TiO$_2$ and Al$_2$O$_3$-based solar cells and corresponding energy levels (reprinted with permission from Lee *et al.*[25]).

Furthermore, we focus on recent advances of CH$_3$NH$_3$-PbI$_3$-based devices using various organic and inorganic HTMs, deposition methods and stability approaches, whose results show significant improvement in power conversion efficiency and stability in last 5 years. Thus, perovskites are considered best materials for commercialization in near future.

Progress in organic–inorganic halide perovskite devices

Although, perovskites are known to the scientific community since over a century[21], they received attention only when Miyasaka and co-workers used methylammonium lead halide (perovskite) as a light harvesting material in excitonic solar cells[22].

Miyasaka and co-workers reported first time in 2009, perovskites utilized as sensitizers in DSSCs and achieved the solar-to-power conversion efficiency of 3.2% for (CH$_3$NH$_3$)PbBr$_3$ and 3.8% for (CH$_3$NH$_3$)PbI$_3$ (ref. 22). However, these devices are unstable due to the degradation of perovskites in liquid electrolyte containing lithium halide. Subsequently, Park and co-workers developed the quantum-dot-sensitized solar cell using perovskite (CH$_3$NH$_3$)PbI$_3$ sensitizer[23]. These perovskite nanoparticles exhibit better optical properties than standard N719 dye sensitizer and reach an efficiency of 6.5%. However, these devices degrade the solar cell performance in a short span of less time due to the dissolution of halides in liquid electrolytes[23].

In order to avoid corrosive liquid electrolyte in perovskite DSSC, Kim *et al.*[24] developed the solid-state electrolyte, spiro-MeOTAD (2,2′,7,7′-tetrakis(*N*,*N*-di-*p*-methoxyphenylamine)-9,9′-spirobifluorene), which can act as a HTM. The authors developed the one-step solution-processable perovskite solar cells using solid-state electrolyte and successively achieved power conversion efficiency (PCE) 9.7% with excellent long-term stability (Figure 3 *a–d*)[24]. They demonstrated the high efficiency due to charge separation by hole transfer from the excited (CH$_3$NH$_3$)PbI$_3$ nanoparticles to the mesoscopic TiO$_2$ film and spiro-OMeTAD, which was confirmed by femtosecond laser studies. Moreover, the authors highlighted that the solid hole conductor as a HTM in perovskite solar cells (PSCs) considerably improved the PCE and stability when compared to liquid electrolyte-based PSCs.

Further, Snaith and co-workers[25] developed the solution processable perovskite solar cells with non-conducting Al$_2$O$_3$ replacing the conducting nanoporous TiO$_2$ (Figure 4 *a* and *b*). The authors observed high efficiency (~10%), when compared to previous DSSCs, where liquid electrolyte was used. Moreover, four additional advances were introduced. First, mixed-halide CH$_3$NH$_3$PbI$_{3−x}$Cl$_x$ in PSCs demonstrated good stability and carrier transport. Second,
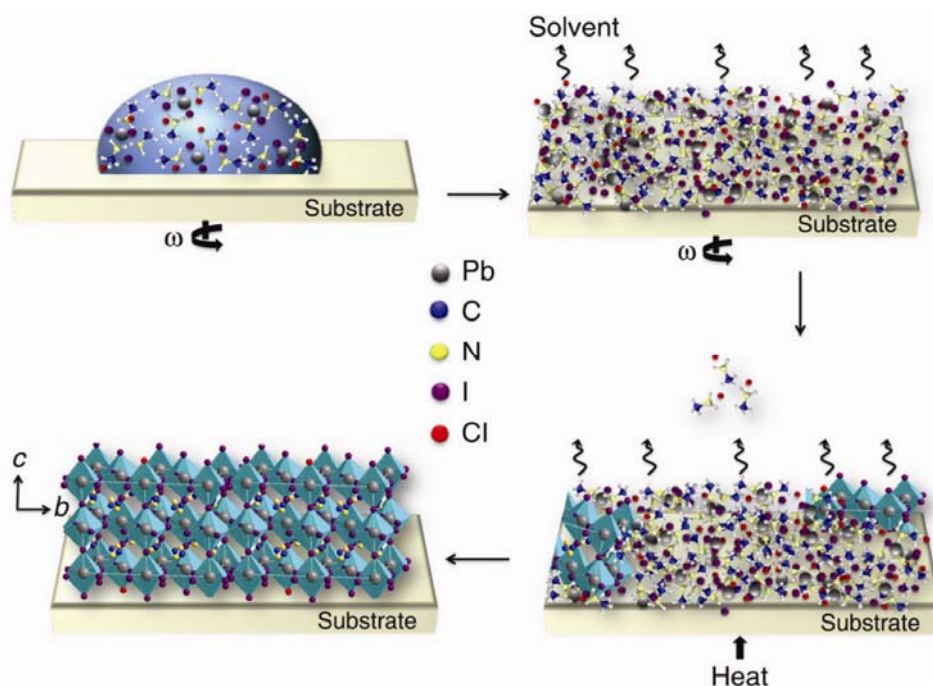
Figure 5. The stages of fabrication of perovskite thin films using excess organic component (reprinted with permission from Zhang *et al.*[28]).

coating thin perovskite layer onto the nanoporous TiO_2 surfaces and preparing the extremely thin absorber (ETA) cells. Third, restoring the conducting nanoporous TiO_2 with non-conducting Al_2O_3, thus improving the open-circuit voltage (V_{oc}) and achieving an efficiency of 10.9%. Fourth, ambiploar transport in simple planar cells with scaffolding eliminated.

Heo *et al.*[26] reported PCE of 12% using both flexible layers, consisting of perovskite layer overlying the scaffolding TiO_2 infiltrated by perovskite. They studied several HTMs-based PSCs, including spiro-OMeTAD and poly-triarylamine, and found that poly triarylanine (PTA)-based PSCs achieved highest efficiency compared to others. Later, Seok and co-workers further improved PCE to 12.3% using mixed-halide $CH_3NH_3PbI_{3-x}Br_x$ perovskites[27]. In this report, subsequent addition of low ionic radius of Br (10–20%) to the mixed halides allowed for significant improvement in efficiency and stability due to the tetragonal to pseudo-cubic structural transition of perovskites.

Zhang *et al.*[28] developed pinhole-free perovskite films and achieved PCE of 15.2% using non-halide ($PbAc_2$) under one Sun illumination (Figure 5)[28]. They prepared films using one-step coating method followed by annealing. Likewise, devices were also fabricated with $PbCl_2$ and PbI_2 and significant improvement in efficiency was observed.

Although one step solution coating process showed significant improvement in efficiency but abandoned precipitation yields morphological defects in photovoltaics, thereby lower PCE. Alternatively, two-step coating deposition method was developed to make smooth films and crystalline. In this method, the film was prepared by using a solution of PbI_2 and coated on the substrate, and then CH_3NH_3I in 2-propanol was spun on the film, resulting high-quality perovskite films (Figure 6 *a*)[29]. Using this method, two groups prepared perovskites films and achieved efficiency of over 15%. Burschka *et al.*[30] developed the sequential deposition method for fabrication of PSCs and achieved PCE of 15% (Figure 6 *b*). Subsequently, Liu *et al.*[31] also developed a method for fabrication of vapour-deposited PSCs based on a planar heterojunction thin-film architecture and reached PCE of over 15% with an V_{oc} of 1.07 V (Figure 6 *c*). These results suggest that deposition approaches significantly influences on PCE of PSCs and achieved the highest efficiency when compared to previously reported solution-processed solar cells.

Later, Jeon *et al.* achieved the PCE of 16.2% by altering the energy levels of mixed-halide $CH_3NH_3PbI_{3-x}Br_x$ with PTAA (HTM)[32]. The efficiency was further improved to 17.9% by adjusting the thickness ratio of perovskite-infiltrated TiO_2 scaffolding relative to the continuous perovskite layer. Recently, Zhou *et al.*[33] have developed perovskite devices and achieved the highest PCE of 19.3% by adjusting the band alignment of HTM/ETM to the perovskite layer (Figure 7 *a–e*). The authors have highlighted that careful selection of HTM and ETM, and film preparation leads to reduced carrier recombination and good carrier transport.
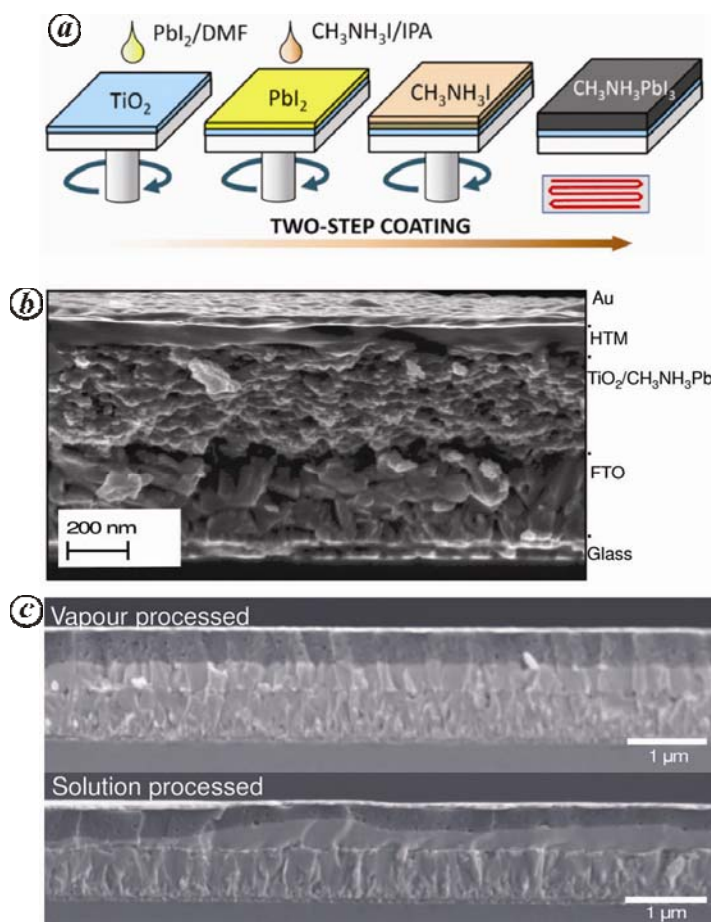
Figure 6. *a*, Schematic illustration of the two-step coating method (reprinted with permission from Im *et al.*[29]). *b*, SEM of a complete photovoltaic device (reprinted with permission from Burschka *et al.*[30]). *c*, SEM of perovskite film under vapour-deposition and solution-process methods (reprinted with permission from Liu *et al.*[31]).

Yan and his group reported that PSCs exhibited maximum efficiency of 26% by maintaining 1 μm thickness of $CH_3NH_3PbI_3$ absorber (phase with *Pm3m* symmetry)[34]. This value is much higher than the reported GaAs solar cell with the same thickness.

Effect of hole transport materials on pervoskite solar cells

Spiro-OMeTAD is extensively used as an HTM in PSCs and has helped achieve remarkable photovoltaic performance using various deposition approaches. However, spiro-OMeTAD cannot be considered for large-scale application due to the multi-step synthesis, purification procedure and moisture sensitivity. In addition, spiro-OMeTAD enhanced PCE only after being doped with a metal complex and/or additives, which might affect the device stability. In order to resolve these issues, several researchers are working on alternatives for spiro-OMeTAD and have developed low-cost and efficient HTMs, particularly inorganic and small organic molecules[35–52]. In this context, inorganic semiconductors are found to be the best alternative in PSCs because of high hole mobility, synthesis feasibility and low production cost. Recently, copper oxide and nickel oxide inorganic HTM-based PSCs have reached an efficiency of approximately 17%, which is close to the value of organic HTM-based PSC. Moreover, stability of inorganic HTMs is relatively better than spiro-OMeTAD. Kamat and co-workers used copper iodide (CuI) as HTM in PSCs and obtained a PCE of ~6.0% (ref. 37). Interestingly, they observed improved open circuit voltage (V_{OC}) when compared to the best spiro-OMeTAD devices. Impedance spectroscopy revealed that CuI exhibited two orders of magnitude higher electrical conductivity than spiro-OMeTAD that allowed appreciably higher fill factor (FF). Recently, CuSCN was used as HTM in PSC and achieved considerably high PCE[38,39]. Ito *et al.*[38] reported that planar $TiO_2/CH_3NH_3PbI_3/CuSCN$ solar cells with J_{SC} of 14.5 mA cm^2, V_{OC} of 0.63 and FF of 0.53, yielded PCE of 4.9%. Qin *et al.*[39] reported PCE of 12.4% with CuSCN as a HTM using well-established sequential deposition method. Sarkar and co-workers developed inverse glass/FTO/NiO/$CH_3NH_3PbI_{3-x}Cl_x$/PCBM solar cells and
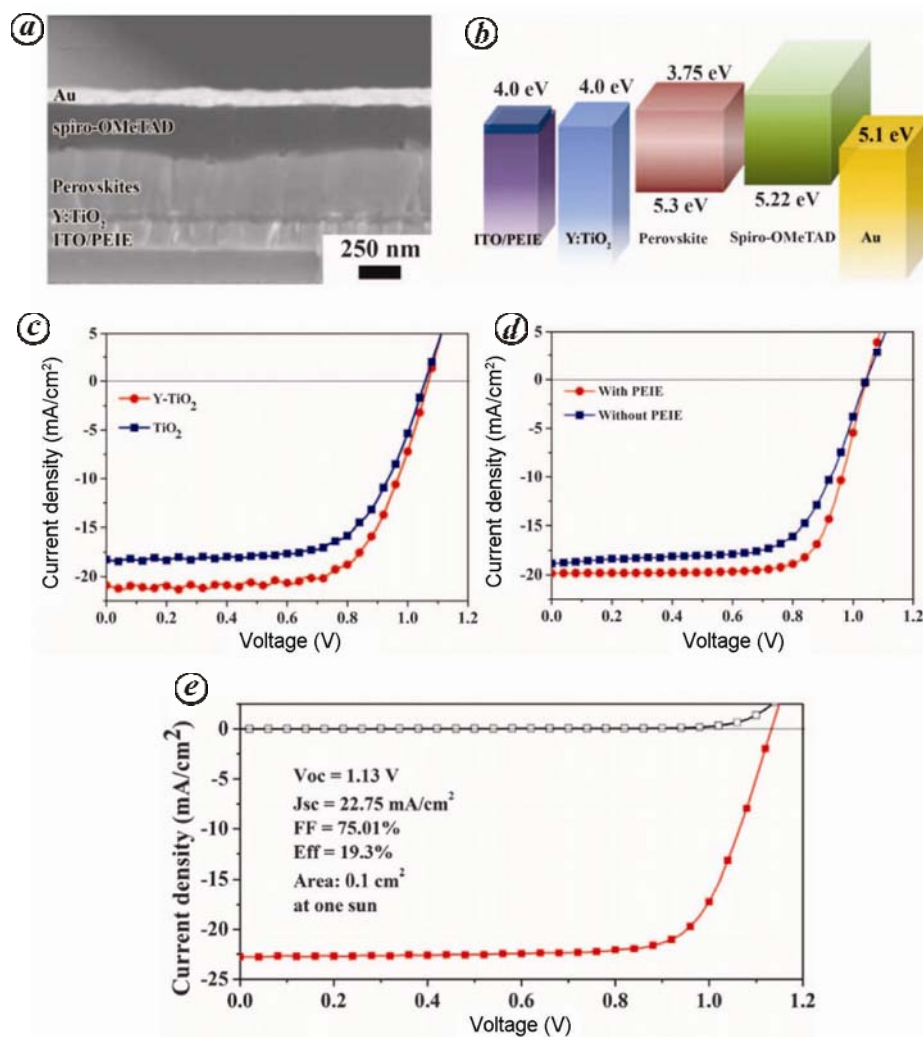
Figure 7. *a*, SEM image of the perovskite device. *b*, Energy level diagram of each layer of the device. *c*, Current density–voltage curves of devices with Y–TiO$_2$ compared with undoped TiO$_2$. *d*, Current density–voltage curves of devices with and without PEIE modification. *e*, Current density–voltage curves for the champion cell without antireflective coating (reprinted with permission from Zhou *et al.*[33]).

achieved PCE of 7.3% (ref. 47). Recently, NiO$_x$-based PSC on an ITO-glass substrate helped achieve optimal PCE of 16.47% by spin coating a presynthesized high-quality NiO$_x$ nanoparticle solution[49].

In addition to inorganic HTM, small-molecule-based HTMs have also been developed, particularly, 3,4-ethylene-dioxythiophene[50], pyrene[51] and other linear π-conjugated structures[52], which provide high PCE of 12–13%. Device description of various spiro-based and polymeric HTMs, together with inorganic HTMs and corresponding PCE values is provided below and tabulated in Table 1.

Improvement in the stability of pervoskites from 2009 till date

Today's pervoskite-based solar cells reached PCE over 20.1%, however, durability still significant concern for

practical applications. The major drawback in PSCs is the relatively short lifetime attained with existing technology. In order to commercialize these solar cells, economically viable extended device lifetime will be necessary.

In 2011, stability of pervoskite-based DSSCs was limited (~10 min) before degradation (about 80% degradation) because perovskite QDs dissolved into redox electrolyte[23]. In 2012, stability of PSCs was enhanced from minutes to over 500 h using spiro-MeOTAD as a solid-state HTM[24]. This progress is attributed to the finding of solid hole conductor. Further improved in the stability over 500 h was achieved by another approach, i.e. long-term light soaking at a light intensity (100 mW cm^{-2}) and a temperature of 45°C. Until now, TiO$_2$-based devices have been used for perovskite solar cells and have attained stability above 500 h. Alternatively, stability of Al$_2$O$_3$-based perovskite solar cells showed improved stability over 1000 h at nearly 15 mA cm^{-2} because

Table 1. Reported efficiency of PSCs since 2009

Year	Pervoskite	HTM	Efficiency (%)	Reference
2009	$CH_3NH_3PbI_3$	I^-/I_3^-	3.8	22
2011	$CH_3NH_3PbI_3$	I^-/I_3^-	6.5	23
2012	$CH_3NH_3PbI_3$	Spiro-OMeTAD	9.7	24
2012	$CH_3NH_3PbI_{3-x}Cl_x$	Spiro-OMeTAD	10.9	25
2013	$CH_3NH_3PbI_3$	PTAA	12.0	26
2013	$CH_3NH_3PbI_{3-x}Br_x$	PTAA	12.3	27
2013	$CH_3NH_3PbI_3$	Spiro-OMeTAD	15.0	30
2013	$CH_3NH_3PbI_3$	Spiro-OMeTAD	15.2	31
2014	$CH_3NH_3PbI_{3-x}Br_x$	PTAA	16.2	32
2014	$CH_3NH_3PbI_{3-x}Cl_x$	Spiro-OMeTAD	19.3	33
2014	$CH_3NH_3PbI_3$	CuI	6.0	37
2014	$CH_3NH_3PbI_3$	CuSCN	4.9	38
2014	$CH_3NH_3PbI_3$	CuSCN	12.4	39
2014	$CH_3NH_3PbI_{3-x}Cl_x$	NiO	7.3	47
2015	$CH(NH_2)_2PbI_3$	Spiro-OMeTAD	20.1	10
2016	$CH_3NH_3PbI_3$	NiO_x	16.47	49

of rapid decay in photocurrent and a small decay in photovoltage[25].

Kwon *et al.*[53] found that the *ex situ* long-term stability attained when exposure to 1000 h at below 20% humidity. In this report, they utilized HTMs such as spiro-OMeTAD, poly 3-hexyl thiophene (P3HT) and PDPPDBTE in PSCs). They found that spiro-MeOTAD-based devices showed a 28% decrease in PCE when ageing extended. This value is lower when compared to the initial PCE value. The authors highlighted that PDPPDBTE-based cells improved the stability remarkably even after 1000 h. This is mainly because of its hydrophobic behaviour, which precluded water flow into the perovskite. In addition to these solar cells, mixed-halide perovskites also improved the stability on nanostructured-TiO_2 (ref. 54). Interestingly, PSC structures show much better stability after inclusion of Br into the mixed-halide, when compared to alone after 30 days, while efficiency of PSCs without Br dropped by 20% than initial PCE. In addition, the equimolar Br/I devices revealed a noteworthy improvement of 37% PCE. This enhancement could be a result of the rearrangement of the 3D configuration of PSCs over time[55].

Mei *et al.*[56] developed a novel device by solution dropcasting method. The device consist of a double-layer of TiO_2 and ZrO_2 in a porous carbon film, which leads to a significantly long-term stability of 1008 h upon direct Sun exposure. Also, stability of mesoporous TiO_2/$CH_3NH_3PbI_3$/C without encapsulated PSCs devices achieved over 2000 h under dark conditions.

During the last few years, stability of PSCs has improved significantly. However, all concerns are not yet well addressed[57]. For commercialization of a PSC solar device, stability is a major issue. Although few reports highlight controlling the device stabilities relating to moisture, temperature, light and oxygen, other concerns like intrinsic stabilities at the interface, and device architecture remain major obstructions to practical applications.

Notably, these latest results show the significant improvement in PCE and stability of PSCs by considering the possibility of using one or two optional layers, three different mixed-halide perovskites and a few diverse HTMs. Another significant aspect in PSCs is ease of fabrication, and similar design strategy of dye-sensitized and organic solar cells has resulted in a rapid increase in the number of researchers working in this field. During the last 5 years, the number of journal papers published on PSC devices has radically increased from two to thousands. Therefore, PSCs play a major role in commercialization of future generated photovoltaics.

Table 1 summarizes the growth of PSCs with change in material composition and improvement in efficiency.

Conclusion and future challenges

Organic–inorganic halide perovskites significant for research and commercialization of solar cells in next few years due to high efficiency and durability. Another advantages of PSCs that low processing cost and simple execution of desirable products such as flexible, transparent or all-perovskite tandem cell modules than existing photovoltaics. Furthermore, PSCs can show the better performance if integrated with other cell technologies.

However, few problems need to be resolved with respect to commercialization: (1) toxicity of Pb atoms, (2) long-term durability, and (3) cost-effectiveness. Until now, the highest efficiency has been obtained only from lead-based perovskites. However, utilization of Pb-based materials in solar cells is restricted due to their toxicity. In order to overcome this issue, majority of research is on lead-free-based materials together with commercialization. Fortunately, Sn-based materials have been developed and reached efficiency of approximately ~7% (refs 58 and 59). Although efficiency of Sn-based perovskite

devices is lower than Pb, the results show the way for commercialization of pervoskite solar cells and provide better durability and eco-friendly paths. Thus, challenging PSC manufacturers to introduce new products into the market with existing technologies.

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