

REVIEW

View Article Online

View Journal | View Issue

Cite this: *Mater. Chem. Front.*,
2021, 5, 7467

Strategies of perovskite mechanical stability for flexible photovoltaics

Yi-Ran Shi,^{†a} Chun-Hao Chen,^{†a} Yan-Hui Lou^{*b} and Zhao-Kui Wang^{id} ^{*ac}

The market's increasing demand for portable electronic products has made the research in flexible devices very attractive. Flexible solar cells are one of the most eye-catching devices in the field of flexible photovoltaic devices. And the perovskite material has become a powerful candidate material for manufacturing flexible solar cells due to its excellent optical properties, low price and the ability to tolerate more stress accumulation. However, as an active layer, the perovskite film still faces the issue that cracks are easily generated when bending and encountering temperature changes for the limited flexibility. There are many factors that affect the mechanical stability of the perovskite layer: the characteristics of the material itself, the influence of the other layers in the device and the presence or absence of a protective layer. This work reviews some reported strategies of improving the perovskite bending durability, classifies them according to the influencing factors mentioned above, and describes them in detail respectively.

Received 25th April 2021,
Accepted 26th August 2021

DOI: 10.1039/d1qm00616a

rsc.li/frontiers-materials

1 Introduction

Flexible photovoltaic devices are considered as the main development direction of the photovoltaic industry in the future. Due to the demands for wearable and portable devices, and the existence of some special requirements in special industries such as the aviation industry, flexible devices have attracted great attention.^{1–3} Materials such as silicon, inorganic salts (gallium arsenide, cadmium sulfide, and copper indium selenium), organic substances (phthalocyanine compounds, porphyrin, and crystals) and perovskites have all been used in flexible solar cells.⁴ Among them, the perovskite material is very striking owing to its excellent optoelectric properties and rapid efficiency increase.^{5–10} The power conversion efficiency (PCE) of the most advanced flexible perovskite solar cells (FPSCs) is approaching 20%,^{10,11} which is higher than that of organic and dye-sensitized based flexible devices. Moreover, many studies have shown that perovskite materials can tolerate more strain than silicon materials and other inorganic semiconductor materials.¹² Thus, perovskite materials become a strong candidate material for fabricating flexible solar cells.^{13–15} But

if we want to make flexible perovskite solar cells realize large-scale application from the laboratory to the industry, there are still many non-negligible problems which need to be faced and solved, such as the performance losses with perovskite crystal growth and defects, and the stability of the device in daily production and operation.^{16–25} The stability, which is the issue that needs to be solved most, includes the environmental stability and the mechanical stability.^{26,27} Environmental stability refers to the influence of moisture and oxygen in the working environment, which would make the perovskite degradation faster and easier. Then the performance of the device would get worse when the equipment is working in the air. Mechanical stability mainly refers to the occurrence of cracks on different layers in the device due to the presence of stress, which would be accumulated when bending, applying an external mechanical force and during thermal expansion generated by temperature changes. And the cracks would affect the device performance seriously as well. Many studies on the strategies for improving environmental and mechanical stabilities have been reported.^{28–35} However, the strategies aimed at improving the mechanical stability of the perovskite layer have been relatively rarely reported.

The mechanical stability of the perovskite layer is affected by many factors. Firstly, different perovskites have different mechanical stabilities. For the perovskite material itself, the chemical compositions have great effects on the bending stability. And for polycrystalline perovskites, the grain boundaries between the crystal lattices are the most prone to crack. Secondly, when an external mechanical force exists, stress accumulation would occur between the perovskite layer and the adjacent layer.

^a Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou 215123, China. E-mail: zkwang@suda.edu.cn

^b College of Energy, Soochow Institute for Energy and Materials Innovations, Soochow University, Suzhou 215006, China. E-mail: yhlou@suda.edu.cn

^c Key Laboratory for Organic Electronics and Information Displays, Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications, 9 Wenyuan Road, Nanjing 210023, China

[†] These two authors contribute equally.

Once the stress accumulates to a certain extent, separation between layers and cracks on layers would occur. Furthermore, the selection of electrodes and substrates is also very important. The stretching and expansion of used electrodes and substrates could have an indirect effect on the perovskite layer. Finally, considering the existence of the neutral surface, the introduction of the protective layer is valuable for improving the mechanical stability as well. In this review, we start from the influencing factors aforementioned, classify the existing recorded strategies for improving the mechanical stability of the perovskite layer and make a narrative.

2 Mechanical stability of the perovskite layer

2.1 Compositional engineering

For the perovskite material, the cationic composition, anionic composition and different combinations of anion and cation all will affect its brittleness. Rolston *et al.* have reported that the most commonly studied perovskite-methylammonium lead iodide (MAPbI₃) is unstable when exposed to heat, moisture and light.^{36–38} As a result, the PCE decreases by 0.1% h^{−1} for MAPbI₃ based perovskite solar cells (PSCs),^{39,40} which is several orders of magnitude higher than that of organic photovoltaics (OPVs, 10^{−3}% h^{−1})⁴¹ and other solar technologies such as c-Si and cadmium indium gallium selenide (CIGS) (<10^{−5}% h^{−1}) as shown in Fig. 1a.^{42,43} So, it is necessary for PSCs to substantially improve the reliability and stability. When measuring the mechanical stability of the perovskite film, the cohesion energy (G_c) is an important factor for device robustness, which

is related to the reliability of the processing through a series of device technologies.^{44–48} Fig. 1b shows the measured average G_c and PCE values corresponding to different cation compositions, showing a balance between reliability and efficiency. Perovskite is a kind of brittle material whose G_c of the single-crystal was found to be 1.05–2.11 J m^{−2} where there are even no grain boundaries.⁴⁴ Smaller grain sizes lead to lower G_c values for double and triple-cation perovskites compared to purely MA-based films because of the increased number of grain boundaries.^{44,49} Also, although an excess of PbI₂ doped in perovskite films can improve the PCE of the device,^{50–56} the smaller grains bring about lower G_c leading to the worse mechanical stability. Triple-cation perovskite compositions incorporating both FA and Cs simultaneously into the MA perovskite resulted in a breakthrough for device reproducibility and efficiency, leading to cells with the best PCE for the cation composition Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}. However, this composition resulted in the lowest G_c among all measured cation configurations at just 0.25 ± 0.07 J m^{−2}, which was almost identical to that of pure PbI₂. To enhance the G_c of the perovskite, *n*-butylammonium (BA) was used to provide structural support for the perovskite whose G_c was greatly improved to 3.06 ± 0.27 J m^{−2}.

For an ABX₃ type organic–inorganic hybrid halide perovskite, the different components of three sites will affect the bending and mechanical stability of perovskite films to a large extent, where A for K, Rb, Cs, CH(NH₂)₂⁺ (FA) and CH₃NH₃⁺ (MA); B for Sn and Pb; X for Cl, Br and I.^{57–62} Cao *et al.* attempted to fabricate a kind of KRBsMAFA-based quintuple-cation perovskite film in FPSCs as shown in Fig. 1c,⁶³ where Cs⁺, MA⁺ and FA⁺ cations were used to maintain the high-quality mixed

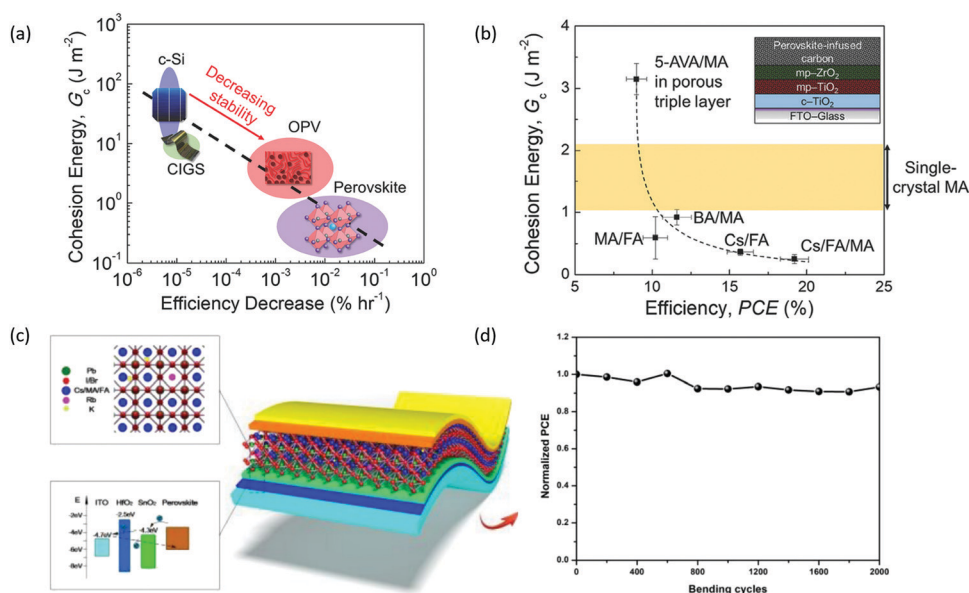


Fig. 1 (a) The measured cohesion (G_c) and degradation rate of different solar cell active materials. Ref. 43. Copyright 2017 Wiley-VCH. (b) The average G_c and PCE values of different cation compositions, showing a trade-off between reliability and efficiency. Ref. 43. Copyright 2017 Wiley-VCH. (c) Schematic diagram of the Rb₁K₄CsFAMA-based flexible device and the corresponding energy diagram. Ref. 63. Copyright 2019 The Royal Society of Chemistry. (d) Normalized PCE of the Rb₁K₄CsFAMA-based flexible device varying with bending cycles with a curvature radius of 10 mm. Ref. 63. Copyright 2019 The Royal Society of Chemistry.

cation perovskite films for better thermal properties and good phase stability. Rb^+ cations were used to minimize the defects by tuning the crystal structure.⁵⁸ And K^+ cations can reduce the number of Frenkel defects of iodine by entering the interstitial sites of the perovskite.⁶² Using this strategy, a champion flexible device presented a PCE as high as 19.11%. Moreover, the flexible device showed good bending resistance which can be seen in Fig. 1d. The device could retain 93% of its original PCE after 2000 bending cycles with a curvature radius of 10 mm.

The Young's modulus is an important index for measuring the mechanical stability of materials. Therefore, it is necessary to conduct an experimental study of the mechanical properties of the organic-inorganic halide perovskites measured using the Young's modulus.^{64–67} Sun *et al.* summarized the Young's moduli and hardness values of the methylammonium lead halide crystals to investigate their mechanical stability as a function of halide in perovskites.⁶⁸ The overall results demonstrated that the elastic moduli of $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{I}, \text{Br}$ and Cl) single crystals varied from 10 to 20 GPa, and a general trend of $E_{\text{Cl}} > E_{\text{Br}} > E_{\text{I}}$ was observed. Feng *et al.* calculated and summarized the Young's modulus, and the Debye temperature of MABX_3 ($\text{B} = \text{Sn}, \text{Pb}$; $\text{X} = \text{Br}, \text{I}$) perovskites.⁶⁹ It can be seen that for tetragonal crystals, the Sn-based perovskite shows a higher value of the Young's modulus than the Pb-based perovskite, implying that the Sn-based perovskite film possesses better stability in mechanical ductility. Also, the Br-based perovskite is better than that of I-based perovskite. In addition, the Debye temperature represents the strength of the average chemical bond of Sn–Br, Sn–I, Pb–Br, and Pb–I, which presents the same trend as the Young's modulus. In summary, the elastic properties are dependent on the compositional element of B^{2+} and X^- ions.

2.2 Grain boundary crosslinking engineering

In addition to the brittleness of the perovskite itself aforementioned, for polycrystalline perovskite crystals, the grain boundaries (GBs) are the places where cracks are most likely to occur when pressed or stretched by an external force.^{70,71} Therefore, adding a stress buffer crosslinking agent at the GBs of the perovskite layer is a highly feasible strategy. Huang *et al.* attempted to incorporate the elastomer polyurethane (PU) into a perovskite film to improve the bendability.⁷² The elastomer PU additive crosslinks the GBs between adjacent perovskite crystals to form a PU network which can effectively improve the bending properties of perovskite films as shown in Fig. 2a. There is almost no damage to the film after mechanical bending for 200 times. The PVSCs fabricated by incorporating PU into the perovskite precursor offer an impressive PCE of 18.7% with almost no photocurrent hysteresis and excellent stability in ambient air. This strategy is of great significance for realizing the flexibility and wearability of perovskite solar cells. Hu *et al.* employed a similar approach that sulfonated graphene oxide (s-GO) was employed to construct cementitious GBs.⁷³ The resulting s-GO- $[\text{PbI}_6]^{4-}$ complex can effectively improve the waterproofness and flexibility of the perovskite film owing to the tough and water-insoluble GBs. In the bending process

(Fig. 2b), s-GO can toughen GBs to release stress and improve ductility and resistant moisture at the same time. The champion PCE of the 1.01 cm^2 flexible devices has reached 20.56% with reduced hysteresis. Moreover, the devices with s-GO exhibit excellent flexibility, retaining about 88% efficiency even when the bending angle reaches 70° . The strategy of ultraviolet radiation promoting polymer cross-linking of the GBs of the perovskite layer was also used by Li *et al.* to improve the mechanical stability of FPSCs. Ultraviolet radiation could induce the crosslinking of [6,6]-phenylC₆₁-butyric oxetane dendron ester (C-PCBOD) molecules *via* ring opening polymerization of the cationic oxetane.⁷⁴ The stretching or bending of the perovskite film on a flexible substrate makes the crevices between GBs larger and the crystal structure distorted. It can be seen from Fig. 2c that as C-PCBOD fills the space between the GBs, the organic network around the perovskite grains is formed, and the crystalline perovskite films turn uniform and dense. The results showed that C-PCBOD could passivate the GBs, reduce the formation of trap states and enhance the environmental stability of MAPbI₃, achieving the record device PCE of 18.1% on a flexible substrate. It is well known that the infiltration of moisture has a great influence on the perovskite film. In order to deeply explore the effect of moisture on the mechanical stability of FPSCs, Du *et al.* boldly attempted to add water into perovskite films of flexible devices.⁷⁵ In this work, they used H_2O additive doped in perovskite precursor solution to optimize $\text{MAPbI}_{3-x}\text{Cl}_x$ in the spin coating process. The results show that H_2O assisted perovskite phase deposition has an important effect on the transformation pathway by affecting the combined GBs of the pre-deposited films and delaying the recrystallization rate of the mesophase as shown in Fig. 2d. The results show that the device maintains more than 90% of its original efficiency after the maximum bending deformation. At a higher degree of curvature (20 mm bending curvature), it will not crack and shut down the cell performance. In addition, when F-PSCs are bent more than 50 times, their efficiency can still reach a comparable value while maintaining more than 85% of their original efficiency. All these findings indicate that the F-PSC based on H_2O -treatment exhibits excellent stability. In summary, the additive engineering for GBs crosslinking is highly feasible to improve the bendability and torsion resistance of FPSCs.

3 Interface engineering

From the upper section, we know that the perovskite material is brittle. Continuous bending will accumulate the stress between the brittle perovskite and the near layer, which makes the perovskite film crack and break easily. Between different layers, the microcracks and delamination would also emerge when bending. Researchers, referring to the “vertebrae” structure of the human body,^{76–78} simulated the articular cartilage and built a bionic structure in PSCs. They introduced a “soft substance” into the connection of the interface or developed a “softer” material as the transporting layer in place of the original layer. The device had the “articular cartilage” – the introduced

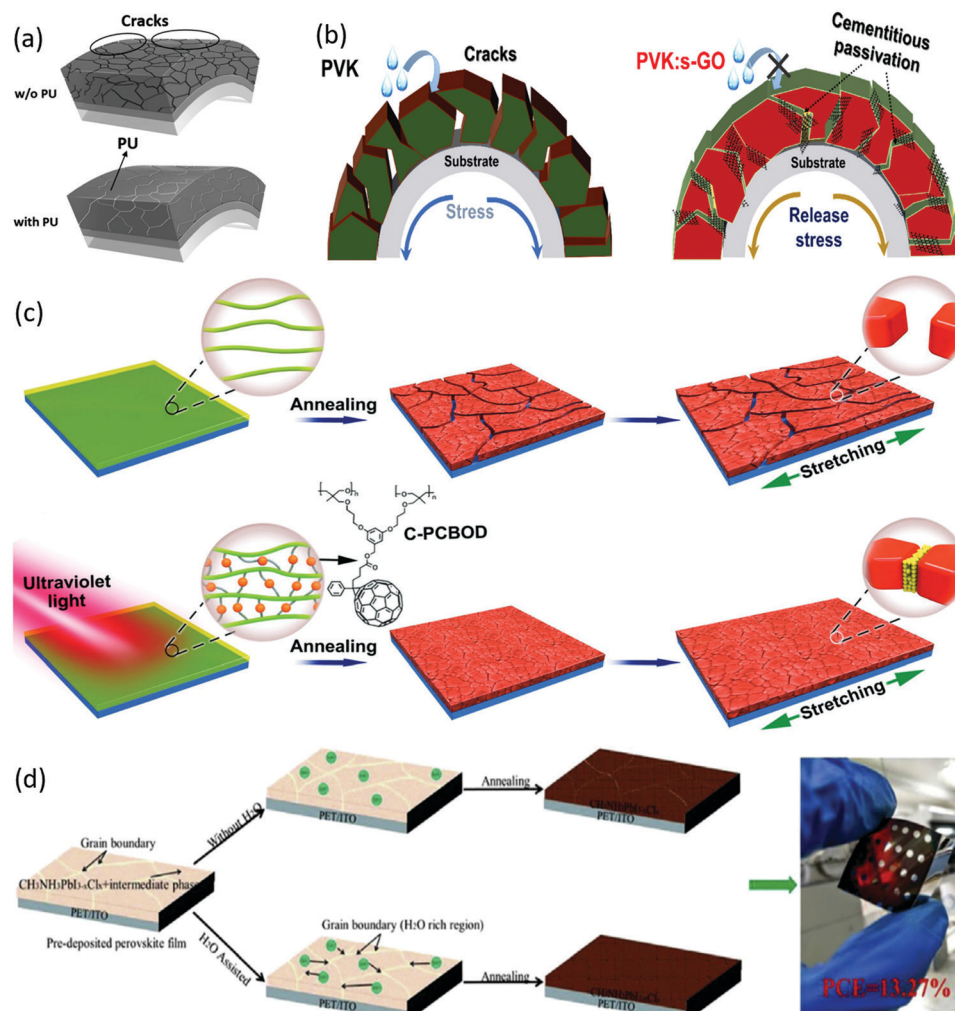


Fig. 2 (a) Schematic illustration of the PU additive in the perovskite layer upon sustainable bending. Ref. 72. Copyright 2017 Wiley-VCH. (b) Schematic diagram of the moisture degradation and fragile nature of the control perovskite, and the enhanced water resistance with flexural endurance due to cementation and passivation of the GBs. Ref. 73. Copyright 2020 Science China Press. (c) Operational mechanism of C-PCBOD in the perovskite GBs. Ref. 74. Copyright 2019 Wiley-VCH. (d) Schematic illustration of the different morphology development for CH₃NH₃PbI_{3-x}Cl_x films with and without H₂O additive. Ref. 75. Copyright 2017 American Chemical Society.

interlayer, which serves as the mechanical buffer layer to protect the film from stress damage. The working mechanism of this type of engineering is subtly different from the one in the upper chapter. The increased flexibility of the device is achieved through formation of the chemical bonding between both layers instead of making mechanical interlocks between the perovskite crystals.

3.1 Replacement of adjacent layer

Meng *et al.* applied a polymer, PEDOT:EVA (poly(3,4-ethylenedioxythiophene):poly(ethylene-co-vinyl acetate)), between ITO and the perovskite layer (Fig. 3a).⁷⁹ Due to the conductive properties, this polymer was used as the hole-transporting layer (HTL). The PEDOT:EVA is a glued polymer; its adhesiveness property could make the mechanical force distributed evenly and the pressure surface enlarged. As a result, the pressure did not reduce accordingly although the amount of force applied to the perovskite layer didn't change. The PEDOT:EVA layer absorbs and

releases the stress efficiently like the spinal cartilage. Moreover, the existence of this polymer could precisely control the nucleation position of the perovskite crystal above the PEDOT:EVA layer, and simultaneously realize better orientation growth of the perovskite crystals. This makes the vertical crystallization of the perovskite easy, improving the flexibility by obtaining closer bonding of the ITO and the active layer.

Besides replacing the hole-transporting layer, it is also possible to change the electron-transporting layer (ETL). Kim *et al.* developed dicyanothiophene (P(NDI2DT-TTCN)) as the ETL in the FPSCs (Fig. 3b).⁸⁰ They performed bending tests on two different ETL based solar cells. As shown in Fig. 3c, we can see that different degrees of cracks and fractures appear on the surfaces of two different devices during the same bending cycles. These results demonstrate that the ETL possessing higher mechanical stability is of great help for the flexibility of the solar cells.

In addition, a bilayer hole-transporting layer, PEDOT:PSS/PTAA, was also introduced into the flexible solar cells,⁸¹ which

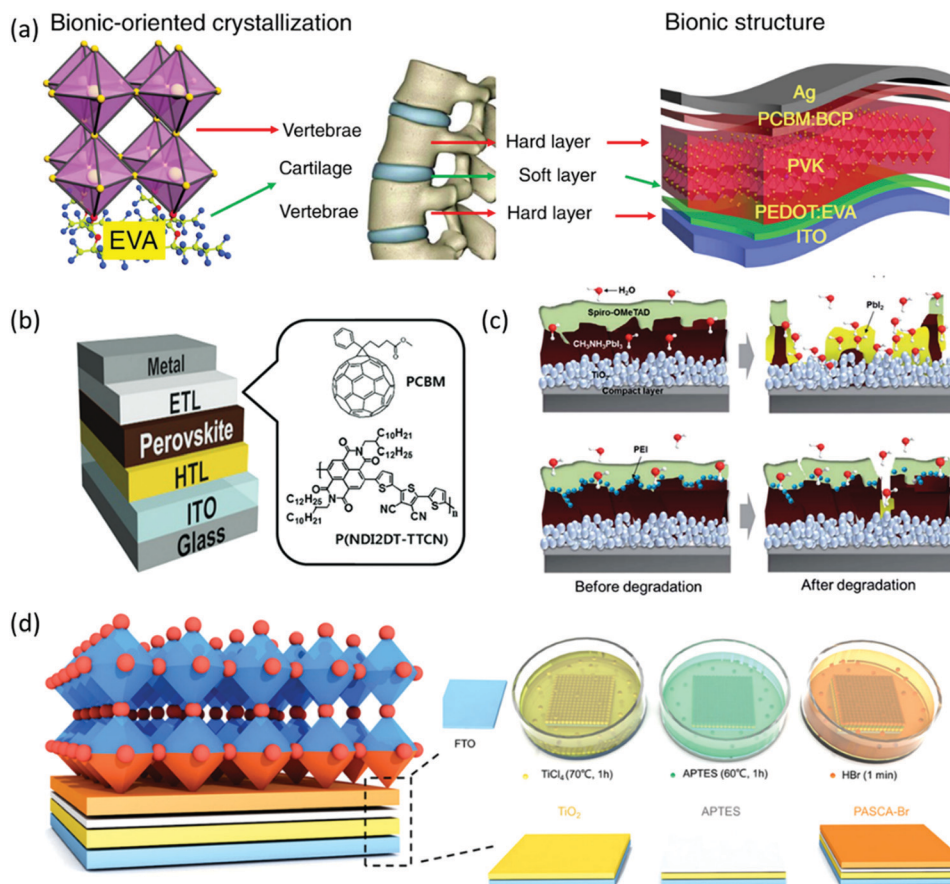


Fig. 3 (a) Biomimetic mechanisms of the vertebrae and PSCs. Ref. 79. Copyright 2020 Springer Nature Limited. (b) Schematic illustration of the p-i-n device architecture based on PCBM and P(NDI2DT-TTCN), respectively. Ref. 80. Copyright 2018 Wiley-VCH. (c) Cartoon depiction of the structural and morphological difference between the solar cell devices without PEI and with PEI upon exposure to 85% humidity. Ref. 83. Copyright 2015 The Royal Society of Chemistry. (d) A schematic of the fabrication process for TiO₂ and PASCA-Br layers. Ref. 82. Copyright 2020 Wiley-VCH.

had a beneficial impact on the mechanical durability of the solar devices *via* lowering of the occurrence of cracks under external mechanical pressure.

3.2 Additional interfacial layer

Apart from directly replacing the material of the transport layer to enhance the bending stability, researchers also found that it is desirable to complete mechanical buffering through the introduction of an intermediate layer between the brittle layer. Zhang *et al.* used PASCA-Br as a connector between TiO₂ and the perovskite layer to tie both of them tightly (Fig. 3d).⁸² The coupling agent (PASCA-Br) is “soft” enough to buffer the stress caused by external mechanical bending and reduce the occurrence of cracks. PASCA-Br is a kind of low-molecular-weight modified organosilicon compound. The PASCA was obtained on TiO₂, because of the condensation reaction during which the covalent bonds would be formed. The R-NH₃Br terminal could passivate the perovskite through targeting for the uncoordinated lead atom. In a word, the PASCA-Br as a molecular interlayer could grasp the TiO₂ and the perovskite simultaneously. This interaction between interfaces is strong enough to release the strain stress and make the rupture harder to happen.

A connector between the upper hole-transport layer (HTL) and the perovskite has been applied as well. Polyethyleneimine (PEI) could play a role of compatibilizer at the perovskite/HTL interface.⁸³ The application of PEI makes the layers adhere strongly to each other (Fig. 3c). PEI is a polymer that can effectively bind Pb due to the existence of amine groups. Moreover, the carbon-based organic polymers like PEI can easily generate intermolecular interactions with spiro-OMeTAD (HTM). Thus, the PEI layer would interact with both the perovskite layer and HTL at the same time to complete a strong adhesion, implying that the device showed a significant increase in mechanical stability. The double cantilever beam (DCB) was used to measure the fracture energies of different samples in this research. The researchers linked the measured data of SEM and EDS with the fracture energy results of different devices, investigated the modification mechanism of PEI, and concluded that the formation of chemical bonds between layers is the way to realize the promoting effect of polyethyleneimine (PEI) compatibilizer.

Aiming at solving the problem of brittleness of the perovskite layer, most researchers have focused on the design engineering of separate interfaces as described above. These additional processing steps may affect the mechanical

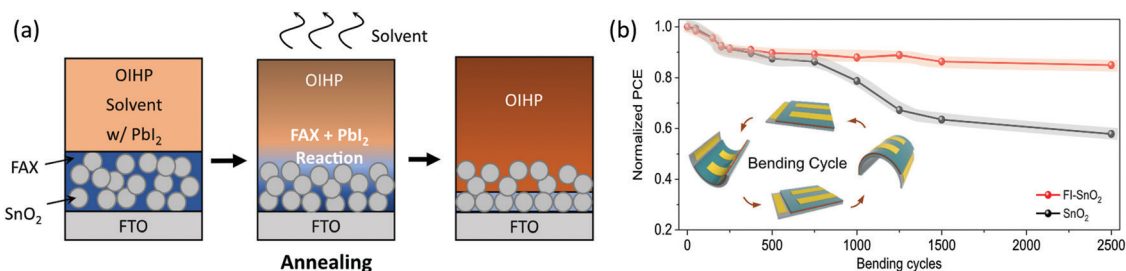


Fig. 4 (a) Schematic illustration showing the formation process of the OIHP/FI-SnO₂ interface by the reaction between the excess PbI₂ in the OIHP layer and the FA halide in the FI-SnO₂ ETL. (b) Durability of FPSC devices based on FI-SnO₂ and pristine SnO₂ ETLs as a function of mechanical bending cycles (40% RH; ambient air; 25 °C; 3 mm minimum *r*); inset illustrates a typical mechanical bending cycle. Ref. 87. Copyright 2021 Springer Nature Limited.

integrity.^{84–86} Thus, holistic design engineering was adopted to get a mechanically robust device interface. Dong *et al.*⁸⁷ mixed the perovskite layer and ETL, and synthesized an interpenetrating interface (Fig. 4a). In device fabrication, they used a SnO₂ ETL containing FAI (FI-SnO₂) and an organic–inorganic halide perovskite layer with excess PbI₂ (OIHP). Then, a reaction between the FA halide and the excess PbI₂ would form the interpenetrating interface. They provided many characterization results to prove that the OIHP/SnO₂ interface contains a mixed intermediate layer. Different bending cycles were applied to the films with and without modification; the pristine film showed a phenomenon of delamination, while the interpenetrating film was still intact and the device still kept a PCE of 85% of the original value (Fig. 4b). Obviously, the characteristics of interpenetrating interface had a positive impact on improving mechanical durability. These research studies opened up more possibilities in interface formation and more approaches to enhance the mechanical tolerance and modify the interfacial brittleness of the perovskite films.

4 Engineering on other functional layers

4.1 Flexible substrate and electrode

In addition to the direct influence of the brittleness of the perovskite itself and its adjacent interface on the mechanical stability of perovskite layers, the substrate and electrode also have an indirect influence on the flexibility, most of which comes from the accumulation of the stress and strain under mechanical power. The expansion coefficient, the thickness, the special structure of the substrate and the selection of electrodes are the main factors which affect the stress accumulation.

An annealing process is necessary in the current mature manufacturing process of perovskite solar cells. At the generally required annealing temperature, the substrate would have a certain degree of thermal expansion, whether a plastic substrate or rigid substrate. The expansion process and even the practical operation could accumulate stress and strain, yielding the impact on the perovskite layer and then forming crack lines in the film.^{88,89} What's more, severe mismatches in

the thermal properties between adjacent layers can impose additional stress on the crystal lattice, resulting in strain and cracks during heating and cooling.⁹⁰ Therefore, the thermal expansion coefficient (CTE) and the thermal transition are important features that we need to consider when selecting a substrate. For example, the flexible willow glass (Corning), which could withstand the high temperature of 500 degrees Celsius, has been used in PSC manufacturing.⁸⁸ Apart from the thermal and thermomechanical properties, there are many other requirements we need to think about for the flexible substrates to obtain an outstanding photovoltaic device, such as light transmittance and chemical properties. Polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polycarbonate (PC), polyethersulfone (PES) and polyimide (PI) are the substrates commonly used in devices. They have their own advantages, so we need to consider comprehensively when choosing.⁹⁰

In addition, the impact factor of substrate thickness has to be taken into account. Lee *et al.*⁹¹ evaluated the performance of the PSCs and confirmed the effect of the applied strain by changing the thickness of the substrate (Fig. 5a). A bending cycle test was conducted on PSCs to compare the efficiency of devices fabricated on substrates with three different thicknesses. Surprisingly, FPSCs with the same initial efficiency but different substrate thicknesses showed completely different final efficiencies after 1000 bending cycles. It is found that the current density–voltage (*J*–*V*) curve of the device prepared on a thinner substrate is almost unchanged after bending, while the performance of the device prepared on a thicker substrate will be severely reduced under the same operation. The significant decrease in PCE mainly originated from the worse MAPbI₃ film with the existence of deep and wide gaps as shown in Fig. 5a. Therefore, to obtain stronger films and devices, we should choose a suitable thickness of the substrate.

The structure of the substrate is also an important factor for stress accumulation. Researchers proposed to adopt a substrate with the inverted nanocone (i-cone) structure (Fig. 5b). In this study, the i-cone structure used is a folded form, which is a highly stretchable structure. For the folded form, the in-plane stretching of the planar material would be transformed into a local small angle bending in the corner. That's why the structure could achieve release of stress caused by stretching

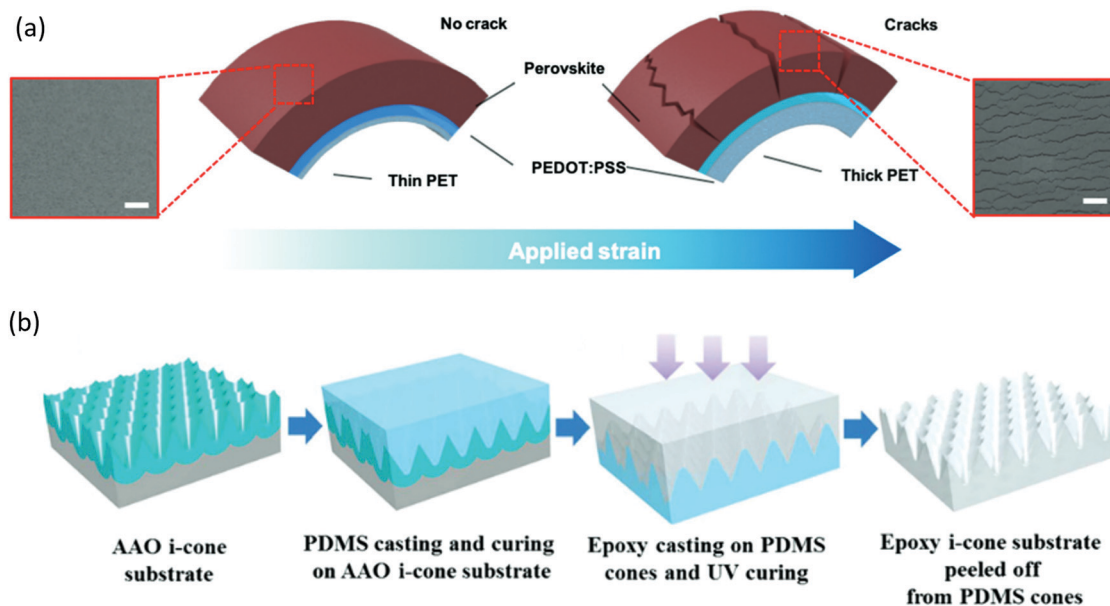


Fig. 5 (a) Schematic illustrations of the influence of substrate thickness on the formation of perovskite film cracks. Ref. 91. Copyright 2019 Royal Society of Chemistry. (b) Schematics of fabrication of the i-cone epoxy substrate. Ref. 92. Copyright 2016 Royal Society of Chemistry.

or thermal expansion.⁹² Thus, the presence of the i-cone structure makes it difficult for the stress and strain of the device to be accumulated when bending. This inhibits the nucleation of cracks in different layers and effectively improves the mechanical durability of the devices. However, this structure will reduce the absorption of light and then affect the efficiency of the device. Therefore, the researchers need to combine the demand for photovoltaic performance and mechanical stability, and then select the most suitable size of the i-cone structure. Therefore, it is limited to improving mechanical stability.

For perovskite layers, the mechanical properties of the electrode would also affect it. Many flexible solar cells have achieved high photovoltaic performance but with weak flexibility from the adoption of brittle electrodes such as the indium-doped-tin oxide (ITO).^{93–96} The cracks of the electrode could damage the other layers as well. To enhance the mechanical durability, many alternative electrodes have been

developed, such as carbon nanotubes, graphenes, Ti foils, metal thin films and the silver nanowires.^{97–99}

4.2 Additional protective layer

When bending, the outer surfaces withstand the tensile stress and the inner surfaces withstand the compression stress. There will be a plane where the tensile stress and the compression stress reach a balance. This plane is defined as the neutral plane (NP).^{90,92} Simply, the neutral surface is the surface where the strains and the total stresses are zero. We only need to adjust the most fragile interface to the neutral surface by adding a protective layer and other measures, and we can get better mechanical durability of the device.¹⁰⁰

As shown in Fig. 6, a thin film, a parylene protective layer, was introduced on the top of the device to relocate the neutral plane onto the perovskite layer. There is an equation used to calculate the thickness of protective layer so that the neutral plane can be exactly on the interface we want to protect.⁹¹ After 100

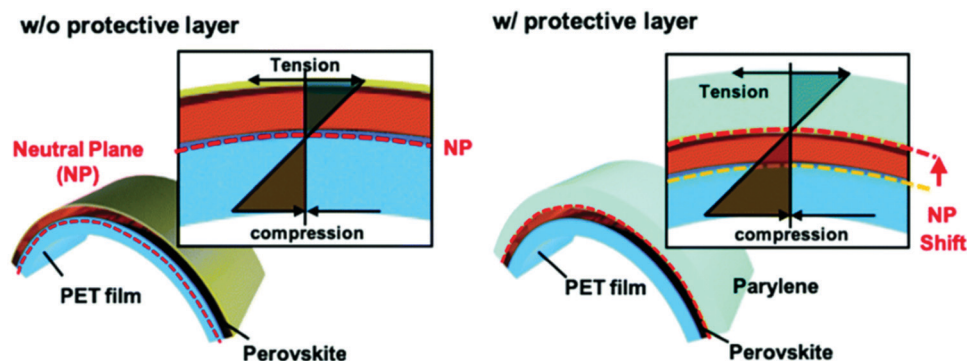


Fig. 6 Schematic diagram of the influence of the introduction of the protective surface on the position of the neutral plane. Ref. 91. Copyright 2019 Royal Society of Chemistry.

cycles of bending, 88% of the initial performance of the device was retained the protective layer. Furthermore, the moisture in the air would also affect the bending durability of the perovskite.¹⁰¹ The protective layer could protect the film from moisture, which means that the introduction of the protective layer is very important for practical application.

However, just like the diagram shows, the change of the neutral plane would increase the stress to the other layers, that is, the stress does not disappear but transfer to other layers, which is a significant limitation. Sometimes, we could use this engineering if we particularly want to protect one layer of the device.

5 Summary and conclusion

In general, the mechanical stability of the perovskite layer of flexible PSCs will be affected by many factors, which will play key roles in flexible PSCs in the future. It will lead to different mechanical stabilities due to the difference in the intrinsic properties of the perovskite. For the perovskite material itself, the difference in chemical composition at different sites A, B, and X has a great influence on its bending stability. However, since perovskite is a polycrystalline film, there are a large number of GBs between the crystal lattices, which are the places where cracks form and locate. Their impact on the mechanical stability is significant. Therefore, some attempts such as cross-linking of polymer chain doping have been applied to improve the stability of grain boundaries. In addition, when the thickness of the perovskite layer film changes and the flexible device is affected by external forces, the mechanical stability of the perovskite will also change. Secondly, when an external force exists, stress accumulation will occur between the perovskite layer and the adjacent functional layer. When the stress accumulates to a certain degree, delamination will occur between different layers, resulting in the formation of cracks. Therefore, articular cartilage-like soft materials are used at the interface to improve the flexibility of the device by forming a chemical bond between the two layers. Additionally, the choice of electrode and substrate is also a very important factor. The stretching and expansion of the two layers may also have an indirect effect on the perovskite layer. Finally, considering the existence of the neutral surface, the introduction of a protective layer also has a certain value for improving the cell stability.

And obviously, each type of project has its advantages and disadvantages. Both compositional engineering and grain boundary crosslinking engineering are the most direct and relevant ways to improve the mechanical durability of perovskite layers. And moreover, it would be of great help in reducing the degradation of the perovskite if we add the stress buffer crosslinking agent at the GBs, since it prevents moisture from entering the perovskite from the grain boundary. However, in general, these measures are accompanied by sacrifices and losses of photoelectric conversion efficiency. The composition of components with good

mechanical stability is generally not the combination with the best efficiency. The stretchable crosslinking agent often has poor conductivity, which would also cause weakening of the photoelectric properties.

Engineering of other functional layers is easy to realize, and there would be many choices for us. However, when choosing, all researchers just consider the reduction of the stress of each individual layer. But they do not consider from the point of view of the entire device structure, and the adaptability of the scratching coefficient between the layers clearly impacts the performance of the device. Simply increasing the scalability of one layer, without paying attention to the adaptability of the layers will only make the layers separate, so that the entire device structure is broken.

Through interface engineering, the above question can be alleviated to some extent. Additionally, if we use appropriate molecules, it can also passivate defects to a certain extent, build a bridge between the layers, and increase the transfer of charge. However, it is difficult to find a mechanical buffer, so this engineering is more difficult to implement.

In conclusion, all reported strategies have shown a great improvement of the mechanical stability. This means these strategies are available and feasible. But it is also obvious that, if we want to actually apply the flexible perovskite solar cells in industry, only one engineering technique to improve the stability is definitely not enough. By combining these methods, absorbing each of the advantages and improving the disadvantages, we believe that people can better achieve the application of flexible perovskite devices one day.

Finally, a standardized representation of mechanical stability is currently lacking. At present, the measurement of mechanical tolerance is carried out under various conditions. They cannot be compared, and they cannot provide references for subsequent research. If the flexible perovskite solar cells are to be commercialized, it is necessary to have a fixed standard for industry. Until now, no one has worked in this regard. Therefore, developing specific standards is also an aspect that needs to break through and be paid attention.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors acknowledge financial support from the National Natural Science Foundation of China (No. 62075148, 52073197), and the Natural Science Foundation of Jiangsu Province (No. BK20201413). This project was also funded by the Collaborative Innovation Center of Suzhou Nano Science and Technology, by the “111” Project of the State Administration of Foreign Experts Affairs of China, and by the open research fund of Key Laboratory for Organic Electronics and Information Displays.

References

- 1 F. D. Giacomo, A. Fakharuddin, R. Jose and T. M. Brown, Progress, challenges and perspectives in flexible perovskite solar cells, *Energy Environ. Sci.*, 2016, **9**, 3007–3035.
- 2 M. Ye, X. Hong and X.-Y. Liu, Recent advancements in perovskite solar cells: Flexibility, stability and large scale, *J. Mater. Chem. A*, 2016, **4**, 6755–6771.
- 3 D. Yang, R. Yang, S. Priya and S. Liu, Recent advances in flexible perovskite solar cells: Fabrication and applications, *Angew. Chem., Int. Ed.*, 2018, **58**, 4466–4483.
- 4 G. Hashmi, K. Miettunen, T. Peltola, J. Halme, I. Asghar, K. Aitola, M. Toivola and P. Lund, Review of materials and manufacturing options for large area flexible dye solar cells, *Renewable Sustainable Energy Rev.*, 2011, **15**, 3717–3732.
- 5 C. C. Zhang, Z. K. Wang, S. Yuan, R. Wang, M. Li, M. F. Jimoh, L. S. Liao and Y. Yang, Polarized ferroelectric polymers for high-performance perovskite solar cells, *Adv. Mater.*, 2019, **31**, 1902222.
- 6 C. Dong, X. M. Li, C. Ma, W. F. Yang, J. J. Cao, F. Igbari, Z. K. Wang and L. S. Liao, Lycopene-based bionic membrane for stable perovskite photovoltaics, *Adv. Funct. Mater.*, 2021, **31**, 2011242.
- 7 H. Tan, F. Che, M. Wei, Y. Zhao, M. I. Saidaminov, P. Todorovic, D. Broberg, G. Walters, F. Tan, T. Zhuang, B. Sun, Z. Liang, H. Yuan, E. Fron, J. Kim, Z. Yang, O. Voznyy, M. Asta and E. H. Sargent, Dipolar cations confer defect tolerance in wide-bandgap metal halide perovskites, *Nat. Commun.*, 2018, **9**, 3100.
- 8 R. Wang, J. Wang, S. Tan, Y. Duan, Z. K. Wang and Y. Yang, Opportunities and challenges of lead-free perovskite optoelectronic devices, *Trends Chem.*, 2019, **1**, 368–379.
- 9 C. H. Chen, Y. H. Lou, K. L. Wang, Z. H. Su, C. Dong, J. Chen, Y. R. Shi, X. Y. Gao and Z. K. Wang, Ternary two-step sequential deposition induced perovskite orientational crystallization for high-performance photovoltaic devices, *Adv. Energy Mater.*, 2021, **11**, 2101538.
- 10 Z. Li, R. Wang, J. Xue, X. Xing, C. Yu, T. Huang, J. Chu, K. L. Wang, C. Dong, Z. Wei, Y. Zhao, Z. K. Wang and Y. Yang, Core-shell ZnO@SnO₂ nanoparticles for efficient inorganic perovskite solar cells, *J. Am. Chem. Soc.*, 2019, **141**, 17610–17616.
- 11 X. Z. Dai, Y. H. Deng, C. H. Van Brackel, S. S. Chen, P. N. Rudd, X. Xiao, Y. Lin, B. Chen and J. S. Huang, Scalable fabrication of efficient perovskite solar modules on flexible glass substrates, *Adv. Energy Mater.*, 2020, **10**, 1903108.
- 12 J. Yu, M. Wang and S. Lin, Probing the soft and nanoductile mechanical nature of single and polycrystalline organic–inorganic hybrid perovskites for flexible functional devices, *ACS Nano*, 2016, **10**, 11044–11057.
- 13 M. Cai, Y. Wu, H. Chen, X. Yang, Y. Qiang and L. Han, Cost-performance analysis of perovskite solar modules, *Adv. Sci.*, 2017, **4**, 1600269.
- 14 B. J. Kim, D. H. Kim, Y. Y. Lee, H. W. Shin, G. S. Han, J. S. Hong, K. Mahmood, T. K. Ahn, Y. C. Joo and K. S. Hong, Highly efficient and bending durable perovskite solar cells: Toward a wearable power source, *Energy Environ. Sci.*, 2015, **8**, 916–921.
- 15 M. Kaltenbrunner, G. Adam, E. D. Glowacki, M. Drack, R. Schwödiauer, L. Leonat, D. H. Apaydin, H. Groiss, M. C. Scharber and M. S. White, Flexible high power-per-weight perovskite solar cells with chromium oxide-metal contacts for improved stability in air, *Nat. Mater.*, 2015, **14**, 1032–1039.
- 16 C. Zhang, S. Wang, H. Zhang, Y. Feng, W. Tian, Y. Yan, J. Bian, Y. Wang, S. Jin, S. M. Zakeeruddin, M. Gratzel and Y. Shi, Efficient stable graphene-based perovskite solar cells with high flexibility in device assembling via modular architecture design, *Energy Environ. Sci.*, 2019, **12**, 3585–3594.
- 17 G. Xu, R. Xue, W. Chen, J. Zhang, M. Zhang, H. Chen, C. Cui, H. Li, Y. Li and Y. Li, New strategy for two-step sequential deposition: Incorporation of hydrophilic fullerene in second precursor for high-performance p–i–n planar perovskite solar cells, *Adv. Energy Mater.*, 2018, **8**, 1703054.
- 18 Z. K. Wang and L. S. Liao, Doped charge-transporting layers in planar perovskite solar cells, *Adv. Opt. Mater.*, 2018, **6**, 1800276.
- 19 C. Chen, Y. Jiang, J. Guo, X. Wu, W. Zhang, S. Wu, X. Gao, X. Hu, Q. Wang, G. Zhou, Y. Chen, J. Liu, K. Kempa and J. Gao, Solvent-assisted low-temperature crystallization of SnO₂ electron-transfer layer for high-efficiency planar perovskite solar cells, *Adv. Funct. Mater.*, 2019, **29**, 1900557.
- 20 Z. Wang, Y. Lou, S. Naka and H. Okada, Bias and temperature dependent charge transport in solution-processed small molecular mixed single layer organic light emitting devices, *Appl. Phys. Lett.*, 2011, **98**, 063302.
- 21 Q. Q. Ye, Z. K. Wang, M. Li, C. C. Zhang, K. H. Hu and L. S. Liao, N-Type doping of fullerenes for planar perovskite solar cells, *ACS Energy Lett.*, 2018, **3**, 875–882.
- 22 X. Liu, L. Hu, R. Wang, J. Li, H. Gu, S. Liu, Y. Zhou and G. Tu, Flexible perovskite solar cells via surface-confined silver nanoparticles on transparent polyimide substrates, *Polymers*, 2019, **11**, 427.
- 23 Z. Yang, C. Chueh, F. Zuo, J. H. Kim, P. Liang and A. K.-Y. Jen, High-performance fully printable perovskite solar cells via blade-coating technique under the ambient condition, *Adv. Energy Mater.*, 2015, **5**, 1500328.
- 24 H. Zhang, J. Cheng, F. Lin, H. He, J. Mao, K. S. Wong, A. K.-Y. Jen and W. C. H. Choy, High-performance fully printable perovskite solar cells via blade-coating technique under the ambient condition, *ACS Nano*, 2016, **10**, 1503–1511.
- 25 Z. Zhu, J. Xu, C. Chueh, H. Liu, Z. Li, X. Li, H. Chen and A. K.-Y. Jen, A low-temperature, solution-processable organic electron-transporting layer based on planar coronene for high-performance conventional perovskite solar cells, *Adv. Mater.*, 2016, **28**, 10786–10793.
- 26 L. Wang, H. Zhou, J. Hu, B. Huang, M. Sun, B. Dong, G. Zheng, Y. Huang, Y. Chen and L. Li, A Eu³⁺–Eu²⁺ ion redox shuttle imparts operational durability to Pb–I perovskite solar cells, *Science*, 2019, **363**, 265–270.

- 27 H. Wang, C. Zhu, L. Liu, S. Ma, P. Liu, J. Wu, C. Shi, Q. Du, Y. Hao, S. Xiang, H. Chen, P. Chen, Y. Bai, H. Zhou, Y. Li and Q. Chen, Interfacial residual stress relaxation in perovskite solar cells with improved stability, *Adv. Mater.*, 2019, **31**, 1904408.
- 28 B. J. Kim, D. H. Kim, Y. Y. Lee, H. W. Shin, G. S. Han, J. S. Hong, K. Mahmood, T. K. Ahn, Y. C. Joo, K. S. Hong, N. G. Park, S. Lee and H. S. Jung, Highly efficient and bending durable perovskite solar cells: Toward a wearable power source, *Energy Environ. Sci.*, 2015, **8**, 916–921.
- 29 S. S. Shin, W. S. Yang, J. H. Noh, J. H. Suk, N. J. Jeon, J. H. Park, J. S. Kim, W. M. Seong and S. I. Seok, High-performance flexible perovskite solar cells exploiting Zn_2SnO_4 prepared in solution below 100 °C, *Nat. Commun.*, 2015, **6**, 7410.
- 30 V. Zardetto, T. M. Brown, A. Reale and A. D. Carlo, Substrates for flexible electronics: A practical investigation on the electrical, film flexibility, optical, temperature, and solvent resistance properties, *J. Polym. Sci. Part B*, 2011, **49**, 638–648.
- 31 D. Yang, R. Yang, K. Wang, C. Wu, X. Zhu, J. Feng, X. Ren, G. Fang, S. Priya and S. Liu, High efficiency planar-type perovskite solar cells with negligible hysteresis using EDTA-complexed SnO_2 , *Nat. Commun.*, 2018, **9**, 3239.
- 32 L. Li, S. Zhang, Z. Yang, E. E. S. Berthold and W. Chen, Recent advances of flexible perovskite solar cells, *J. Energy Chem.*, 2018, **27**, 673–689.
- 33 Y. Fu, T. Wu, J. Wang, J. Zhai, M. J. Shearer, Y. Zhao, R. J. Hamers, E. Kan, K. Deng, X.-Y. Zhu and S. Jin, Stabilization of the metastable lead iodide perovskite phase via surface functionalization, *Nano Lett.*, 2017, **17**, 4405–4414.
- 34 R. Y. F. Liu, D. A. Schiraldi and A. Hiltner, Oxygen-barrier properties of cold-drawn polyesters, *J. Polym. Sci. Part B*, 2002, **40**, 862–877.
- 35 J. Feng, X. Zhu, Z. Yang, X. Zhang, J. Niu, Z. Wang, S. Zuo, S. Priya, S. Liu and D. Yang, Record efficiency stable flexible perovskite solar cell using effective additive assistant strategy, *Adv. Mater.*, 2018, **30**, 1801418.
- 36 G. Niu, X. Guo and L. Wang, Review of recent progress in chemical stability of perovskite solar cells, *J. Mater. Chem. A*, 2015, **3**, 8970–8980.
- 37 E. T. Hoke, D. J. Slotcavage, E. R. Dohner, A. R. Bowering, H. I. Karunadasa and M. D. McGehee, Reversible photo-induced trap formation in mixed-halide hybrid perovskites for photovoltaics, *Chem. Sci.*, 2015, **6**, 613–617.
- 38 D. J. Slotcavage, H. I. Karunadasa and M. D. McGehee, Light-induced phase segregation in halide-perovskite absorbers, *ACS Energy Lett.*, 2016, **1**, 1199–1205.
- 39 R. G. Wilks and M. Bär, Perovskite solar cells: Danger from within, *Nat. Energy*, 2017, **2**, 16204.
- 40 M. Zhong, Y. Liang, J. Zhang, Z. Wei, Q. Li and D. Xu, Highly efficient flexible MAPbI_3 solar cells with a fullerene derivative-modified SnO_2 layer as the electron transport layer, *J. Mater. Chem. A*, 2019, **7**, 6619.
- 41 C. H. Peters, I. T. Sachs-Quintana, J. P. Kastrop, S. Beaupré, M. Leclerc and M. D. McGehee, High efficiency polymer solar cells with long operating lifetimes, *Adv. Energy Mater.*, 2011, **1**, 491–494.
- 42 D. C. Jordan and S. R. Kurtz, Photovoltaic degradation rates—an analytical review, *Prog. Photovoltaics*, 2013, **21**, 12.
- 43 N. Rolston, A. D. Printz, J. M. Tracy, H. C. Weerasinghe, D. Vak, L. J. Haur, A. Priyadarshi, N. Mathews, D. J. Slotcavage, M. D. McGehee, R. E. Kalan, K. Zielinski, R. L. Grimm, H. Tsai, W. Nie, A. D. Mohite, S. Gholipour, M. Saliba, M. Grätzel and R. H. Dauskardt, Effect of cation composition on the mechanical stability of perovskite solar cells, *Adv. Energy Mater.*, 2017, **8**, 1702116.
- 44 N. Rolston, B. L. Watson, C. D. Bailie, M. D. McGehee, J. P. Bastos, R. Gehlhaar, J. E. Kim, D. Vak, A. T. Mallajosyula, G. Gupta, A. D. Mohite and R. H. Dauskardt, Mechanical integrity of solution-processed perovskite solar cells, *Extreme Mech. Lett.*, 2016, **9**, 353–358.
- 45 L. Pei, H. Yu, Q. Zhang, J. Li, K. Wang and B. Hu, Concave and convex bending influenced mechanical stability in flexible perovskite solar cells, *J. Phys. Chem. C*, 2020, **124**, 2340–2345.
- 46 L. Qiu, J. Deng, X. Lu, Z. Yang and H. Peng, Integrating perovskite solar cells into a flexible fiber, *Angew. Chem., Int. Ed.*, 2014, **53**, 10425–10428.
- 47 Y. Li, L. Meng, Y. (Michael) Yang, G. Xu, Z. Hong, Q. Chen, J. You, G. Li, Y. Yang and Y. Li, High-efficiency robust perovskite solar cells on ultrathin flexible substrates, *Nat. Commun.*, 2016, **7**, 10214.
- 48 R. H. Dauskardt, M. Lane, Q. Ma and N. Krishna, Adhesion and debonding of multi-layer thin film structures, *Eng. Fract. Mech.*, 1998, **61**, 141–162.
- 49 M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt and M. Grätzel, Cesium-containing triple cation perovskite solar cells: Improved stability, reproducibility and high efficiency, *Energy Environ. Sci.*, 2016, **9**, 1989–1997.
- 50 W. Wu, P. N. Rudd, Z. Ni, C. H. Van Brackle, H. Wei, Q. Wang, B. R. Ecker, Y. Gao and J. Huang, Reducing surface halide deficiency for efficient and stable iodide-based perovskite solar cells, *J. Am. Chem. Soc.*, 2020, **142**, 3989–3996.
- 51 B.-W. Park, N. Kedem, M. Kulbak, D. Y. Lee, W. S. Yang, N. J. Jeon, J. Seo, G. Kim, K. J. Kim, T. J. Shin, G. Hodes, D. Cahen and S. I. Seok, Understanding how excess lead iodide precursor improves halide perovskite solar cell performance, *Nat. Commun.*, 2018, **9**, 3301.
- 52 T. J. Jacobsson, J. P. Correa-Baena, E. H. Anaraki, B. Philippe, S. D. Stranks, M. E. F. Bouduban, W. Tress, K. Schenk, J. Teuscher, J. E. Moser, H. Rensmo and A. Hagfeldt, Unreacted PbI_2 as a double-edged sword for enhancing the performance of perovskite solar cells, *J. Am. Chem. Soc.*, 2016, **138**, 10331–10343.
- 53 T. Meier, T. P. Gujar, A. Schönleber, S. Olthof, K. Meerholz, S. van Smaalen, F. Panzer, M. Thelakktat and A. Köhler,

- Impact of excess PbI_2 on the structure and the temperature dependent optical properties of methylammonium lead iodide perovskites, *J. Mater. Chem. C*, 2018, **6**, 7512–7519.
- 54 S. Chen, X. Wen, J. S. Yun, S. Huang, M. Green, N. J. Jeon, W. S. Yang, J. H. Noh, J. Seo, S. I. Seok and A. Ho-Baillie, Spatial distribution of lead iodide and local passivation on organo-lead halide perovskite, *ACS Appl. Mater. Interfaces*, 2017, **9**, 6072–6078.
 - 55 B. Shi, X. Yao, F. Hou, S. Guo, Y. Li, C. Wei, Y. Ding, Y. Li, Y. Zhao and X. Zhang, Unraveling the passivation process of PbI_2 to enhance the efficiency of planar perovskite solar cells, *J. Phys. Chem. C*, 2018, **122**, 21269–21276.
 - 56 Q. Jiang, L. Zhang, H. Wang, X. Yang, J. Meng, H. Liu, Z. Yin, J. Wu, X. Zhang and J. You, Enhanced electron extraction using SnO_2 for high-efficiency planar-structure $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ -based perovskite solar cells, *Nat. Energy*, 2017, **2**, 16177.
 - 57 I. K. Popoola, M. A. Gondal and T. F. Qahtan, Recent progress in flexible perovskite solar cells: Materials, mechanical tolerance and stability, *Renewable Sustainable Energy Rev.*, 2018, **82**, 3127–3151.
 - 58 M. Saliba, T. Matsui, K. Domanski, J. Y. Seo, A. Ummadisingu, S. M. Zakeeruddin, J. P. Correa-Baena, W. R. Tress, A. Abate and A. Hagfeldt, Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance, *Science*, 2016, **354**, 206–209.
 - 59 Z. Tang, S. Uchida, T. Bessho, T. Kinoshita, H. Wang, F. Awai, R. Jono, M. M. Maitani, J. Nakazaki, T. Kubo and H. Segawa, Modulations of various alkali metal cations on organometal halide perovskites and their influence on photovoltaic performance, *Nano Energy*, 2018, **45**, 184–192.
 - 60 T. J. Jacobsson, S. Svanström, V. Andrei, J. P. H. Rivett, N. Kornienko, B. Philippe, U. B. Cappel, H. Rensmo, F. Deschler and G. Boschloo, Extending the compositional space of mixed lead halide perovskites by Cs, Rb, K, and Na doping, *J. Phys. Chem. C*, 2018, **122**, 13548–13557.
 - 61 G. Zheng, C. Zhu, J. Ma, X. Zhang, G. Tang, R. Li, Y. Chen, L. Li, J. Hu, J. Hong, Q. Chen, X. Gao and H. Zhou, Manipulation of facet orientation in hybrid perovskite polycrystalline films by cation cascade, *Nat. Commun.*, 2018, **9**, 2793.
 - 62 D. Y. Son, S. G. Kim, J. Y. Seo, S. H. Lee, H. Shin, D. Lee and N. G. Park, Universal approach toward hysteresis-free perovskite solar cell via defect engineering, *J. Am. Chem. Soc.*, 2018, **140**, 1358–1364.
 - 63 B. B. Cao, L. K. Yang, S. S. Jiang, H. Lin, N. Wang and X. Li, Flexible quintuple cation perovskite solar cells with high efficiency, *J. Mater. Chem. A*, 2019, **7**, 4960–4970.
 - 64 W. Li, M. S. R. N. Kiran, J. L. Manson, J. A. Schlueter, A. Thirumurugan, U. Ramamurty and A. K. Cheetham, Mechanical properties of a metal–organic framework containing hydrogen-bonded bifluoride linkers, *Chem. Commun.*, 2013, **49**, 4471–4473.
 - 65 J. C. Tan, T. D. Bennett and A. K. Cheetham, Chemical structure, network topology, and porosity effects on the mechanical properties of zeolitic Imidazolate Frameworks, *Proc. Natl. Acad. Sci. U. S. A.*, 2010, **107**, 9938–9943.
 - 66 B. J. Kim, D. H. Kim, Y. Y. Lee, H. W. Shin, G. S. Han, J. S. Hong, K. Mahmood, T. K. Ahn, Y. C. Joo, K. S. Hong, N. G. Park, S. Lee and H. S. Jung, Highly efficient and bending durable perovskite solar cells: Toward a wearable power source, *Energy Environ. Sci.*, 2015, **8**, 916.
 - 67 W. C. Oliver and G. M. Pharr, Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology, *J. Mater. Res.*, 2004, **19**, 3–20.
 - 68 S. Sun, Y. Fang, G. Kieslich, T. J. White and A. K. Cheetham, Mechanical properties of organic–inorganic halide perovskites, $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{I}, \text{Br}$ and Cl), by nanoindentation, *J. Mater. Chem. A*, 2015, **3**, 18450–18455.
 - 69 J. Feng, Mechanical properties of hybrid organic–inorganic $\text{CH}_3\text{NH}_3\text{BX}_3$ ($\text{B} = \text{Sn}, \text{Pb}$; $\text{X} = \text{Br}, \text{I}$) perovskites for solar cell absorbers, *APL Mater.*, 2014, **2**, 081801.
 - 70 A. F. Castro-Mendez, J. Hidalgo and J. P. Correa-Baena, The role of grain boundaries in perovskite solar cells, *Adv. Energy Mater.*, 2019, **9**, 1901489.
 - 71 C. Liu, L. Zhang, X. Zhou, J. Gao, W. Chen, X. Wang and B. Xu, Hydrothermally treated SnO_2 as the electron transport layer in high-efficiency flexible perovskite solar cells with a certificated efficiency of 17.3%, *Adv. Funct. Mater.*, 2019, **29**, 1807604.
 - 72 Z. Q. Huang, X. T. Hu, C. Liu, L. C. Tan and Y. W. Chen, Nucleation and crystallization control via polyurethane to enhance the bendability of perovskite solar cells with excellent device performance, *Adv. Funct. Mater.*, 2017, **27**, 1703061.
 - 73 X. Hu, X. Meng, X. Yang, Z. Huang, Z. Xing, P. Li, L. Tan, M. Su, F. Li, Y. Chen and Y. Song, Cementitious grain-boundary passivation for flexible perovskite solar cells with superior environmental stability and mechanical robustness, *Sci. Bull.*, 2020, **66**, 527–535.
 - 74 M. Li, Y. G. Yang, Z. K. Wang, T. Kang, Q. Wang, S. H. Turren-Cruz, X. Y. Gao, C. S. Hsu, L. S. Liao and A. Abate, Perovskite grains embraced in a soft fullerene network make highly efficient flexible solar cells with superior mechanical stability, *Adv. Mater.*, 2019, **31**, 1901519.
 - 75 Y. Du, H. Cai, X. Bao, Z. Xing, Y. Wu, J. Xu, L. Huang, J. Ni, J. Li and J. Zhang, Flexible Perovskite Solar Cells onto Plastic Substrate Exceeding 13% Efficiency Owing to the Optimization of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ Film via H_2O Additive, *ACS Sustainable Chem. Eng.*, 2018, **6**, 1083–1090.
 - 76 S. Yao, B. Jin, Z. Liu, C. Shao, R. Zhao, X. Wang and R. Tang, Biomineralization: From material tactics to biological strategy, *Adv. Mater.*, 2017, **29**, 1605903.
 - 77 X. Wang, C. Sun, P. Li, T. Wu, H. Zhou, D. Yang, Y. Liu, X. Ma, Z. Song, Q. Nian, L. Feng, C. Qin, L. Chen and R. Tang, Vaccine engineering with dual-functional mineral shell: A promising strategy to overcome preexisting immunity, *Adv. Mater.*, 2016, **28**, 694–700.
 - 78 C. Shao, R. Zhao, S. Jiang, S. Yao, Z. Wu, B. Jin, Y. Yang, H. Pan and R. Tang, Citrate improves collagen mineralization via interface wetting: A physicochemical

- understanding of biomineralization control, *Adv. Mater.*, 2018, **30**, 1704876.
- 79 X. Meng, Z. Cai, Y. Zhang, X. Hu, Z. Xing, Z. Huang, Z. Huang, Y. Cui, T. Hu, M. Su, X. Liao, L. Zhang, F. Wang, Y. Song and Y. Chen, Bio-inspired vertebral design for scalable and flexible perovskite solar cells, *Nat. Commun.*, 2020, **11**, 3016.
 - 80 H. Il Kim, M.-J. Kim, K. Choi, C. Lim, Y.-H. Kim, S.-K. Kwon and T. Park, Improving the performance and stability of inverted planar flexible perovskite solar cells employing a novel NDI-based polymer as the electron transport layer, *Adv. Energy Mater.*, 2018, **8**, 1702872.
 - 81 Z. Wang, L. Zeng, C. Zhang, Y. Lu, S. Qiu, C. Wang, C. Liu, L. Pan, S. Wu, J. Hu, G. Liang, P. Fan, H.-J. Egelhaaf, C. J. Brabec, F. Guo and Y. Mai, Rational interface design and morphology control for blade-coating efficient flexible perovskite solar cells with a record fill factor of 81%, *Adv. Funct. Mater.*, 2020, **30**, 2001240.
 - 82 C. C. Zhang, S. Yuan, Y.-H. Lou, Q.-W. Liu, M. Li, H. Okada and Z.-K. Wang, Perovskite films with reduced interfacial strains via a molecular-level flexible interlayer for photovoltaic application, *Adv. Mater.*, 2020, 200147.
 - 83 J. H. Yun, I. Lee, T.-S. Kim, M. J. Ko, J. Y. Kimae and H. J. Son, Synergistic enhancement and mechanism study of mechanical and moisture stability of perovskite solar cells introducing polyethylene-imine into the $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{HTM}$ interface, *J. Mater. Chem. A*, 2015, **3**, 22176.
 - 84 A. Rajagopal, K. Yao and A. K.-Y. Jen, Toward perovskite solar cell commercialization: A perspective and research roadmap based on interfacial engineering, *Adv. Mater.*, 2018, **30**, 1800455.
 - 85 A.-N. Cho and N.-G. Park, Impact of interfacial layers in perovskite solar cells, *ChemSusChem*, 2017, **10**, 3687–3704.
 - 86 H. Tan, A. Jain, O. Voznyy, X. Lan and E. H. Sargent, Efficient and stable solution-processed planar perovskite solar cells *via* contact passivation, *Science*, 2017, **355**, 722–726.
 - 87 Q. Dong, C. Zhu, M. Chen, C. Jiang and Y. Zhou, Interpenetrating interfaces for efficient perovskite solar cells with high operational stability and mechanical robustness, *Nat. Commun.*, 2021, **12**, 973.
 - 88 M. M. Tavakoli, K.-H. Tsui, Q. Zhang, J. He, Y. Yao, D. Li and Z. Fan, Highly efficient flexible perovskite solar cells with antireflection and self-cleaning nanostructures, *ACS Nano*, 2015, **10**, 10287–10295.
 - 89 M. M. Tavakoli, Q. Lin, S.-F. Leung, G. C. Lui, H. Lu, L. Li, B. Xiang and Z. Fan, Efficient, flexible and mechanically robust perovskite solar cells on inverted nanocone plastic substrates, *Nanoscale*, 2016, **8**, 4276–4283.
 - 90 X. Hu, X. Meng, L. Zhang, Y. Zhang, Z. Cai, Z. Huang, M. Su, Y. Wang, M. Li, F. Li, X. Yao, F. Wang, W. Ma, Y. Chen and Y. Song, A mechanically robust conducting polymer network electrode for efficient flexible perovskite solar cells, *Joule*, 2019, **3**, 2205–2218.
 - 91 G. Lee, M. Kim, Y. W. Choi, N. Ahn, J. Jang, J. Yoon, S. M. Kim, J.-G. Lee, D. Kang, H. S. Jung and M. Choi, Ultra-flexible perovskite solar cells with crumpling durability: Toward a wearable power source, *Energy Environ. Sci.*, 2019, **12**, 3182–3191.
 - 92 M. M. Tavakoli, Q. Lin, S.-F. Leung, G. C. Lui, H. Lu, L. Li, B. Xiang and Z. Fan, Efficient, flexible and mechanically robust perovskite solar cells on inverted nanocone plastic substrates, *Nanoscale*, 2016, **8**, 4276–4283.
 - 93 B. J. Kim, D. H. Kim, Y.-Y. Lee, H.-W. Shin, G. S. Han, J. S. Hong, K. Mahmood, T. K. Ahn, Y.-C. Joo and K. S. Hong, Highly efficient and bending durable perovskite solar cells: Toward a wearable power source, *Energy Environ. Sci.*, 2015, **8**, 916–921.
 - 94 D. Liu and T. L. Kelly, Perovskite solar cells with a planar heterojunction structure prepared using room-temperature solution processing techniques, *Nat. Photon.*, 2014, **8**, 133–138.
 - 95 J. You, Z. Hong, Y. M. Yang, Q. Chen, M. Cai, T.-B. Song, C.-C. Chen, S. Lu, Y. Liu and H. Zhou, Low-temperature solution-processed perovskite solar cells with high efficiency and flexibility, *ACS Nano*, 2014, **8**, 1674–1680.
 - 96 Y. Chen, T. Chen and L. Dai, Layer-by-layer growth of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ for highly efficient planar heterojunction perovskite solar cells, *Adv. Mater.*, 2014, **27**, 1053.
 - 97 M. Lee, Y. Jo, D. S. Kim and Y. Jun, Flexible organo-metal halide perovskite solar cells on a Ti metal substrate, *J. Mater. Chem. A*, 2015, **3**, 4129–4133.
 - 98 Z. Li, S. A. Kulkarni, P. P. Boix, E. Shi, A. Cao, K. Fu, S. K. Batabyal, J. Zhang, Q. Xiong and L. H. Wong, Laminated carbon nanotube networks for metal electrode-free efficient perovskite solar cells, *ACS Nano*, 2014, **8**, 6797–6804.
 - 99 J. Han, S. Yuan, L. Liu, X. Qiu, H. Gong, X. Yang, C. C. Li, Y. Hao and C. Bingqiang, Fully indium-free flexible Ag nanowires/ZnO: F composite transparent conductive electrodes with high haze, *J. Mater. Chem. A*, 2015, **3**, 5375–5384.
 - 100 G. Lee, M. C. Kim, Y. W. Choi, N. Ahn, J. Jang, J. Yoon and M. Choi, Ultra-flexible perovskite solar cells with crumpling durability: Toward a wearable power source, *Energy Environ. Sci.*, 2019, **12**, 3182–3191.
 - 101 N. Rolston, B. L. Watson and R. H. Dauskardt, Mechanical integrity of solution-processed perovskite solar cells, *Extreme Mech. Lett.*, 2016, **9**, 353–358.