Recent advances in flexible perovskite solar cells

B. Susrutha, Lingamallu Giribabu and Surya Prakash Singh

Flexible and low-weight thin-film perovskite solar cells have attracted considerable attention for developing large-area, roll-to-roll and differently shaped photovoltaics with improved power conversion efficiencies. In this review, we describe how researchers have adopted different approaches to enhance the device performance of the flexible perovskite solar cells to compete with rigid substrates with tailored electron/hole transport materials and flexible substrates.

1. Introduction

Solar energy is one of the most abundant and renewable energy sources and has minimum harmful impact on the environment compared to other sources like fossil fuels and nuclear energy. A solar cell (also called a photovoltaic cell or a photoelectric cell) is a solid-state electrical device that directly converts solar energy into electricity. An ideal solar cell requires low-cost, trouble-free, abundant material resources with good stability and high power conversion efficiency (PCE), and should also be able to be integrated into a large area device. Based on this criteria, many photovoltaic technologies have been developed such as crystalline silicon based solar cells, thin-film vapour-deposited semiconductor-based solar cells, for example, CdTe or CIGS, and solution-processed solar cells based on organic semiconductors, hybrid composites, or inorganic semiconductors, which are denoted as first, second, and third generation photovoltaics (PVs), respectively. Moreover, crystalline Si-based solar cells play a major role in the commercial photovoltaic market and

Dr B. Susrutha is a Research Associate at the CSIR-Indian Institute of Chemical Technology, Hyderabad, India, in the group of Dr L. Giribabu and Dr Surya Prakash Singh. She gained her masters at Osmania University, Hyderabad, and then received her PhD from the Indian Institute of Technology, Kharagpur, in 2014. Her research interests are focused on the synthesis and fabrication of perovskite solar cells, and the synthesis of nanofluids and nanocomposites.

Lingamallu Giribabu received his PhD degree in chemistry from the University of Hyderabad in 2000. Before joining the CSIR-Indian Institute of Chemical Technology, Hyderabad, India, as a Scientist in 2003, he worked with Dr. Martin R. Johnston (Central Queensland University, Australia) and Prof. Karl M. Kadish (University of Houston, Houston, USA) as a postdoctoral fellow. He has been working as a senior scientist at the Indian Institute of Chemical Technology, India, since 2003. His research interests include the development of low-cost new efficient materials for dye-sensitized solar cells, donor-acceptor systems, and the non-linear optical properties and photoelectrochemistry of tetrapyrrolic compounds. He has published over 100 research articles, patents, review articles and a book chapter.
have efficiencies of 12% to 16%. However, their high manufacturing costs limit their use in large-scale PVs. Recently, perovskite solar cells has promised to break the current paradigm by ultimately combining both low cost and high efficiency. Following the pioneering work by Grätzel et al. on the discovery of 9.7% solid-state perovskite solar cell, which has attained 500 h verified stability, more interest is now being shown by researchers in this area.\textsuperscript{14,15}

In general, fluorine-doped tin oxide (FTO) or indium tin oxide (ITO) coated glass substrates are used for the fabrication of solar cells, which provide an extremely effective barrier towards water and oxygen penetration into the solar cell device, but they require high-temperature processes to fabricate PVs with excellent PCEs.\textsuperscript{14–18} However, the main drawbacks of this type of substrates concern their rigidity, weight, and fragility, which limit the potential integration of PV devices into large-scale and roll-to-roll modules. Instead, flexible substrates can be easily moulded into different shapes, and thin-film PV panels containing these substrates can be integrated with infrastructures of various shapes and sizes for innovative energy-generating products. Hence, nowadays, researchers have focused more on designing low-cost, lightweight, and mechanically flexible thin-film PVs, which enable the implementation of portable, reduced dimensions, and also roll-to-roll fabrication of solar devices on a large scale.\textsuperscript{19–31} To date, a lot of different PV materials have been developed with various deposition methods on a variety of substrates for the manufacture of flexible solar cells. Based on the PV materials used, flexible solar cells are usually categorized as (1) Si-based flexible solar cells; for example, amorphous Si-based PVs,\textsuperscript{32–35} polycrystalline Si-based PVs,\textsuperscript{36–38} and monocrystalline Si-based PVs,\textsuperscript{39–41} (2) compound flexible solar cells; for example, CdTe,\textsuperscript{42–44} Cu(In,Ga)Se\textsubscript{2} (CIGS),\textsuperscript{45–47} and III–V semiconductors,\textsuperscript{48–50} (3) organic solar cells; for example, dye-sensitized solar cells,\textsuperscript{51–54} or (4) organic–inorganic hybrid solar cells; for example, Si with poly[(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS), ZnO with poly(3-hexylthiophene) (P3HT), and perovskite solid-state solar cells.\textsuperscript{55–61,99,105} In this review, we focus our attention on the progress that has been made in the field of flexible perovskite solar cells.

2. Crystal structure and mechanism of perovskite solar cells

Perovskite materials have a specific crystal structure with the ABX\textsubscript{3} formula (X = oxygen, halogen). The larger A cation occupies a cubo-octahedral site shared with twelve X anions, whereas the smaller B cation is stabilized in an octahedral site shared with six X anions. Organic–inorganic halide perovskites materials are usually used for solar energy applications. Herein, the larger A cation is organic; it is generally methylammonium (CH\textsubscript{3}NH\textsubscript{2}+) and the X anion is a halogen, generally iodine, although Br and Cl are also commonly used. For efficient cells, cation B, Pb is universally used. The crystal structure of the organic–inorganic perovskite is shown in Fig. 1. A typical perovskite is thus CH\textsubscript{3}NH\textsubscript{3}PbX\textsubscript{3}, with the mixed halides CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3−x}Cl\textsubscript{x} and CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3−x}Br\textsubscript{x} also being important.

The basic device architecture of the perovskite solar cell consists of a FTO- or ITO-coated glass substrate deposited with compact TiO\textsubscript{2} and mesoporous TiO\textsubscript{2} or Al\textsubscript{2}O\textsubscript{3} as the electron-transport material (ETM) and then coated with perovskite, followed by a hole transport material (HTM), usually 2,2’/7,7’-tetrakis(N,N-di-p-methoxyphenylamine)9,9’-spirobifluorene (spiro-OMeTAD), and furthermore an Au/Ag metal layer as the electrode. When the device is irradiated under solar light, the perovskite material absorbs light and ejects an electron into the conduction band (CB) of the TiO\textsubscript{2} film with an energy gap E\textsubscript{g} \sim 1.5 eV. It has been shown that the electrons can easily transfer from CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} to the CB of the TiO\textsubscript{2} film, and the holes thus generated in CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} transfer to the HTM layer. In mixed-halide perovskites, Al\textsubscript{2}O\textsubscript{3} plays a significant role and acts as a mesoporous scaffold for the perovskites. When CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}Cl is irradiated, the photogenerated electrons cannot inject into the Al\textsubscript{2}O\textsubscript{3} film due to the very large band gap (E\textsubscript{g} \sim 7–9 eV) of Al\textsubscript{2}O\textsubscript{3} and the holes produced in the perovskite are thus transported to the HTM layer. A schematic of the perovskite solar cell architecture is shown in Fig. 2.

![Fig. 1 Structural representation of an organic–inorganic perovskite](image-url)
3. Why perovskite solar cells are important?

Perovskite materials possess a high extinction coefficient over the visible spectrum and low exciton binding energy, which make them superior light harvesters for photovoltaic applications within the nano-scale. The main advantage of the perovskite solar cell is the high output voltage close to the optical band gap, which reduces the energy redundancy that exists in most excitonic solar cells like organic PVs. Since perovskite shows an ambipolar nature, which means it can work as either an electron or a hole transporter, it allows for a versatile design of device architectures. For example, Bi et al. used perovskite as an electron transporter to form a junction in contact with various HTMs. Lee et al. deposited perovskite on the surface of meso-structured Al₂O₃ layers, where Al₂O₃ acted as a non-injecting electrode scaffold and perovskite as the electron-transport medium. Etgar et al. observed that perovskite can play the role of a light harvester and a hole conductor by applying it in contact with an electron acceptor (TiO₂) to realize a charge separation junction.

In the early 1990s, Mitzi, and co-workers carried out extensive investigations into the optoelectronic properties of organic–inorganic perovskites. Their research focused on layered organo-metal perovskites that exhibited strong excitonic features and demonstrated good operation in transistors and light-emitting diodes. In 2009, Kojima et al. first attempted to use methylammonium lead halide (CH₃NH₃PbX₃) as a semiconductor sensitizer in dye-sensitized solar cells and achieved a PCE of 3–4%, which was, however, a much low efficiency compared to that achieved with conventional Ru-based molecular dyes with PCEs of more than 11%. Two years later, Park’s group reported a 6.5% efficient CH₃NH₃PbI₃ perovskite solar cell, which was slightly more stable in electrolytes, and they showed its use in more advanced technology to form the perovskite sensitizer on a thinner TiO₂ film. Currently, the performance of perovskite-based solar cells has rapidly improved with a PCE as high as 20.1% according to National Renewable Energy Laboratory efficiency chart. Moreover, they can be conformed to curved surfaces to enhance power conversion densities. A brief overview of the achievements of flexible perovskite is provided in Fig. 3. In addition, we describe the device structures that correspond to each published efficiency record from 2.62% to 12.20%.
4. Low-temperature approach for making TiO$_2$ films over flexible substrates

In general, solar cell architectures with mesostructured TiO$_2$ or Al$_2$O$_3$ scaffold have typically shown superior efficiency and stability on glass substrates upon annealing at high temperatures. The Al$_2$O$_3$ layer does not require careful annealing since no charge injection occurs in Al$_2$O$_3$. The development of large-scale devices requires low temperatures to yield high quality compact hole blocking layers and well-connected mesoporous nanocrystalline materials, which is applicable to plastic substrates to attain enhanced efficiencies. Recently, Zardetto et al. proposed a UV irradiation process on a customized TiO$_2$ nanoparticle paste for the fabrication of efficient dye-sensitized solar cells. The atomic layer deposition (ALD) method has also been used for the fabrication of ultra-thin, uniform, and conformal layers at low temperatures in several PV technologies. The plasma approach offers several advantages over conventional thermal processes, in particular it enables the deposition of higher quality films, i.e. in terms of lower pinhole density in the range of temperatures compatible with conductive plastic substrates. Recently, Giacomo et al. prepared a compact TiO$_2$ layer/scaffold at low temperature (150 °C) by UV irradiation in combination with ALD to fabricate flexible perovskite solar cells on an ITO-coated poly(ethylene terephthalate) (PET) substrate with an active area of 0.12 cm$^2$ with a PCE of 8.4%. This value was low compared to glass/ITO-based devices (9.9%), wherein the scaffold was prepared by thermal annealing at 450 °C.

After developing the most efficient compact layer/scaffold combination at the cell level, they subsequently scaled up the process over large areas for the fabrication of a flexible photovoltaic module consisting of four series-connected cells on a 5.6 × 5.6 cm PET/ITO substrate, which is shown in Fig. 4. For this, they used a screen printable mesoporous scaffold and patterning procedures compatible with the delicate PET/ITO substrates. The prepared module exhibited a PCE of 3.1%, with a fill factor of 71%, an open circuit voltage ($V_{oc}$) of 3.4 V, and a short circuit current density ($J_{sc}$) of 5.2 mA cm$^{-2}$. The obtained device showed good mechanical resistance to the bending test and maintained its initial PCE after a sequence of 100 bending cycles at large radii of curvature. At smaller radii (<5 mm), the PCE significantly decreased because of the increased sheet resistance, which might be due to the formation of cracks in the brittle ITO. These in turn could damage the active layers over the ITO, leading to a lower PCE.

In another report, Kim et al. fabricated highly bendable (up to 1 mm bending radius) mixed-halide perovskite (CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$) solar cells based on polyethylene naphthalate (PEN)-deposited ITO flexible substrates with an excellent PCE of 12.2%. This is the highest PCE reported to date in flexible perovskite solar cells. Herein, a ~20 nm-thick amorphous TiO$_2$ compact layer was deposited on PEN/ITO substrate via a plasma enhanced-ALD (PEALD) technique. They observed a high photocurrent density of more than 20 mA cm$^{-2}$, which was responsible for the high PCE and attributed to the superior recombination-blocking and electron-transport properties of the PEALD-TiO$_2$ layer. A cross-sectional scanning electron microscopy (SEM) image with an image of the device is shown in Fig. 5(a and b). As shown in Fig. 6, this solar cell shows superior mechanical endurance properties, i.e., its energy conversion efficiency does not change after 1000 cycles of bending tests under conditions of a bending radius of 10 mm, demonstrating that using the ALD technique for the preparation of scaffold nanolayers at low temperature is a good initiation to produce efficient flexible perovskite solar cells, which can potentially be used for a power solution for future wearable devices.

5. ZnO-based flexible perovskite solar cells

ZnO is a feasible alternative to TiO$_2$/Al$_2$O$_3$ due to its comparable energy levels as well as good electron-transport properties. In addition, a ZnO nanoparticle layer can be deposited easily by spin-coating and requires no heating or sintering step, which makes it ideal for deposition on thermally sensitive substrates. Based on this, Kumar et al. synthesized flexible and low-temperature (≤ 100 °C) solid-state perovskite CH$_3$NH$_3$PbI$_3$ solar cells with a PCE of 8.90% on FTO-based glass substrates and a PCE of 2.62% on flexible PET/ITO-based substrates. They used
enhanced PbI₂ loading, when compared to the planar ZnO films. SEM studies demonstrated that ZnO nanorods with a diameter of 100–150 nm and lengths between 400 and 500 nm showed a homogeneous structure when it was converted into perovskite. The bigger-sized perovskite islands have poor loading of perovskite in the ZnO substrate compared to the nanorod sample. In general, bigger-sized perovskite islands have poor loading of perovskite in the ZnO compact layer on FTO, (e) cross-sectional view of perovskite islands on the ZnO compact layer, (f) cross-sectional view of the complete ZnO nanorod device; FTO (blue), ZnO BL (red), ZnO nanorod + perovskite (purple), spiro (light green), gold (yellow) (Kumar et al. in ref. 95).

Table 1 Photovoltaic parameters of devices with FTO-planar/nanorod architectures and with PET/ITO-planar/nanorod architectures

<table>
<thead>
<tr>
<th>Device</th>
<th>J_{sc} (mA cm⁻²)</th>
<th>V_{oc} (V)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTO-planar</td>
<td>11.27</td>
<td>1.08</td>
<td>45.44</td>
<td>5.54</td>
</tr>
<tr>
<td>FTO-nanorod</td>
<td>16.98</td>
<td>1.02</td>
<td>51.11</td>
<td>8.90</td>
</tr>
<tr>
<td>PET/ITO-planar</td>
<td>5.57</td>
<td>0.99</td>
<td>39.58</td>
<td>2.18</td>
</tr>
<tr>
<td>PET/ITO-nanorod</td>
<td>7.52</td>
<td>0.80</td>
<td>43.14</td>
<td>2.62</td>
</tr>
</tbody>
</table>

η = 8.90%) demonstrated a higher conversion efficiency than the planar device (J_{sc} = 11.27 mA cm⁻², V_{oc} = 1.08 V, FF = 45.44%, η = 5.54%) on FTO. The less irregular perovskite overlayer found in the nanorod sample allowed the formation of a thinner spiro-OMeTAD layer, which in turn increases the fill factors. Such an improvement in the nanorod device compared to the planar device was also observed for the PET/ITO substrates. The complete PV parameters of both devices are shown in Table 1. In this study, the ZnO nanorod morphology facilitates more charge collection and increased perovskite loading with the homogenous perovskite layer, which in turn improves the PCE compared to the planar ZnO device.

Kelly et al.⁹⁶ also used ZnO as the ETL for CH₃NH₃PbI₃-based solar cells and achieved a PCE as high as 15.7% on rigid substrates and above 10% on flexible substrates under AM 1.5G illumination. They prepared different ETLs with varied thicknesses from 0 to 70 nm to probe the effect of the ZnO layer thickness on the device performance. As can be seen from the data (Table 2), without a ZnO layer, the device produced very low FF and V_{oc} due to the increased charge recombination at the ITO surface and a correspondingly low shunt resistance. Incorporating even a very thin (10 nm) ZnO layer into the device substantially improved both V_{oc} and FF, and for a ZnO thickness of 25 nm, PCEs in excess of 14% were obtained. Further increasing the thickness of the ZnO layer did not result in any improvements in device performance (Table 2). An optimized ZnO thickness of 25 nm was considered for the fabrication of flexible devices. The bending tests of a flexible device are shown in Fig. 9 and demonstrate that the device performs well even after bending repeatedly to lower radii of curvature. The device performance is decreased by 15% compared to the original one, when it was bent to the radius of curvature to such a point where the ITO/PET substrate could no longer recover its original shape.

Table 2 Device parameters for solar cells prepared with varying thicknesses of ZnO

<table>
<thead>
<tr>
<th>No. of layers</th>
<th>ZnO thickness (nm)</th>
<th>J_{sc} (mA cm⁻²)</th>
<th>V_{oc} (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>16.5</td>
<td>0.46</td>
<td>31.7</td>
<td>2.4</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>18.0</td>
<td>0.99</td>
<td>62.4</td>
<td>11.1</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>20.5</td>
<td>1.01</td>
<td>69.6</td>
<td>14.4</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>18.9</td>
<td>1.01</td>
<td>70.0</td>
<td>13.3</td>
</tr>
<tr>
<td>4</td>
<td>70</td>
<td>18.4</td>
<td>1.01</td>
<td>69.5</td>
<td>12.9</td>
</tr>
</tbody>
</table>

6. Metal-oxide-free flexible perovskite solar cells

The metal-oxide-free low-temperature (≤100 °C) solution processing of organic–inorganic solid-state perovskite solar cells...
provides a new route to synthesize flexible large-scale and roll-to-roll hybrid solar cells. In addition to metal oxides, one of the fullerene derivatives, phenyl-C61-butyric acid methyl ester (PCBM), has attracted more interest as an n-type material for use in solar cells and has already been utilized in the P–I–N architecture.97–104 PCBM layers deposited on perovskites can effectively passivate the charge trap states and eliminate the notorious photocurrent hysteresis, which produces enhanced PCEs. In this perspective, Carmona et al. reported a perovskite solar cell based on a flexible PET substrate coated with a transparent silver electrode, PEDOT:PSS as HTM, and PCBM as the electron-transport layer (ETL) with a gold top electrode.105 The cross-sectional SEM image with an image of this device is shown in Fig. 10.

The J–V characteristics of a typical small area (0.12 cm²) flexible perovskite solar cell measured under light intensities of 100 mW cm⁻² showed $J_{sc}$, $V_{oc}$ and FF of 14.3 mA cm⁻², 1.04 V and 0.47, respectively, leading to a PCE of 7%. Previously, Malinkiewicz et al. reported values on glass substrates with $J_{sc}$, $V_{oc}$ and FF of 16.1 mA cm⁻², 1.05 V and 0.67, respectively, leading to a PCE of 12%.100 Hence, the main difference between the devices on the glass substrates and on the flexible foils is the lower FF, which causes a strong reduction in the PCE. The reduction in FF and PCE is due to the thicker hole and electron blocking layers in the flexible cells. This can be avoided when a larger substrate is used in either a batch or roll-to-roll process. Moreover, this solar cell is very strong, leading to a slight decrease in PCE of only 0.1% after 50 bending cycles.

An inverted flexible perovskite solar cell with PEDOT:PSS as a hole selective contact and a PCBM layer as the n-type contact was developed by Docampo et al.,99 and its device architecture is shown in Fig. 11. To examine the performance of the inverted architecture, they designed regular as well as inverted perovskite devices in FTO/glass substrates. The inverted architecture achieved a $J_{sc}$ of 16 mA cm⁻², a $V_{oc}$ of 0.9 V, and a PCE of 9.8%, which closely match with initial reports with devices based on the standard architecture.8,106,107 A key difference between these two device architectures is the annealing of the TiO₂ layer at 500 °C in the regular devices. In order to check whether this could affect device performance, they fabricated regular ones with non-sintered compact TiO₂ layers, and the same significant reduction in all photovoltaic performance parameters, especially FF, was noted. This led to the conclusion that the inverted perovskite solar cell architecture should be capable of attaining the same efficiencies as the best performing regular devices once a suitably effective TiO₂ or air-stable n-type collection layer is employed.

In the case of inverted flexible devices based on ITO-covered PET substrates, they exhibited a $J_{sc}$ of over 14 mA cm⁻², a $V_{oc}$ of 0.9 V and PCE of over 6.3%. The main difference between devices fabricated on an ITO- or FTO-covered substrate is the lower FF and current of the ITO devices. This may arise from the poor perovskite film formation and lower surface coverage upon the PEDOT:PSS-coated ITO as opposed to the PEDOT:PSS-coated FTO. The main difference between FTO and ITO is the surface roughness, with the latter being much smoother. Therefore, roughness of FTO is an important factor in enabling a more uniform perovskite coating and resulting in a better PCE of the inverted perovskite solar cells.

In another study, You et al.101 designed an inverted flexible perovskite solar cell using PCBM as the ETL. They chose a mixed-halide perovskite (CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$) due to its long carrier lifetime and good electrical properties. All the layers of the device are solution-processed under 120 °C. Based on the proposed device structure, a PCE of 11.5% was obtained on a glass/ITO substrate, and a 9.2% PCE was achieved for a PET/ITO flexible substrate. Schematic of the device structure and a cross-sectional SEM image are shown in Fig. 12. They measured the photoluminescence (PL) and time-resolved photoluminescence (TRPL) in order to observe the charge generation in the perovskite photovoltaic cells. The PL data showed that a significant quenching effect occurs when the perovskite layer establishes contact with either the PEDOT:PSS or the PCBM layer.
The PCBM-coated perovskite film shows a completely quenched PL, and the PEDOT:PSS-based sample exhibits roughly 10% PL, indicating that charge generation is possible at both interfaces with the carrier generation at the perovskite/PEDOT:PSS interface slightly less than at the perovskite/PCBM interface.

To further confirm these charge transport processes, they performed a TRPL measurement and observed a PL lifetime as high as 200.1 ns, which is consistent with previous reports. This long lifetime is essential for longer exciton/carrier diffusion lengths, which are necessary to allow large film thicknesses for light harvesting. When the perovskite film forms a contact with PEDOT:PSS or PCBM, it was observed that the PL lifetime is reduced significantly; for instance, for the PEDOT:PSS case, the lifetime decreases to 50 ns, and when coating the PCBM layer on the perovskite layer, the carrier lifetime further drops to 25.4 ns, indicating that charge transfer from perovskite to PCBM could be faster than that for the PEDOT:PSS. Considering the strong quenching effect of PEDOT:PSS and PCBM to the PL emission from the perovskite layer, the PL lifetime of the PEDOT:PSS/perovskite layer/PCBM further decreases to 18 ns. This strong PL quenching happens with fast charge transfer at the interface, which may be the mechanism for charge separation and collection in these devices. The PV performance of the flexible device showed an efficiency of 9.2% with a Voc of 0.86 V, Jsc of 16.5 mA cm⁻², and FF of 64%, thereby retaining 80% of the rigid device performance. The mechanical bending tests show that the device maintains its performance through mechanical bending up to twenty times.

To date, all researchers have reported that the perovskite solar cells on flexible substrates exhibit lower PCEs compared to that on glass substrates. This may be due to charge recombination at imperfect interfaces and due to structural or chemical defects in the flexible perovskite films. However, recently, Chiang et al. studied planar perovskite–fullerene heterojunction solar cells on both glass/ITO and PET/ITO substrates, and they observed a higher PCE of 4.34% in a PET/ITO-based device compared to 3.10% with a glass/ITO. They assumed that the main difference in the two materials was the energy level of the work function. Through UV photo electron spectroscopic measurements, the work functions of the glass/ITO and PET/ITO were found to be 4.8 eV and 5.2 eV, respectively. From this study, it was found that PET/ITO has a higher work function of 0.4 eV than glass/ITO, which results in a closer alignment between the photovoltaic active layer and the contact material and reduces the energy loss from the hole transfer between the HOMO level of perovskite and the Fermi level of PET/ITO. Consequently, this promotes an increased Voc in the PET/ITO device, which in turn improves the PCE value.

In general, there are more reports on inverted (P–I–N) perovskite–C₆₀ heterojunction solar cells. However, in N–I–P architectures, using C₆₀/PCBM as the ETL is not very common due to the lack of acceptable processes for deposition of a uniform and dense perovskite layer on PCBM or C₆₀. Furthermore, the performance of P–I–N solar cells employing PEDOT:PSS and PCBM as the HTM and ETL is still low compared to N–I–P devices employing compact TiO₂ and ZnO layers. Moreover, the acidic and hygroscopic nature of PEDOT:PSS has a negative impact on the long-term stability. Therefore, positioning PCBM as a single ETL in front of the perovskite layers, i.e., the N–I–P architecture, is important for the fabrication of efficient and stable perovskite solar cells. Therefore, to apply a uniform and dense layer of perovskite on PCBM, Ryu et al. used a modified solvent engineering process, employing a diethyl ether drip as an orthogonal solvent to enable the fabrication of a multi-layered device comprising FTO/polyethyleneimine (PEI)/PCBM/MAPbI₃/poly(triaryl amine)(PTA)/Au at low temperature (<100 °C). Herein, PEI acts as an interfacial material that can modify the work function of the FTO or ITO cathode due to the strong electrostatic self-assembled dipoles, and it facilitates electron extraction into the electrode via fullerene derivatives. Optimization of the thickness of the PCBM layer yielded a steady-state efficiency of 13.9% under AM 1.5G 100 mW cm⁻² illumination on a glass substrate and 11.1% on a flexible substrate.

To optimize the PCBM layer thickness, four devices with varied PCBM layer thicknesses (45, 55, 80, and 100 nm) were fabricated, keeping the other conditions constant. The PCE increased from 9.8% to 14.4% with the decreasing thickness of the PCBM layer. The Jsc, Voc, and FF also followed the same trend. This can probably be attributed to increased recombination when the dissociated electrons are extracted towards the FTO/PEI electrode over the longer distance in the thick PCBM layer. A 55 nm thickness PCBM layer was further optimized to achieve a PCE of 15.3% with a Jsc of 21.8 mA cm⁻², a Voc of 0.98 V, and an FF of 72%, as shown in Fig. 13a. To provide more justified results on the role of single-layered PCBM as the ETL, the authors introduced a double ETL of low-temperature-fabricated TiO₂ and PCBM instead of a single PCBM layer. A PCE of 15.2% was achieved for the double ETL device, which is slightly lower than the device employing the single PCBM layer. These comparable efficiencies envisage that the single PCBM layer works well as an ETL in the N–I–P configuration. They extended this configuration to a flexible ITO/polyethylene naphthalate (PEN) substrate and successfully achieved a PCE of 11.1% with a Jsc of 18.7 mA cm⁻², a Voc of 0.99 V, and an FF of 60 (Fig. 13b).
7. Flexible perovskite solar cells with metal substrates

There are many disadvantages of applying ITO or FTO on flexible substrates such as degradation of the device performance due to crack formation in the ITO/FTO layer upon bending the device, chemical instability under acidic or basic conditions, and high cost of indium. Therefore, devices with ITO electrodes are unsuitable for providing a cost-effective and flexible system. Metal substrates can be a viable alternative to ITO-PET substrates, offering advantages such as high-temperature control without the use of expensive ITO. However, the opaque nature of metal substrates hinders the light absorption from the photoanode, so the device will not work using a conventional metallic counter-electrode and therefore a transparent counter-electrode is required. Recently, Lee et al. used titanium (Ti) foil of 127 \( \mu \text{m} \) thickness with an ultra-thin metal film (UTMF) of silver as the top semi-transparent electrode. A regular fabrication procedure was applied for the CH\(_3\)NH\(_3\)PbI\(_3\) film (UTMF) of silver as the top semi-transparent electrode. A stainless steel fiber of diameter 127 \( \mu \text{m} \) was used as the collecting electrode, the highest efficiency of 6.15% was achieved. Further increasing the thickness could not improve the efficiency of the solar cells. Evidently, it was observed that the thickness of the Ag layer controls the number of photons penetrating into the active layer and the collecting charge ability, which consecutively improves the PCE.

To highlight the significance of the Ti substrate, the authors measured the \( I-V \) curves with and without the Ti substrate for the devices. The solar cells with Ti substrate at the back showed a slightly higher \( J_{sc} \) (9.8 mA cm\(^{-2}\)) compared to the device without Ti substrate (9.2 mA cm\(^{-2}\)). This might be due to the increased light harvesting from reflection by the Ti substrate. The extent of flexibility of these solar cells measured at a bending radius of \( \sim 6 \text{ mm} \) was 98.5% of the efficiency from the beginning value, which is excellent compared with ITO-based flexible photovoltaic cells for roll-to-roll processing. There is another report on Ti-foil-based solar cells by Troughton et al., who used Ti foil as a substrate and transparent conductive adhesive (TCA) onto a PET film embedded with Ni grid as a counter electrode to prepare an indium-free flexible perovskite solar cell with a PCE of 10.3%. The TCA counter electrode avoids the ITO coating in favour of the electrodeposited nickel grid, which is cheaper at scale and more mechanically robust in comparison. Schematic of the metal foil cell architecture and the device image are shown in Fig. 14.

In this study, they adopted a new PEDOT:PSS interlayer spray deposited on to the HTM, which plays a critical role in transporting charge from the HTM to the small “islands” of PEDOT:PSS within the TCA. They found the influence of this interlayer dramatically increases the \( J_{sc} \) and FF of the solar cells, which will ultimately increase the efficiency of the device.

A cross-sectional SEM image and schematic of the fiber shaped perovskite solar cell are shown in Fig. 15.
The symmetric coaxial structure facilitated the photovoltaic performance of the optimized device, which remain unchanged with increasing the angle of the incident light from 0 to 180° under the same light intensity. Moreover, these coaxial fiber shaped perovskite solar cells were flexible and can be bent into various shapes without fatigue, and the energy conversion efficiencies remained at 95% after bending for 50 cycles.

Recently, Wang et al. demonstrated flexible perovskite solar cells with TiO$_2$ nanotubes coated on to Ti foil with a transparent carbon nanotube electrode, yielding an efficiency of 8.31%. Highly-ordered TiO$_2$ nanotube arrays were prepared by electrochemical anodization at 20 V for 10 min at room temperature (~20 °C) and the perovskite absorber was sequentially deposited on TiO$_2$ nanotube arrays. Furthermore, CNT films prepared by the chemical vapour deposition method were coated on the perovskite absorber, which acts as a hole collector and transparent electrode. For better hole collection, the hole transport material spiro-OMeTAD was infiltrated in to the CNTs network. Schematic of the device architecture is shown in Fig. 16.

To observe the influence of foil thickness on the device flexibility, two types of Ti foils were used during cell fabrication (125 μm and 25 μm). For both thick and thin Ti-foil-based perovskite devices, TiCl$_4$ treatment was employed to improve the photovoltaic performance. TiCl$_4$ can fill the voids and cracks in the TiO$_2$ blocking layer and therefore decrease recombination in solar cells. Solar cells fabricated on 25 μm Ti foil exhibited a higher photovoltage (0.83 V vs. 0.70 V for non-TiCl$_4$-treated tubes; 0.99 V vs. 0.78 V for TiCl$_4$-treated tubes) and improved fill factor (0.63 vs. 0.62 for non-TiCl$_4$-treated tubes; 0.68 vs. 0.62 for TiCl$_4$-treated tubes) compared to 125 μm Ti-foil-based solar cells. The $V_{oc}$ and fill factor improvement can be attributed to the smaller surface roughness of the thinner Ti foil. This envisages that the smoother Ti surface improves the flatness of

### Table 4: Year-wise efficiency chart of flexible perovskite solar cells

<table>
<thead>
<tr>
<th>Year</th>
<th>Device structure</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>Efficiency (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2013</td>
<td>14.4</td>
<td>0.88</td>
<td>0.51</td>
<td>6.40</td>
<td>95</td>
<td>Docampo$^99$</td>
</tr>
<tr>
<td>2014</td>
<td>14.30</td>
<td>1.04</td>
<td>0.47</td>
<td>7.00</td>
<td>Carmona$^{105}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14.10</td>
<td>0.85</td>
<td>0.70</td>
<td>8.40</td>
<td>Giacomo$^89$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.20</td>
<td>0.66</td>
<td>0.48</td>
<td>3.30</td>
<td>Qiu$^{124}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.93</td>
<td>0.92</td>
<td>0.61</td>
<td>4.54</td>
<td>Chiang$^{109}$</td>
<td></td>
</tr>
<tr>
<td>2014</td>
<td>14.36</td>
<td>0.99</td>
<td>0.68</td>
<td>8.30</td>
<td>Wang$^{128}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16.5</td>
<td>0.86</td>
<td>0.64</td>
<td>9.20</td>
<td>You$^{101}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.40</td>
<td>1.03</td>
<td>0.73</td>
<td>10.20</td>
<td>Liu$^{96}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>21.40</td>
<td>0.95</td>
<td>0.60</td>
<td>12.20</td>
<td>Kim$^{91}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.50</td>
<td>0.88</td>
<td>0.73</td>
<td>6.15</td>
<td>Lee$^{121}$</td>
<td></td>
</tr>
</tbody>
</table>
the perovskite layer and reduces the unfavourable series resistance. Thus, the thin 25 μm Ti-foil-based perovskite solar cell obtained the best PCE of 8.31%. The device also showed good performance after 100 mechanical bending cycles, indicating its excellent flexibility.

Although we have discussed about the recent progress in flexible perovskite solar cells, in Table 4 we list the annual efficiencies achieved with device architectures, for readers’ convenience.

8. Conclusions and future perspectives

This article has reviewed recent progress in the fabrication of flexible perovskite solar cells from different approaches, including the low-temperature synthesis of TiO2 by the ALD technique, using ZnO as the ETL, the metal-oxide-free approach with C60/PCBM as the ETL, and using flexible metal substrates. We observed high efficiencies (up to 12.2%) in the case of metal-oxide-based solar cells with good device performance over mechanical bending, even at a low bending radius of <1 mm as compared to metal-oxide-free devices. However, we noticed that the use of C60/PCBM as the ETL instead of TiO2 predominantly eliminates the notorious photocurrent hysteresis and produces a PCE as high as 11.1%. Further improvements in efficiency could be achieved by fine-tuning the perovskite layer morphology by adopting slow growth and using additives. Flexible metal-substrate-based devices also showed better efficiencies of up to 8.3%, and can permit high-temperature processes, for more effective charge collection.

As of now, large commercial silicon modules convert 17–25% of solar radiation into electricity, while much smaller perovskite cells in the lab scale have already reached a PCE as high as 20.1% on rigid substrates and 12.2% on flexible substrates. Fabrication costs are also low compared to the silicon modules. Therefore, fabrication of these cells on a large scale with good efficiency is emerging and will expand the solar energy market throughout the world.

Long-term stability is the major issue in perovskite solar cells and restricts their outdoor photovoltaic applications. The issues of degradation and the stability of these perovskites should be urgently addressed to achieve good reproducibility and a long lifetime with high conversion efficiency. Without studying the stability, one cannot transfer these exciting achievements from the laboratory to industry and to outdoor applications. Selecting a suitable flexible substrate also plays a major role in fabricating different shaped flexible devices and also to resist the mechanical bending up to extreme bending limits. Hence, extensive research is required in terms of the PCE, long-term stability, and flexibility of these devices to compete with other flexible devices to fabricate low-cost and large-area solar panels for upcoming solar energy applications.

Acknowledgements

Authors are thankful to the CSIR/TAPSUN for financial support. We also gratefully acknowledge DST-UK (APEX) for their support. Authors show their gratitude to all the researchers who contributed to the work cited in this article.

Notes and references