

Cite this: *J. Mater. Chem. A*, 2021, 9, 19554Received 16th May 2021
Accepted 22nd July 2021

DOI: 10.1039/d1ta04130d

rsc.li/materials-a

Advances in SnO₂-based perovskite solar cells: from preparation to photovoltaic applications

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Perovskite solar cells (PSCs) have recently demonstrated a rapid power conversion efficiency of above 25%. In terms of physical properties, SnO₂ is similar to TiO₂ but with stronger charge extraction at the interface. Furthermore, the SnO₂ electron transporting layer (ETL) is prepared using new, simple, and efficient methods, resulting in high-performance PSCs. This review initially described recent progress in SnO₂ nanostructures and preparation methods. The passivation options were then divided into elemental doping, bilayer alterations, and interfacial modifications. Finally, we discussed the challenges and limitations of SnO₂ ETL-based PSCs and made recommendations for further research.

1. Introduction

Nowadays, perovskite solar cells (PSCs) have attracted substantial attention due to low expense, facile production, and high power conversion efficiency (PCE).^{1–5} Besides, the rapid development of theoretical and practical research has boosted its PCE from 3.8%⁶ to 25.5%^{3,7–12} in just ten years, which is close to that of polycrystalline silicon solar energy cells (Fig. 1a).

The general chemical formula of perovskite is ABX₃, in which A involves an organic cation group or inorganic metal cations such as Methylammonium (CH₃NH₃⁺), formamidinium (NH₂CH=NH₂⁺), as well as cesium (Cs⁺); B is generally a heavy metal cation such as lead(II) (Pb²⁺) and tin(II) (Sn²⁺); X is

commonly a halide ion including chlorine (Cl⁻), bromide (Br⁻), or iodine (I⁻).^{13,14} (Fig. 1b) The Goldschmidt tolerance factor (*t*),¹⁵ is a simple way to check whether or not specific compositions can form a stable perovskite structure.

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$

where *r*_A, *r*_B, and *r*_X represent the corresponding ionic radius of A, B and X, respectively. The 3D perovskite structure can be stable only when *t* is located in the range of ~0.8–1.0.¹⁶

PSC structures are always classified into two types: n-i-p structures and p-i-n structures. The n-i-p structures are of two types: n-i-p mesoporous and n-i-p planar structures, whereas the p-i-n structures are only p-i-n planar structures (Fig. 1c–e).^{4,17,18} The n-i-p mesoporous structures are usually composed of a transparent conductive electrode such as fluorine-doped tin oxide (FTO) and indium tin oxide (ITO), an electron transporting layer (ETL), a mesoporous scaffold layer (which is

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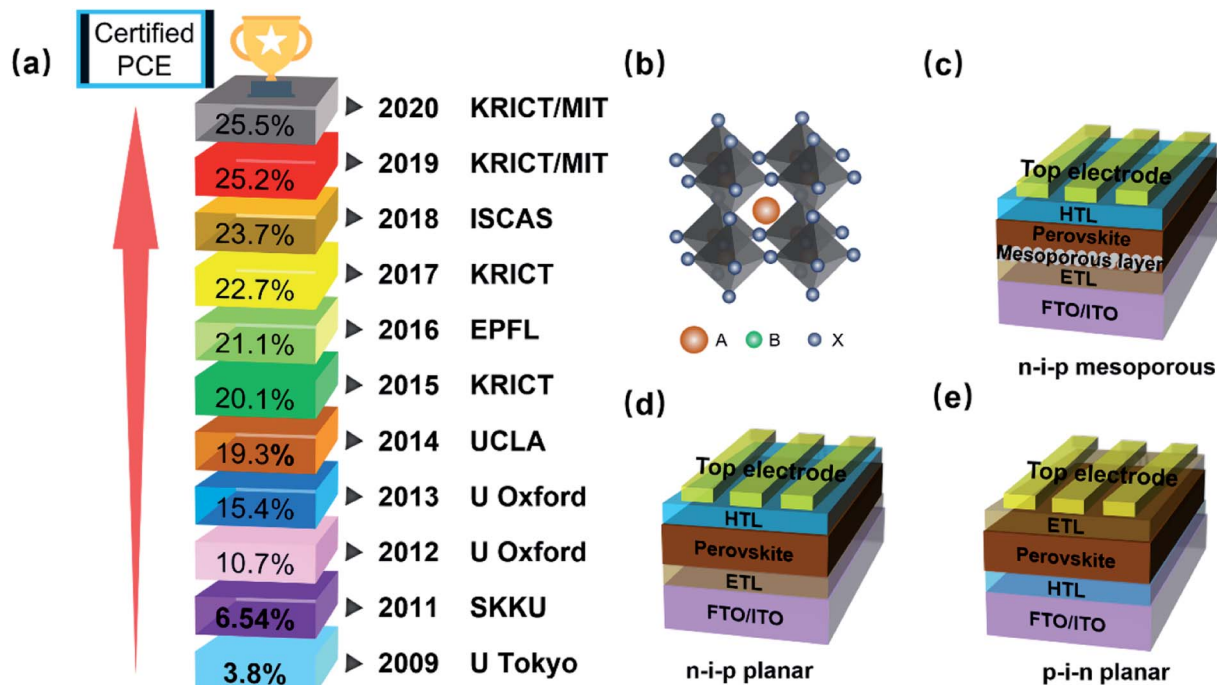


Fig. 1 (a) Brief development history of PSCs (2009,⁶ 2011,²⁸ 2012,²⁹ 2013,³⁰ 2014,³¹ 2015,³² 2016,³³ 2017,³⁴ 2018,³⁵ 2019,³⁶ and 2020,⁷). (b) Crystal structure of cubic for metal halide perovskite. (c) PSCs with an n-i-p mesoporous structure. (d) PSCs with a regular n-i-p planar structure. (e) PSCs with a p-i-n planar structure.

always TiO_2 or Al_2O_3), a perovskite absorption layer, a hole transporting layer (HTL) and a top electrode. However, the TiO_2 mesoporous layer is always post-treated at high temperatures (typically above 450°C) to increase the conductivity and remove the organic material.^{19–25} By contrast, the planar structure of n-i-p PSCs without a mesoporous scaffold also achieves a similar efficient power output and long-term stability to the device with the mesoporous configuration.^{26,27}

TiO_2 is a widely utilized ETL in PSCs for n-i-p planar structures due to its proper bandgap and good transmittance.^{37–40} However, when tested under continuous light illumination, TiO_2 obtains electrons from I^- , leading to perovskite cubic structural damage and generation of I_2 .^{41–43} Furthermore, TiO_2 has a disadvantage of poor electron mobility ($10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) due to impaired intrinsic electron mobility ($<1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).⁴⁴ Furthermore, organic residuals must be removed using high-



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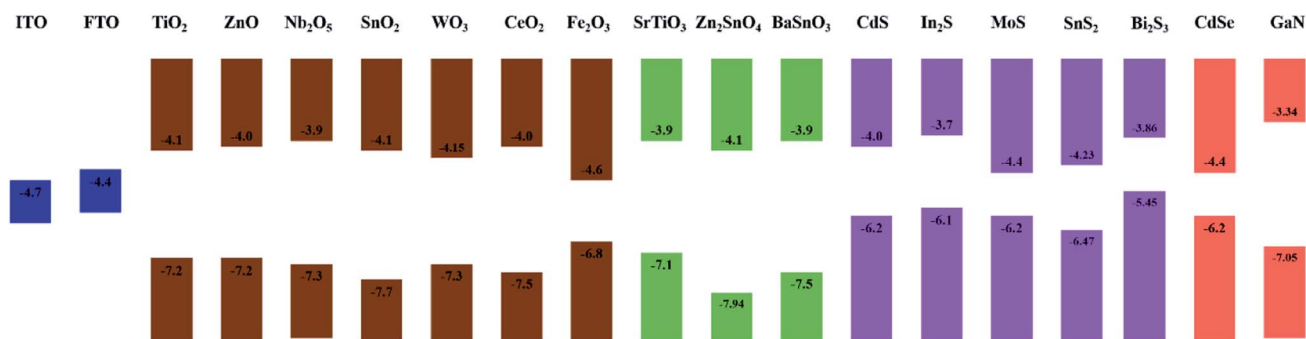


Fig. 2 Conduction band (CB) and valence band (VB) of widely introduced inorganic metal materials as ETLs in PSCs. (blue: metal oxides; green: ternary metal; yellow: metal sulfide; pink: CdSe; and purple: GaN).

temperature procedures, which will take a significant amount of time and energy. For high-performance PSCs, an appropriate and chemically stable ETL is required.

For efficient and stable PSCs, we must adhere to key ETL material principles: (a) high transmittance with minimum optical energy loss, (b) appropriate bandgap matching, (c) high conductivity, (d) low cost and (e) good reproducibility.^{45–48} Many metal oxides with unique optical and electrical properties have been reported as potential candidates for replacing TiO₂ (Fig. 2), including metal oxides (ZnO,^{49–53} In₂O₃,⁵⁴ Nb₂O₅,^{55,56} WO₃,^{57,58} Fe₂O₃,^{59–62} and CeO₂^{63,64}) ternary metal oxides (Zn₂SnO₄,^{65,66} BaSnO₃,^{67–69} and SrTiO₄^{70,71}), metal sulfides (MoS,^{72,73} CdS,^{74–76} In₂S,⁷³ SnS₂⁷⁷ and Bi₂S₃⁷⁸), GaN⁷⁹ and CdSe,^{80,81} and InGaZnO₄.⁸² However, some drawbacks still exist, like low PCE, poor interfacial contact, or high energy consumption.

Since the first report of 6.5% by Dai *et al.* and the subsequent report of above 15% by Yan *et al.* in 2015,^{83,84} the performance of SnO₂-based PSCs has exceeded 25%, making SnO₂ an appealing ETL in PSCs and is considered a potential alternative instead of TiO₂. SnO₂ possesses the following remarkable properties: (1) depth CBM and optimal energy level alignment;⁸⁵ (2) high bulk electron mobility (significantly greater than TiO₂ ETL) and high conductivity;^{86,87} (3) large bandgap (3.6–4.5 eV) and high optical transparency;^{88,89} (4) high-temperature flexible deposition; and (5) outstanding stability under light, heat, and moisture, with minimal photoactivity.^{90,91} TiO₂ in PSCs usually requires a mesoporous layer and especially high-temperature post-treatment (above 450 °C) to get dense with superior conductivity and crystallinity whether in a spin coating or spraying method, which costs more energy and expense. The SnO₂ ETL is often achieved using spin coating and chemical bath deposition, requiring just post-treatment at low temperatures (≤ 200 °C), which is advantageous for a large-scale preparation.

In this review, we present an overview of the use of SnO₂ in PSCs, including standard preparation procedures, SnO₂ nanostructures, and performance optimization techniques such as elemental doping, surface modifications, and bilayer design. Then, we go into hysteresis and stability issues in further detail. Finally, we explore the problems and limits of SnO₂ ETL-based PSCs, as well as possible future research directions.

2. Preparation methods of SnO₂

The SnO₂ film is typically prepared through solution processing, chemical bath deposition (CBD), and atomic layer deposition (ALD). Recently, emerging methods for deposition of SnO₂ such as e-beam evaporation, magnetron sputtering, and electrochemical deposition are also reported to improve the conformability of SnO₂ for flexible and large-scale PSCs. Fig. 3 shows the schematic illustration of various processing methods for SnO₂ ETLs. We just picked some of the representative data of reported different preparation methods, even though other factors may have an impact on the performance. So, here, we have talked more about performance optimization strategies in detail in Section 4. Aside from these, the PCE is also influenced by the rigid or flexible substrate, preparation environment (N₂ or air), and electrode types.

2.1 Solution-processable method

The solution process contains the thermal decomposition method, sol-gel method, deposition of synthesized SnO₂ nanoparticles (NPs), and commercialized SnO₂ colloidal precursors.^{92–94} In the meantime, spin-coating,^{95–98} spray-coating,^{99–101} slot-die coating,^{100,102,103} roll-to-roll microgravity printing,¹⁰⁴ blade-coating^{105,106} and inkjet-printing^{107,108} are valuable technologies to fabricate quality SnO₂ films.

2.1.1 Thermal decomposition method. For thermal decompositions, Sn-based salts (SnCl₂,^{109,110} or SnCl₄,^{111–113} or their hydrates SnCl₂·2H₂O^{114,115} or SnCl₄·5H₂O^{116,117}) were first dissolved in polar solvents such as alcohol and deionized water, which were then deposited on an ITO or a FTO substrate by spin-coating and gradually converted into SnO₂ through thermal annealing in ambient air. It should be noticed that the humidity and temperature of the environment significantly influence the annealing process and the quality of the obtained SnO₂ films.

Zhang and co-workers prepared SnO₂ thin films using SnCl₄ as the tin source at low temperatures.¹¹² Furthermore, they compared the passivation by SnCl₄ at FTO/ETL with that at the ETL/perovskite interface to study the effect of the SnCl₄ pre-treatment and post-treatment on SnO₂ (Fig. 4a). With the assistance of SnCl₄ pre-treatment, the devices based on Cl-SnO₂

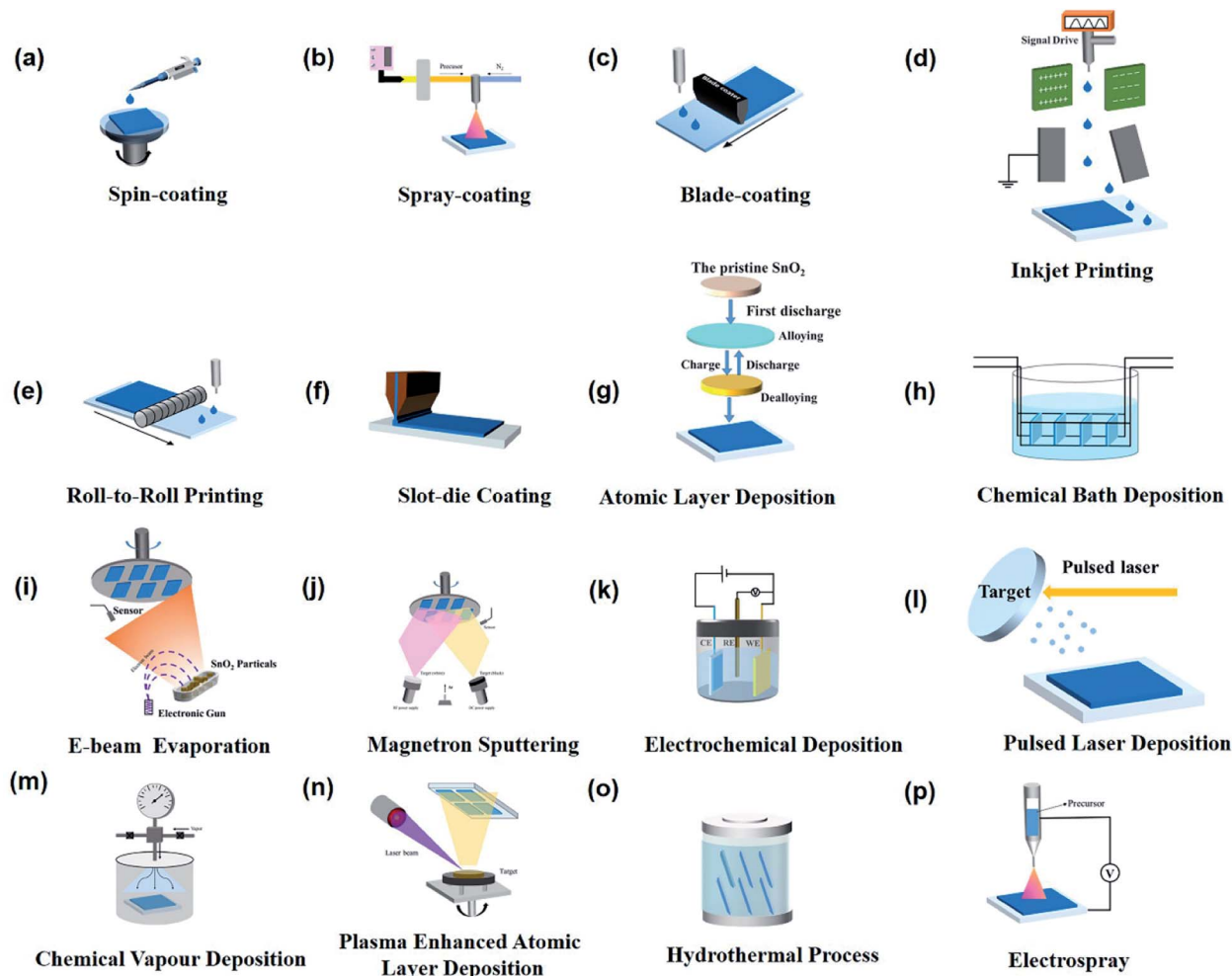


Fig. 3 Schematic illustration of common SnO_2 deposition processes in PSCs. (a) Spin-coating. (b) Spray-coating. (c) Blade-coating. (d) Inkjet-printing. (e) Roll-to-roll printing. (f) Slot-die coating. (g) Atomic layer deposition. (h) Chemical bath deposition. (i) E-beam evaporation electro-spray. (j) Magnetron sputtering. (k) Electrochemical deposition. (l) Pulsed laser deposition. (m) Chemical vapor deposition. (n) Plasma enhanced atomic layer deposition. (o) Hydrothermal process. (p) Electro-spray.

ETL obtained the best efficiency of 18.6% as compared to the post-treatment process (17.3%). The results confirmed that both modifications could boost the photovoltaic performance of the PSCs. However, SnCl_4 pre-treatment increased SnO_2 ETL in electron coupling with FTO, leading to higher electron mobility and better charge extraction efficiency.¹¹²

Annemarie Pucci and co-workers prepared SnO_2 thin films using $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ as the tin source. Their work elucidated the influence of two different solvents and various annealing temperatures on the layer morphology of SnO_2 thin films. It was found that different morphologies were mainly observed during the spin-coating process and not the subsequent annealing process. Furthermore, high annealing temperatures ($\approx 400^\circ\text{C}$) do not entirely omit the differences in morphology, which were processed from the two kinds of solution systems. Although this device still showed severe hysteresis, the device with inkjet-printed SnO_2 layers presented the highest output efficiency of about 19%.¹⁰⁷

2.1.2 Sol-gel method. Sol-gel is one of the most commonly used methods to produce thin dense films and powder catalysts

at large homogeneous concentrations and under stoichiometry control because of the simplicity, low energy, reliability, reproducibility, and relatively mild fabrication conditions.^{118–121}

Lee and co-workers introduced a simple sol-gel method to form a SnO_2 bilayer (Bi-SnO_2) as ETL with dopant-free and amorphous-crystalline heterophase properties by a sequential spin-coating process. Bi-SnO_2 demonstrated a smooth morphology, low density of energy level traps, and appropriate bandgap matching. As a consequence, Bi-SnO_2 PSCs with active areas ($\approx 3.55\text{ cm}^2$) reached up to about 15% with less hysteresis.¹²² Xu *et al.* optimized the aging time, and the PSCs based on the sol-gel SnO_2 film yielded the best PCE of 19% with excellent light trapping ability and a textured SnO_2 structure. But the sol-gel SnO_2 film suffered from poor interfacial contact electrical properties with the perovskite absorber layer because of the annealing effects, resulting in the degradation of performance of PSCs.¹²³

Wang *et al.* reported a whole sol-gel crystallized SnO_2 fabrication process below 80°C (Fig. 4b).¹¹⁴ Participation of environmental O_2 and H_2O via various methods of refluxing is

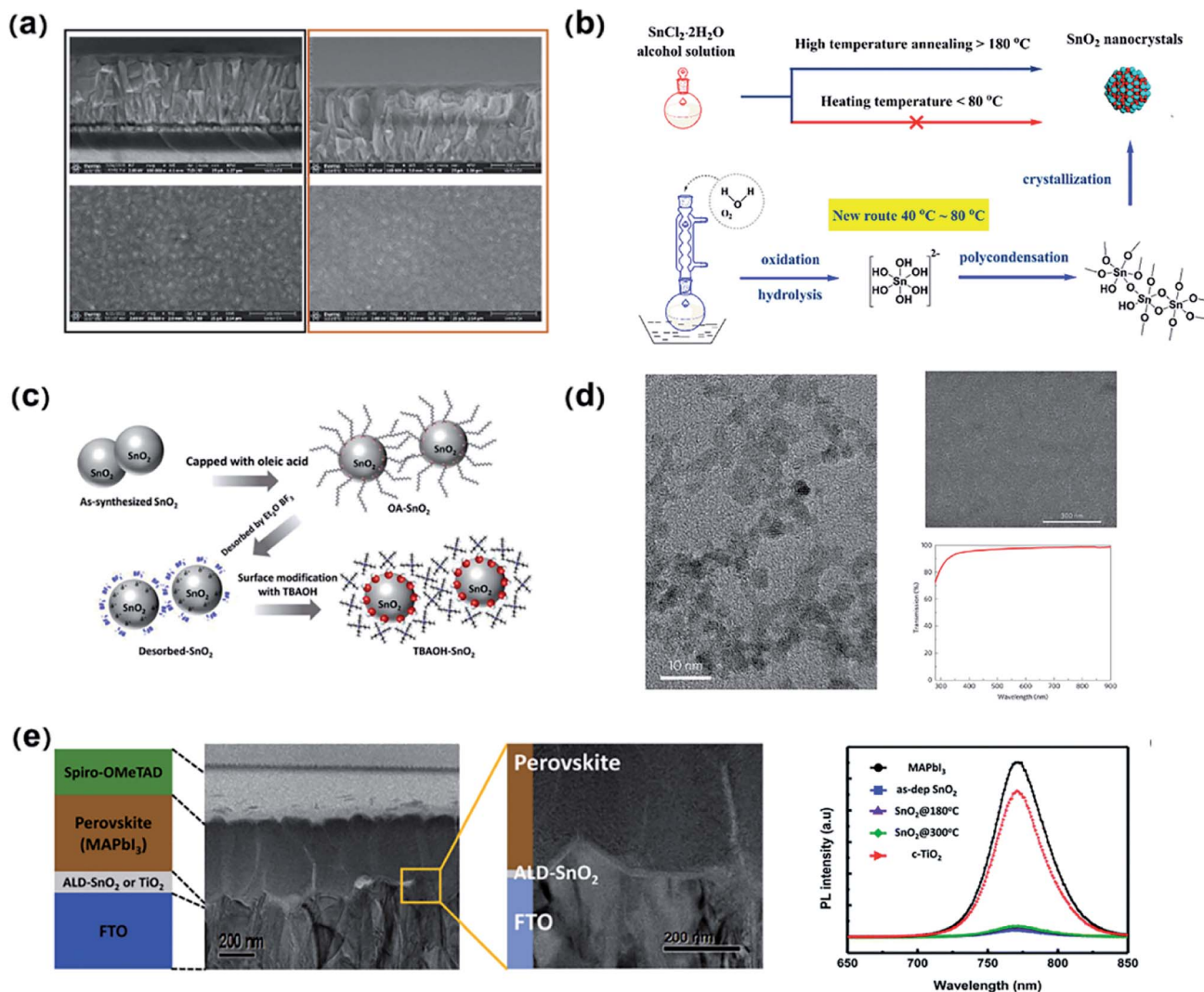


Fig. 4 (a) Cross-sectional and top-view SEM images (left) of the FTO/SnO₂ NC substrate and (right) FTO/Cl-SnO₂. Reproduced with permission.¹¹² Copyright 2020, Elsevier. (b) Schematic diagram of the wet chemical route to synthesize SnO₂ nanocrystals. Reproduced with permission.¹¹⁴ Copyright 2017, Elsevier. (c) Schematic illustration of the ligand exchange procedure for TBAOH-capped SnO₂ nanoparticles. Reproduced with permission.¹²⁴ Copyright 2017, ACS Publishing Group. (d) TEM and SEM images of SnO₂ nanoparticles and the transmission spectrum of SnO₂ films. Reproduced with permission.⁴⁴ Copyright 2017, Nature Publishing Group. (e) Device architecture and cross-sectional TEM images, and PL spectra of the device based on the ALD-SnO₂ films. Reproduced with permission.¹²⁵ Copyright 2019, Royal Society of Chemistry.

essential as it could substantially lower the Sn²⁺ oxidation and lead to the hydrolysis of SnCl₂·2H₂O alcohol solution, alternatively establishing an energetically favorable pathway for SnO₂ crystallization at low temperatures. The devices had a PCE and a steady-state PCE of 19.20% and 18.48%, respectively, which are significantly better than those of the devices based on high temperature annealed TiO₂ ETLs (16.61% and 15.03%).

2.1.3 SnO₂ nanoparticle synthesis method. It is an efficient method to prepare a compact SnO₂ film by depositing synthesized SnO₂ nanoparticles (NPs) for high performance PSCs.^{126,127} To reduce the recombination centers in the SnO₂ film, SnO₂ NPs should be washed prior to the removal of residuals after synthesizing SnO₂. The main issues for the utilization of SnO₂ NPs are the dispersibility and the choice of solvent. A suitable

solvent should be able to disperse NPs nicely and should not damage the perovskite layer.

Lee and co-workers selected tetrabutylammonium hydroxide (TBAOH) to successfully disperse SnO₂ NPs (TBAOH-SnO₂) well in ethanol *via* the ligand exchange method (Fig. 4c).¹²⁴ Using this TBAOH-SnO₂ NPs as ETL, the PSCs effectively reached up to 18.77% because of minor charge accumulation and good energy level alignment. Besides, the device with a TBAOH-SnO₂ NPs layer only reduced approximately 10% in PCE, which showed improved thermal stability by TBAOH treatment.¹²⁴ For SnO₂ deposition, the crystallinity and morphology of the SnO₂ films significantly relied on the annealing temperature.

Park and co-workers investigated the SnO₂ formation at different annealing temperatures (RT, 80 °C, 120 °C, 160 °C, and

200 °C). It was found that when SnO₂ was annealed at 120 °C, the champion PCE was obtained (19.0%). Using AFM and UPS, both the smooth surface and suitable band alignment of SnO₂ film deposition at low temperatures have been observed, contributing to obtaining a high PCE and long stability of the device.⁷³ However, traditional deposition of the SnO₂ film imposes restrictions on the substrate choice and commercial applications because of a relatively high temperature and/or a long-duration sintering step. Many scientists came up with other creative post-annealing processes to deal with this problem, including microwave-assisted annealing,¹²⁶ intense pulsed photonic annealing,¹²⁸ and UV-sintering methods.^{129,130}

2.1.4 SnO₂ colloidal precursor. You *et al.* formed a compact and uniform SnO₂ film by using a commercialized SnO₂ colloidal precursor (Fig. 4d).⁴⁴ The process was that the SnO₂ colloidal nanoparticle precursor was spin-coated at the medium speed rate on top of the ITO electrode. These substrates were annealed at 150 °C for 30 min to evaporate water. The device with SnO₂ film deposition at low temperatures initially achieved 19.9% certified efficiency. Later on, introducing a surface passivation layer of PbI₂ and an organic halide salt phenethylammonium iodide (PEAI) boosted the certified efficiency to 20.9%¹³¹ and 23.32%.³⁵ Tan and co-worker added KCl to the SnO₂ colloidal precursor to passivate the ETL/perovskite interface and at the grain boundaries by K/Cl ions (SnO₂-KCl).¹³² The strategy can enhance the *V*_{oc} from 1.077 to 1.137 V, and a corresponding PCE increased from 20.2% to 22.2% for the devices using SnO₂-KCl composite ETL.

2.2 Atomic layer deposition (ALD)

ALD is considered a promising deposition technique to fabricate ultra-thin and dense metal oxide layers with increased light transmittance based on a self-limiting surface reaction. Due to the precise control at the atomic level, the high-quality film of metal oxides has the merits of promoting charge transfer, suppressing the degradation caused by the external environment and internal ionic migration, and enhancing the photoelectric properties of the device.^{133,134}

Lee and co-workers prepared planar SnO₂-based PSCs using ALD by modulating the deposition and post-annealing temperatures. It was found that the post-annealing process can effectively passivate the perovskite and SnO₂ interface, leading to reduced charge recombination. As a result, SnO₂ based PSC with post-annealing achieved a PCE of 20% with high reproducibility and stability.¹³⁵ Grätzel and co-workers prepared an amorphous SnO₂ film by ALD, which can maintain its dense morphological characteristics even during the annealing process at 450 °C.⁸⁷

Jeong and co-workers deposited thin SnO₂ films by ALD with subsequent annealing at 180 °C as ETLs. In the cross-sectional image by transmission electron microscopy (TEM), the thicknesses of the SnO₂ film were around 12 nm, similar to those of TiO₂ (Fig. 4e). Compared with the c-TiO₂/MAPbI₃ sample, SnO₂@180 °C/MAPbI₃ showed a much decrease in PL intensity (≈ 94%), which exhibited an increase in photo-generated electron extraction from perovskite. Finally, PSCs based on SnO₂

with annealing at 180 °C showed the highest PCE (>18%) with better reproducibility.¹²⁵ Although ALD has these attractive advantages, it is necessary to deposit thin films under vacuum conditions and a matched operating space for scalable fabrication, resulting in high preparation costs.

2.3 Chemical bath deposition (CBD)

CBD is seen as a valuable technique to deposit a thin film of metal oxides as a buffer layer in photovoltaic cells, which has many advantages such as low fabrication cost, low-temperature process, suitability for different electrodes, and great reproducibility.¹³⁶⁻¹³⁸

Jun Hong Noh and co-workers prepared SnO₂ by CBD as ETL and employed poly(3-hexylthiophene) (P3HT) with gallium(III) acetylacetonate (Ga(acac)₃) additives. Consequently, they boosted the performance of free-doping PCE over 24% with a *V*_{oc} of 1.15 V and a FF of 83.8%. It also showed superior water-resistant property for 2000 h under 85% RH without any encapsulation.¹³⁹ Ko and co-workers fabricated a self-controlled SnO₂ through a convenient CBD.¹⁴⁰ It was found that the common-ion and precursor concentrations can effectively tune the growth of the SnO₂ film on FTO, leading to a uniform and compact SnO₂ layer. Finally, the device with a hydrolyzed SnO₂ layer presented an excellent PCE of 20.21%.

Yoo and co-workers first prepared SnO₂ as the ETL using CBD by controlling the formation of Sn intermediate species, which depended on the decomposition pathway of the Sn²⁺ precursor (SnCl₂), including four stages. Their SEM images of the SnO₂ layer showed that as the reaction time increases, the pH of the reaction solution increased, and the size of the SnO₂ domain increased from around 50 nm to about 100 nm. Especially, a SnO₂ layer formed a complete coverage on FTO at stage A-ii (pH 1.5), which can be observed from TEM images. The XRD confirmed the presence of various Sn intermediate species, which relied on the pH of the reaction solution (Fig. 5). Moreover, they added the MAPbBr₃ + MACl additive in perovskite to stabilize the intermediate phase, enhance the perovskite orientation, and introduce alkylammonium bromide for the 2D perovskite passivation. Due to the holistic method, they obtained a certified PCE of 25.2% (Table 1).³⁶ Despite the merits of simple operation and low cost, the quality of films in CBD is strongly determined by the processing parameters, including the temperature, concentration, and pH. In the meantime, the pollution of residual precursors after fabrication and the necessity for frequent bath replacement are also critical issues for the commercialization of PSCs.

2.4 E-beam evaporation

E-beam evaporation is one of the high vacuum techniques, which generates more compact films and minimal waste of resources in contrast to the spin-coating process and ALD, and is beneficial to the large-scale application and commercialization of PSCs.¹⁴¹

Ma and co-worker fabricated SnO₂ as ETL by e-beam evaporation for possible commercialization of PSCs with large-scale manufacture. As the SnO₂ target source evaporated, the e-beam

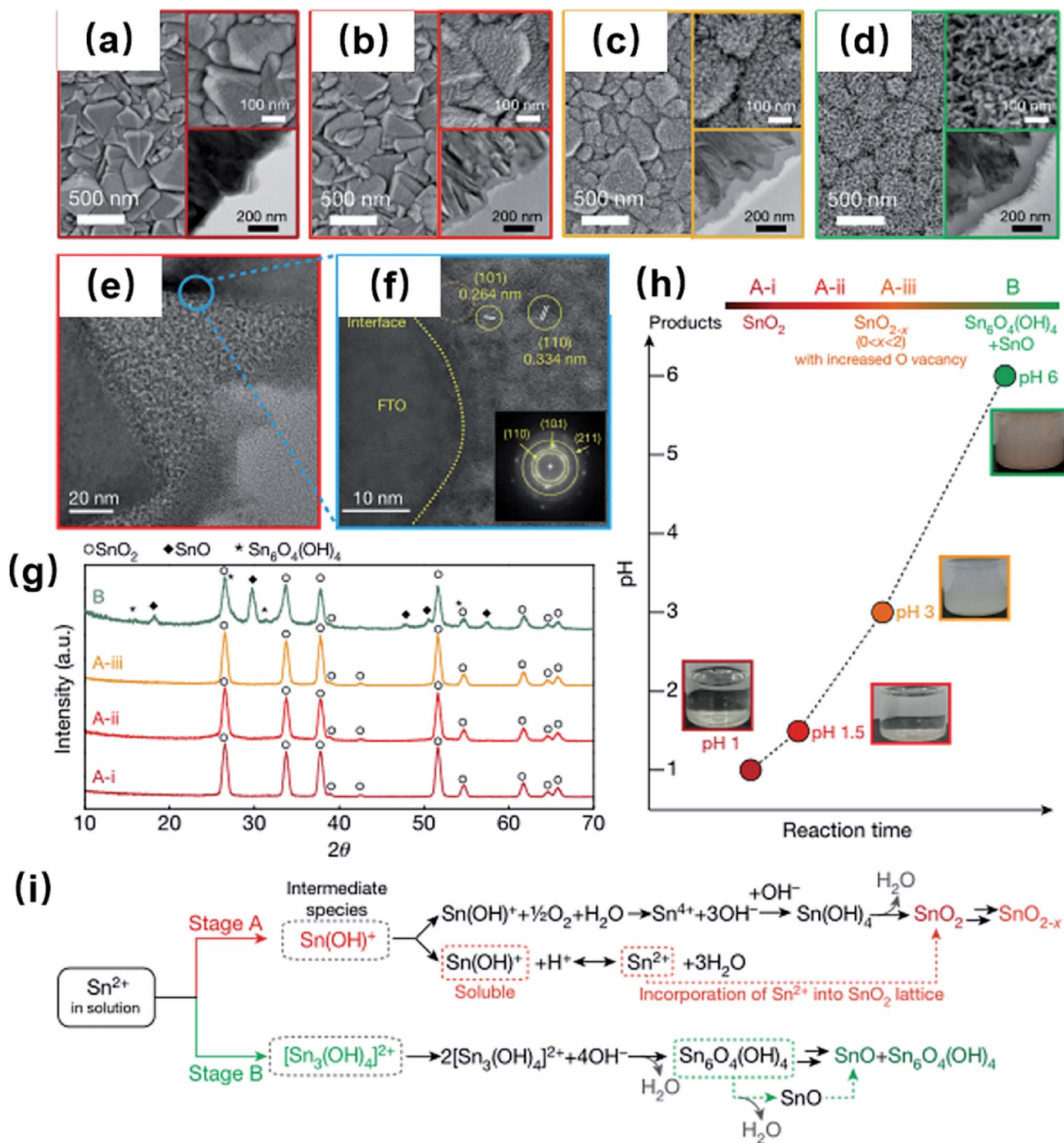


Fig. 5 (a–d) SEM images of SnO₂ at different stages: (a) A-i; (b) A-ii; (c) A-iii; and (d) B. The insets shown are SEM (top-right) and the corresponding cross-sectional TEMs (bottom-right). (e) and (f) High-resolution TEM images of SnO₂ at stage A-ii (the inset: a fast Fourier transform pattern of the TEM image). (g) XRD patterns of the SnO₂ films at different reaction stages. (h) Schematic illustration of the reaction progress with a photograph of the reaction solution at each stage. (i) Schematic illustration of the overall reaction mechanism for forming the SnO₂-based films. Reproduced with permission.³⁶ Copyright 2021, Nature Publishing Group.

evaporation process could simulate thousands of SnO₂ film substrates at one time by changing the position of the substrate holder. The advantages of e-beam evaporation were that the thickness and the crystallinity of the SnO₂ film could be controlled precisely. Consequently, the PSCs with a uniform SnO₂ film by e-beam evaporation demonstrated excellent performance of 18.2%

and remarkable waterproof, which retained 97% of its original efficiency value with a relative humidity of 85% for over 34 days.¹⁴² Despite the relatively high deposition rates, e-beam evaporation has the disadvantage of controlling the film composition precisely.

Later, to reduce the resistivity of SnO₂, Song and co-workers prepared SnO₂ ETL by e-beam evaporation combined with Zn

Table 1 Representative PSCs based on SnO₂ ETL fabricated by different preparation methods^a

| Device structure | Perovskite | Deposition method | Tin source | J_{sc} (mA cm ⁻²) | V_{oc} (V) | FF (%) | PCE (%) | Ref. |
|--|--|--------------------------------------|--|---------------------------------|--------------|--------|---------|------|
| ITO/SnO ₂ /PCBM:Bphen/perovskite/HTL(a)/Au | Cs _{0.04} FA _{0.92} MA _{0.04} PbI ₃ | Spin-coating | SnO ₂ colloidal precursor | 25.15 | 1.167 | 78.64 | 20.39 | 122 |
| ITO/SnO ₂ /perovskite/HTL(a)/Au | MAPbI ₃ | Spin-coating | SnCl ₄ | 23.2 | 1.12 | 71.4 | 18.6 | 112 |
| FTO/SnO ₂ /perovskite/HTL(a)/Au | MAPbI ₃ | Spin-coating | SnCl ₂ ·2H ₂ O | 22.88 | 1.06 | 82.54 | 18.89 | 123 |
| ITO/SnO ₂ /perovskite/HTL(a)/Au | Cs _{0.05} FA _{0.79} MA _{0.16} PbI _{2.45} Br _{0.55} | Spray-coating | SnO ₂ colloid dispersion | 22.2 | 1.17 | 76.1 | 19.8 | 100 |
| FTO/SnO ₂ :GQDs/perovskite/HTL(a)/Au | (FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} | Spray-coating | SnCl ₂ ·2H ₂ O | 22.5 | 1.12 | 65.8 | 17.08 | 99 |
| FTO/SnO ₂ /perovskite/HTL(a)/Au | MAPbI ₃ | Spray-coating | SnO ₂ colloid dispersion | 21.63 | 1.002 | 78 | 16.91 | 101 |
| ITO/SnO ₂ /perovskite/HTL(a)/Au | Cs _{0.05} (FA _{0.85} MA _{0.15}) _{0.95} Pb(I _{0.85} Br _{0.15}) ₃ | Slot-die-coating | SnO ₂ colloid dispersion | 22.60 | 1.148 | 79 | 20.50 | 103 |
| PEN/ITO/SnO ₂ /perovskite/HTL(a)/Ag | FA _x MA _y Cs _{1-x-y} Pb(I _z Br _{1-z}) ₃ | Roll-to-roll | SnO ₂ colloid dispersion | 19.96 | 1.07 | 70.09 | 16.60 | 104 |
| ITO/SnO ₂ /perovskite/HTL(a)/Ag | Cs/FA _x MA _{1-x} PbI _y Br _{3-y} | Blade-coating | SnO ₂ colloid dispersion | 23.1 | 1.08 | 72 | 18 | 106 |
| FTO/SnO ₂ /perovskite/HTL(a)/Au | CsPbI ₃ | Blade-coating | SnO ₂ colloid dispersion | 20.67 | 1.12 | 81.98 | 19 | 105 |
| ITO/SnO ₂ /perovskite/HTL(a)/Au | Cs _{0.10} FA _{0.75} MA _{0.15} Pb(Br _{0.15} I _{0.85}) ₃ | Inkjet-printing | SnCl ₂ ·2H ₂ O | 23.6 | 1.11 | 72 | 18.8 | 107 |
| FTO/SnO ₂ /perovskite/HTL(a)/Au | MAPbI ₃ | ALD | C ₈ H ₂₄ N ₄ Sn | 22.6 | 1.07 | 75.6 | 18.3 | 125 |
| FTO/SnO ₂ /TiO ₂ /perovskite/HTL(a)/Au | (FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} | ALD | C ₈ H ₂₄ N ₄ Sn | 22.67 | 1.13 | 78 | 20.03 | 135 |
| FTO/SnO ₂ /perovskite/HTL(a)/Au | FAPbI ₃ | CBD | SnCl ₂ ·2H ₂ O | 25.09 | 1.194 | 84.7 | 25.4 | 36 |
| FTO/SnO ₂ /perovskite/HTL(b)/Au | (FAPbI ₃) _{0.95} (MAPbBr ₃) _{0.05} | CBD | SnCl ₂ ·2H ₂ O | 25.5 | 1.15 | 83.8 | 24.6 | 139 |
| FTO/SnO ₂ /perovskite/HTL(a)/Au | Cs _{0.05} (MA _{0.17} FA _{0.83}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ | E-beam evaporation | SnO ₂ powders | 22.47 | 1.08 | 71 | 17.38 | 142 |
| FTO/Zn-SnO ₂ /perovskite/HTL(a)/Au | FA _x MA _y Cs _{1-x-y} Pb(I _z Br _{1-z}) ₃ | E-beam evaporation | SnO ₂ powders | 22.72 | 1.11 | 75 | 18.95 | 143 |
| FTO/SnO ₂ /perovskite/HTL(a)/Au | Cs _{0.06} MA _{0.27} FA _{0.67} PbI _{2.7} Br _{0.3} | Magnetron sputtering | SnO ₂ target | 23.7 | 1.08 | 79 | 20.2 | 148 |
| FTO/SnO ₂ /perovskite/HTL(a)/Au | FA _{0.85} MA _{0.15} Pb(I _{0.85} Br _{0.15}) ₃ | Magnetron sputtering | SnO ₂ target | 22.58 | 1.065 | 75.6 | 18.2 | 149 |
| FTO/SnO ₂ /PCBM/perovskite/HTL(a)/Au | MAPbI ₃ | PLD | SnO ₂ target | 21.51 | 1.11 | 73 | 17.29 | 164 |
| FTO/SnO ₂ /C ₆₀ -SAM/perovskite/HTL(a)/Au | MA _{0.7} FA _{0.3} PbI ₃ | PEALD | SnO ₂ target | 22.71 | 1.113 | 80.75 | 20.41 | 156 |
| ITO/SnO ₂ /PCBM/perovskite/HTL(a)/Ag | MAPbI ₃ | Electrodeposition | SnCl ₂ | 19.75 | 1.08 | 65 | 13.88 | 150 |
| FTO/SnO ₂ /perovskite/HTL(a)/Au | Cs _{0.05} (MA _{0.17} FA _{0.83}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ | Combustion | SnCl ₂ ·2H ₂ O | 23.85 | 1.122 | 78.2 | 20.92 | 165 |
| FTO/SnO ₂ /PCBM/perovskite/HTL(a)/Ag | MAPbI ₃ | CVD | SnCl ₂ | 14.7 | 1.03 | 67.51 | 10.2 | 159 |
| FTO/SnO ₂ /C60/perovskite/HTL(a)/Au | MAPbI ₃ | Electrospray | SnCl ₂ ·2H ₂ O | 23.7 | 1.103 | 77.3 | 20.2 | 163 |
| FTO/SnO ₂ /perovskite/HTL(a)/Au | Cs _{0.05} (MA _{0.17} FA _{0.83}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ | Hydrothermal | SnCl ₄ ·5H ₂ O | 22.69 | 1.129 | 72.70 | 18.62 | 117 |
| FTO/SnO ₂ /perovskite/HTL(a)/Au | MAPbI ₃ | Thermal evaporation | SnO ₂ powder | 23.36 | 1.04 | 69.2 | 16.79 | 161 |
| P-FTO/perovskite/HTL(a)/Au | MAPbI ₃ | <i>In situ</i> plasma etching of FTO | Commercial FTO substrate | 23.85 | 1.11 | 77.12 | 20.39 | 160 |
| FTO/G-SnO ₂ /C-SnO ₂ /perovskite/HTL(a)/Au | Cs _{0.05} (MA _{0.17} FA _{0.83}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ | Ball-milling | SnO ₂ powder | 21.16 | 1.22 | 80.09 | 21.09 | 158 |

^a HTL(a): spiro-OMeTAD; HTL(b): poly(3-hexylthiophene) (P3HT); C₈H₂₄N₄Sn: tetrakis(dimethylamido)tin(IV); GQDs: graphene quantum dots; CBD: chemical bath deposition; PLD: pulse laser deposition; ALD: atomic layer deposition; CVD: chemical vapor deposition; PEALD: plasma-enhanced atomic-layer deposition.

doping (Zn-SnO₂). Following Zn doping, the Zn-SnO₂ layer improved the charge mobility, inhibited the charge accumulation at the interface, and optimized the SnO₂ energy level structure, resulting in a PCE increase from 18.95% to 20.16% with long-term stability. More importantly, after 100 bending tests, the flexible device maintained a PCE of over 15% (Fig. 6a and b).¹⁴³ Furthermore, Li and co-workers used an oxygen

plasma-triggered e-beam evaporation approach to create SnO₂ films at ambient temperature without annealing. The oxygen plasma can precisely tune the stoichiometry of SnO₂ films in the evaporation process due to its intense oxidation activity, thereby endowing SnO₂ with uniformity, high transmittance, high Hall mobility, and good hydrophilicity.¹⁴⁴ Aside from the requirement

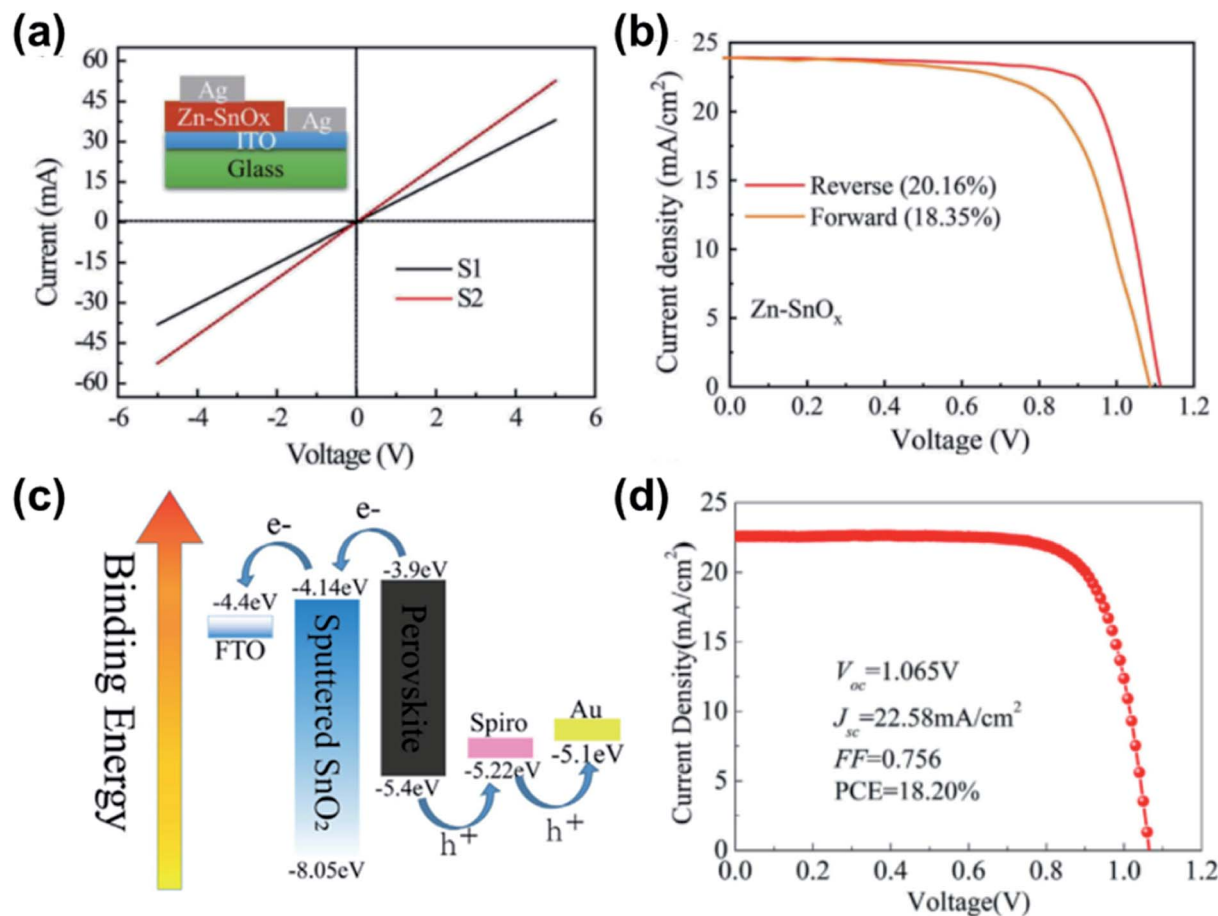


Fig. 6 (a) Conductivity of bare SnO_x (S1) and Zn-SnO_x (S2); (b) the reverse scan J - V curves of the device based on Zn-SiO_x. Reproduced with permission.¹⁴⁵ Copyright 2020, Wiley-VCH. (c) Energy level scheme for various layers in a sputtered SnO₂ based device. (d) J - V curves under the reverse voltage scan of the best device with sputtered SnO₂. Reproduced with permission.¹⁴⁹ Copyright 2019, Elsevier.

for a high vacuum, this approach is limited by X-ray damage on substrates and slow conduction speeds.

2.5 Magnetron sputtering

Magnetron sputtering is a mature and reliable deposition method with the use of low-cost metal-oxide targets to prepare metal-oxide thin films in the lab- and industrial-scale.^{145,146} SnO₂ particles are sputtered by high energy argon ions, react with the reaction gas (like high purity oxygen), and then deposited on the top of the FTO, which is a continuous process. Magnetron sputtering has excellent merits, including the precise control of film density and thickness, low waste of raw materials, a mild deposition process, and low production cost. Besides, the deposition process is usually operated in a high vacuum chamber, leading to high repeatability with minor damage to the natural environment.¹⁴⁷

Qiu and co-workers systematically investigated the chemical and physical characteristics of sputtered SnO₂. It played a significant role in the formation of high quality to control the oxidizing process. Through improvement in the device architecture, the device with sputtered SnO₂ ETL exhibited the champion PCE of 20.2% and a useful life of 625 h under T_{30} measurement,

confirming the enhanced conductivity of SnO₂.¹⁴⁸ Meanwhile, Bai and co-workers discovered that while changing the working gas ratio of Ar/O₂ can result in identical shape and crystallinity of sputtered SnO₂, it can also result in different trap states and carrier transit dynamics in PSC devices. The devices based on sputtered SnO₂ ETL demonstrated a champion PCE (up to 18.20%) (Fig. 6c and d).¹⁴⁹ Additionally, Otoufi and co-workers introduced sputtered SnO₂ on the TiO₂ layer to form TiO₂/SnO₂ bilayers to improve electron extraction further and achieve a better PCE of 12.3% in comparison with only TiO₂ as ETL (8.18%).¹⁴⁶ The gas flows played a crucial role in controlling the oxygen vacancies. On the other hand, tail states within the bandgap are caused by the amorphous or nanocrystallinity in the films, which are effectively suppressed by interface passivation.

2.6 Other deposition methods

Besides the solution-processable and vacuum evaporation methods, other creative methods are emerging for high-quality SnO₂ films due to demands for different applications. For example, Chen *et al.* prepared PSCs with SnO₂-ETLs by electrochemical deposition. The PSCs using MAPbI₃ as the light-absorbing layer obtained a PCE of 13.88% with negligible

hysteresis.¹⁵⁰ The electrochemical deposition was beneficial for SnO₂ preparation at low temperatures (50 °C) without introducing a seed layer or a post-treatment process.¹⁵¹ The dual-fuel combustion method was usually an excellent choice to control the SnO₂ growth.^{152,153} Compared to the conventional solution-process method, as combustion synthesis was ignited, the method not only requires significant external energy input but also is exothermic, leading to reduced production cost.

Additionally, other physical and chemical preparation technologies were also used to deposit SnO₂ ETLs, including plasma-enhanced atomic layer deposition (PEALD),^{154–157} high energy ball-milling,¹⁵⁸ chemical vapor deposition (CVD),¹⁵⁹ *in situ* plasma etching of FTO,¹⁶⁰ thermal evaporation,¹⁶¹ hydrothermal processes,^{117,162} and electro spray method.¹⁶³ In these methods, the SnO₂ film crystallized well during the deposition process on the substrates without further post-heating treatment. Thus, these methods demonstrate significant advantages for the mass production of flexible PSCs, even though the process tends to take much time.

3. Nanostructures of SnO₂

3D SnO₂ materials such as SnO₂ nanoparticles or nanocrystals are commonly exploited as ETL.⁸³ However, Zhao *et al.* found that 0D–2D SnO₂ ETLs can reduce light scattering from rough FTO and enlarge the perovskite grain size, leading to improved performance.¹⁶⁶ Nanostructured SnO₂ is a critical factor for high-efficiency PSCs to scale up planar PSCs for industrial applications. On the one hand, it can optimize the surface wettability for smooth perovskite coverage on the substrate. On the other hand, nanostructured SnO₂ (Fig. 7) enhances the interfacial contact to eliminate the notorious electronic trap states, which removes the energy level traps at the interface. So, the dimensional control of SnO₂ is a promising strategy to prepare SnO₂ ETL with a high photoelectrical property.

3.1 SnO₂ nanowires

SnO₂ nanowires (NWs), a one-dimensional (1D) semiconductor material, are a good ETL in the field of PSCs due to their

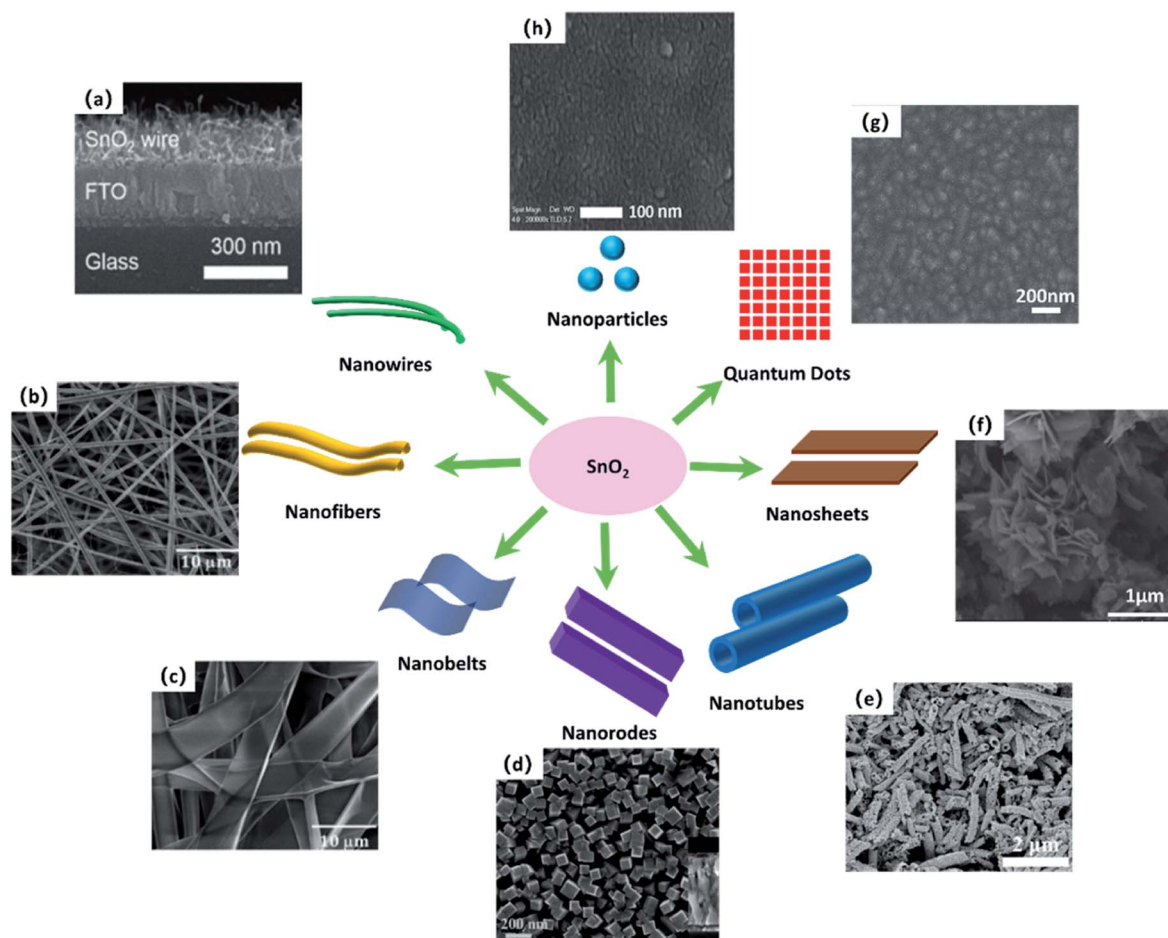


Fig. 7 Schematic diagram of various nanostructures of SnO₂ in accordance with SEM images of various SnO₂ nanostructures: (a) nanowires reproduced with permission.¹⁶⁷ Copyright 2015, Royal Society of Chemistry. (b) Nanofibers and (c) nanobelts. Reproduced with permission.¹⁶⁸ Copyright 2018, Royal Society of Chemistry. (d) Nanorods. Reproduced with permission.¹⁶⁹ Copyright 2018, Wiley-VCH. (e) Nanotubes. Reproduced with permission.¹⁷⁰ Copyright 2020, Elsevier. (f) Nanosheets. Reproduced with permission.¹⁷¹ Copyright 2016, Elsevier. (g) Quantum dots. Reproduced with permission.⁹⁵ Copyright 2018, Wiley-VCH; (h) nanoparticles. Reproduced with permission,⁸³ Copyright 2015, ACS Publishing Group.

efficient extraction and collection capacity. Besides, 1D nanomaterials have fewer defects like grain boundaries which significantly decrease in dead-ends.^{172–176}

Han and co-workers synthesized 1D SnO₂ as the ETL by a vapor–liquid–solid (VLS) reaction for realizing high conductivity for SnO₂ (Fig. 7a). The SnO₂ NWs showed a high transmittance of about 80%, similar to that of the bare FTO substrate, as observed from the UV-vis transmittance spectrum. SnO₂ NWs were modified with TiO₂ nanoshells as TiO₂/SnO₂ NW ETL *via* plasma-enhanced atomic layer deposition (PEALD). Consequently, the TiO₂/SnO₂ NW ETL device displayed over 95% absorbed photon-to-current conversion efficiency (APCE) at 750 nm with a PCE of 14.2% and decreased the electron transport time by one order of magnitude in comparison with that of mp-ETL-based devices.¹⁶⁷

3.2 SnO₂ nanofibers and nanobelts

1D SnO₂ nanofibers (NFs) and nanobelts (NBs) demonstrate fast electron transport rate and light scattering ability used in the dye-sensitized solar cells (DSSCs).^{177–179} Mali and co-workers prepared SnO₂ NFs and NBs with a smooth and uniform morphology as ETL *via* the electrospinning technique.¹⁶⁸ The pure tetragonal rutile phase in SnO₂ NFs and NBs was presented by structural analysis. SEM micrographs exhibited that both the lengths of SnO₂ NFs and NBs reached up to 500 μm with a diameter of about 450–500 nm and a thickness of 180–200 nm, respectively (Fig. 7b and c). Their optimized devices yielded a PCE of >16% based on SnO₂ NBs with good shelf-life stability.¹⁶⁸

3.3 SnO₂ nanorods

Due to a particular open porous structure, SnO₂ nanorods (NRs) provide more expansive space to effectively fill the pores with the perovskite crystals^{180–183} and enhance the light-induced photo utilization of the perovskite layer with good light scattering ability.¹⁸⁴

Xu and co-workers reported good crystalline SnO₂ NRs as the ETL with a high aspect ratio through the sophisticated solvothermal approach to promote PSCs' stability and photovoltaic performance. They showed that oleic acid (OA) ligands could precisely control the length and the diameter of SnO₂ NRs without complex treatments. Besides, the insulating OA ligands had a weaker impact on the electron mobility of SnO₂ NRs than on TiO₂ NRs. The OA-capped SnO₂ NRs ETL-based PSCs with a planar structure achieved the best efficiency of over 18%, which was much higher than that of PSCs with an OA-capped TiO₂ NR ETL (14.27%).¹¹⁷ Zhang *et al.* prepared the *in situ* SnO₂ NRs as ETL *via* a convenient hydrothermal method in an acidic solution.¹⁶² The average diameters of SnO₂ NRs increased from 15 to 25 nm by controlling the precursor concentration, and the corresponding area density drops down to several hundreds of μm⁻². Later on, to simplify the SnO₂ NR fabrication process and remove the OA ligand, Lv and co-workers reported a facile hydrothermal method to synthesize highly crystalline SnO₂ SRs with good light-harvesting ability (Fig. 7d). In the hydrothermal process, the reaction time and temperature are

vital process parameters that determine the morphology of SR, such as the length and the diameter. In addition, a TiO₂ interlayer was inserted between the perovskite absorber layer and the SnO₂ ETL, forming a graded heterojunction configuration, leading to the power output of up to 18.7% with better ambient stability and repeatability.¹⁶⁹

3.4 SnO₂ nanotubes

SnO₂ nanotubes (NTs) as ETL have higher conductivity and a required conduction band edge (3.6 eV) that can induce superior electrochemical properties than TiO₂ (3.2 eV) (Fig. 7e).^{185–188} Gao and co-workers created SnO₂ NTs as ETL *via* an *in situ* template self-etching strategy. The ZnO₂ nanorods as sacrificial templates were covered by smooth nanoporous SnO₂ shells by spin coating. The corresponding EQE spectrum suggested that SnO₂ NTs based PSCs exhibited a high photocurrent of 15.9 mA cm⁻² with a stable efficiency of 12.1% in more than 1000 s under simulated light illumination.¹⁸⁹

3.5 SnO₂ nanosheets

The SnO₂ nanosheets (NSs) demonstrate lots of advantages such as improving photo-induced carrier collection, promoting interfacial charge transfer, and processing good weathering performance of PSCs.^{163,171,190–192}

Hydrothermal growth is a standard method to synthesize SnO₂ nanosheets. Zhou and co-workers prepared SnO₂ NSs as ETL *via* the hydrothermal method in place of the traditional mesoporous TiO₂ layer in PSCs for the first time (Fig. 7f). The device achieved a maximum efficiency of over 7% by optimizing the perovskite's crystallization time and treating it with TiCl₄ aqueous solution.¹⁷¹ Liu and co-workers deposited a mesoporous layer of SnO₂ NSs on a thin, compact SnO₂ layer by using the low-temperature hydrothermal method to improve the PSC stability. The device with the highest efficiency of 16.17% was obtained through such a facile method and retained 90% of its initial PCE value in ambient after 130 d of storage without encapsulation.¹⁹⁰ To optimize the interfacial contact with the perovskite, doping with yttrium and introduction of a C₆₀ interlayer are done in SNS ETL-based devices. Yang and co-workers synthesized a yttrium-doped SnO₂ (Y-SnO₂) as ETL *via* an *in situ* hydrothermal approach at 95 °C. As a result, the Y-SnO₂ based PSC achieved a champion PCE of 17.29% with free hysteresis.

Furthermore, it clearly showed that SnO₂ nanosheet films demonstrated a slightly wider bandgap and a more homogeneous distribution of SnO₂ nanosheet arrays after Y-doping.¹⁹² The introduction of a C₆₀ interlayer (Y:SnO₂) between SNS ETL and perovskite was reported by Wu.¹⁹¹ They found that the C₆₀ interlayer can tune the energy level matching, reduce the charge accumulation and thus prolong the electron lifetime and enhance the V_{oc}. The champion PCE obtained was 18.31%, and the device with C₆₀-NSs preserved over 90% of its champion PCE after 500 h of storage at RT in open air.

3.6 SnO₂ quantum dots

Due to the low crystallinity, inferior electron mobility at lower annealing temperatures as well as instability of the SnO₂ film

deposited *via* colloidal SnO₂ solution, many researchers synthesized high-crystallinity SnO₂ quantum dots (QDs) as ETL by a facile mild solution method combined with spin coating on FTO to improve the light scattering and electron transport and reduce the charge recombination, leading to a dramatic increase in PCE.^{193–197}

Yang and co-workers reported colloidal SnO₂ QDs as ETLs by a facile and repeatable two-step solution-processable method (Fig. 7g). First, they obtained the low concentration of SnO₂ QDs solution by controlling the amount of thiourea in the SnCl₂·2H₂O water solution, and then spin-coated SnO₂ QDs and changed the annealing temperature to eliminate a mass amount of thiol- and amino-groups, leading to an appropriate energy level matching and changeable carrier dynamics. Finally, the planar PSCs with SnO₂ QDs ETLs achieved a maximum power output of over 20% for the planar PSCs.⁹³ Vijayaraghavan and co-workers chose SnO₂ QDs as ETL to replace the commonly used mesoporous TiO₂ owing to their excellent electron extraction and hole blocking ability. For low-cost production and superior stability in air for PSCs, they designed the structure of glass/ITO/SnO₂ QDs/perovskite/carbon as HTL-free PSCs and deposited carbon electrodes *via* low-temperature curing to substitute the widely used vacuum-deposition. As a result, the highest power output of 13.64% was obtained.¹⁹⁸ Wang and co-workers used SnO₂ QDs as ETL, which was combined with potassium hexafluorophosphate (KPF6) treatment. KPF6 had the dual-passivation in which organic cation groups were reoriented or redistributed *via* the strong hydrogen bonds between the PF₆[−] group and organic cations. Moreover, KPF6 passivated the interfacial traps to suppress the energy level traps to improve the conductivity of SnO₂ through the solid ionic bonds between the PF₆[−] group and Sn⁴⁺/Sn²⁺.¹⁹⁹

4. Passivation strategies of SnO₂ ETLs

Although SnO₂ films have several advantages over other metal oxide films, they also have comparable interface difficulties when used as the ETLs of PSCs. There are many flaws at the interfaces due to the bungle between the metal oxides and perovskite films, which degrade the presentation of PSCs. Therefore, passivations on the SnO₂ film are often used to improve the performance of SnO₂ based perovskite solar cells that include elemental doping, bilayer design, and interface modification. The following are the consequences on passivation: (1) tuning of the energy level that promotes electron transfer at the ETL/perovskite interface; (2) passivation of the interfacial defects and suppress nonradiative recombination; (3) control of the crystallization process and improvement of the crystallinity of the perovskite film; and (4) endowing devices with improved humidity tolerance and long-term stability.

4.1 Elemental doping

Owing to intrinsic defects such as Sn interstitials or O vacancies, there is serious charge recombination and contact resistance at the interface between SnO₂ ETL and perovskite, resulting in a low charge transportation rate.^{200–203} To suppress the traps on the SnO₂ film as well as for better energy-level alignment, the researchers demonstrated several halides and metal ions as dopants to improve the conductivity properties of ETL including the halogen ions (Cl[−]^{204–206} and F[−]^{207–211}), metal ions (Li⁺^{212–215} Mg²⁺^{196,216} Al³⁺^{217,218} Zn²⁺^{143,219} Sb³⁺^{215,220,221} Mo²⁺²²² Ru²⁺^{209,223} Ga³⁺^{224,225} Zr²⁺^{226,227} Nb⁵⁺^{228–230} and Ta⁵⁺²³¹) and rare earth ions (Y³⁺^{192,232} La³⁺²³³) and Nd³⁺¹⁶⁵ (Table 2).

Gong and co-workers introduced Cl in SnO₂ nanoparticles (SnO₂-Cl) with a chloroform-D/2-methoxy ethanol solvent (Fig. 8a).²⁰⁵ The SnO₂-Cl film had a hydrophobic surface as the

Table 2 Representative PSCs based on elemental doped SnO₂ ETL

| Doped element | Doping raw material | Device architecture | Perovskite | PCE (%) | Ref. |
|------------------|--|--|--|---------|------|
| Cl [−] | Chloroform-D/2-methoxy ethanol solvent | FTO/Cl-SnO ₂ /perovskite/spiro-OMeTAD/Au | (FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} | 18.1 | 205 |
| F [−] | NH ₄ F | FTO/F-SnO ₂ /perovskite/spiro-OMeTAD/Au | (FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} | 20.2 | 207 |
| Li ⁺ | Li-TFSI | FTO/SnO ₂ /Al ₂ O ₃ /perovskite/spiro-OMeTAD/carbon | MAPbI ₃ | 10.01 | 214 |
| Mg ²⁺ | MgAc·4H ₂ O | FTO/Mg-SnO ₂ /perovskite/spiro-OMeTAD/Au | MAPbI ₃ | 19.21 | 196 |
| Al ³⁺ | Al(NO ₃) ₃ | FTO/Al-SnO ₂ /perovskite/spiro-OMeTAD/Au | Cs _{0.05} (MA _{0.17} FA _{0.83}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ | 17.66 | 218 |
| Zn ²⁺ | ZnCl ₂ | FTO/ZnSnO ₂ /perovskite/CuPc/carbon | Cs _{0.05} FA _{0.79} MA _{0.16} PbI _{2.5} Br _{0.5} | 17.78 | 143 |
| Sb ³⁺ | SbCl ₃ | ITO/Sb-SnO ₂ /perovskite/spiro-OMeTAD/Au | Cs _{0.05} (FA _{0.85} MA _{0.15}) _{0.95} Pb(I _{0.85} Br _{0.15}) ₃ | 20.73 | 221 |
| Mo ⁵⁺ | MoCl ₅ | FTO/Mo-SnO ₂ /perovskite/spiro-OMeTAD/Au | MAPbI ₃ | 10.52 | 222 |
| Ru ²⁺ | RuCl ₃ ·5H ₂ O | FTO/Ru-SnO ₂ /perovskite/spiro-OMeTAD/Au | Cs _{0.05} (MA _{0.10} FA _{0.90}) _{0.95} Pb(I _{0.90} Br _{0.10}) ₃ | 22.0 | 223 |
| Ga ³⁺ | Ga(NO ₃) ₃ ·6H ₂ O | ITO/Ga-SnO ₂ /perovskite/spiro-OMeTAD/Ag | (FAPbI ₃) _{0.97} (MAPbBr ₃) _{0.03} | 18.18 | 224 |
| Zr ²⁺ | ZrCl ₂ ·8H ₂ O | ITO/Zr-SnO ₂ /perovskite/spiro-OMeTAD/Au | (FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} | 19.54 | 226 |
| Nb ⁵⁺ | NbCl ₅ | FTO/Nb-SnO ₂ /perovskite/spiro-OMeTAD/Au | FA _{0.75} MA _{0.2} Cs _{0.05} Pb(I _{0.14} Br _{0.86}) ₃ | 20.5 | 228 |
| Ta ⁵⁺ | TaCl ₅ | ITO/Ta-SnO ₂ /perovskite/spiro-OMeTAD/Au | Cs _{0.05} (MA _{0.10} FA _{0.90}) _{0.95} Pb(I _{0.90} Br _{0.10}) ₃ | 20.8 | 231 |
| Y ³⁺ | Y(OC ₄ H ₉) ₃ | FTO/Y-SnO ₂ /perovskite/spiro-OMeTAD/Au | Cs _{0.05} (MA _{0.15} FA _{0.85}) _{0.95} Pb(I _{0.85} Br _{0.15}) ₃ | 20.71 | 232 |
| La ³⁺ | LaCl ₃ ·5H ₂ O | FTO/La-SnO ₂ /perovskite/spiro-OMeTAD/Au | MAPbI ₃ | 17.08 | 233 |
| Nd ³⁺ | Nd(NO ₃) ₃ ·6H ₂ O | FTO/Nd-SnO ₂ /perovskite/spiro-OMeTAD/Au | Cs _{0.05} (MA _{0.17} FA _{0.83}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ | 20.92 | 165 |

effect of Cl, which increased the grain size of perovskite crystals (Fig. 9). Furthermore, $\text{SnO}_2\text{-Cl}$ as an ETL dramatically reduced the electron trap density and inhibited the charge recombination. In contrast to untreated SnO_2 based PSCs, $\text{SnO}_2\text{-Cl}$ based PSCs achieved a PCE of 18.1%, with significant improvements in J_{sc} and reduced hysteresis. Later, Wang *et al.* reported F-doped SnO_2 (F: SnO_2) nanocrystals as the ETL by spin-coating $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and NH_4F solution onto fresh FTO substrates in a facile solution-processable method at low temperatures (Fig. 8b).²⁰⁷ They found that the band offset between the ETL and the perovskite absorber is related to the F doping level in SnO_2 nanocrystals; the band offset was effectively tailored by doping F into the SnO_2 film, which led to an increasing built-in electric field for maximizing the V_{oc} and charge collection simultaneously. Consequently, a champion PCE of 20.2% with a V_{oc} of 1.13 V can be obtained for n-i-p planar PSCs using an F-doped SnO_2 bilayer ETL.

Jung and coworkers reported doped SnO_2 NPs by Zr element, improving the multiple optoelectronic properties of SnO_2 (Fig. 8c). Zr doping reduced the current leakage and suppressed the charge recombination, facilitating the interfacial transfer between the ETL and the perovskite layer. Consequently, they obtained the best PCE of 19.54% with reduced hysteresis. The research demonstrated that the controlled Zr-doping SnO_2 film

led to adjusted energy levels, increased electrical conductivities, and decreased surface defect densities for optimal interface properties of PSCs.²²⁶ Some other elements also showed similar positive results.^{209,214,223,231}

Fang and co-workers designed a Zr/F co-doped SnO_2 ETL due to its low conduction band position and limited intrinsic carriers; they found that the doping of Zr can increase the CB of SnO_2 for higher V_{oc} , which decreased the energy traps in electron extraction and restrained the interface recombination between the ETL and the perovskite (Fig. 8d). Moreover, as n-type doping, F doping endowed SnO_2 with a mass of free electrons and facilitated the conductivity of the ETL for improvement in short-circuit current (J_{sc}). With the merits of Zr/F co-doping, the device boosted the PCE by over 19% with free hysteresis, which surpassed the undoped device. This result demonstrated the effect of Zr/F co-doping on the regulation of energy level match and conductivity of SnO_2 .²³⁴

4.2 Bilayer ETLs

A mass of pinholes and cracks appear in the SnO_2 film during the fabrication process. The traps reduce the current leakage energy and retard the carrier transfer at the interface, resulting in current leakage in PSCs and a poor photovoltaic

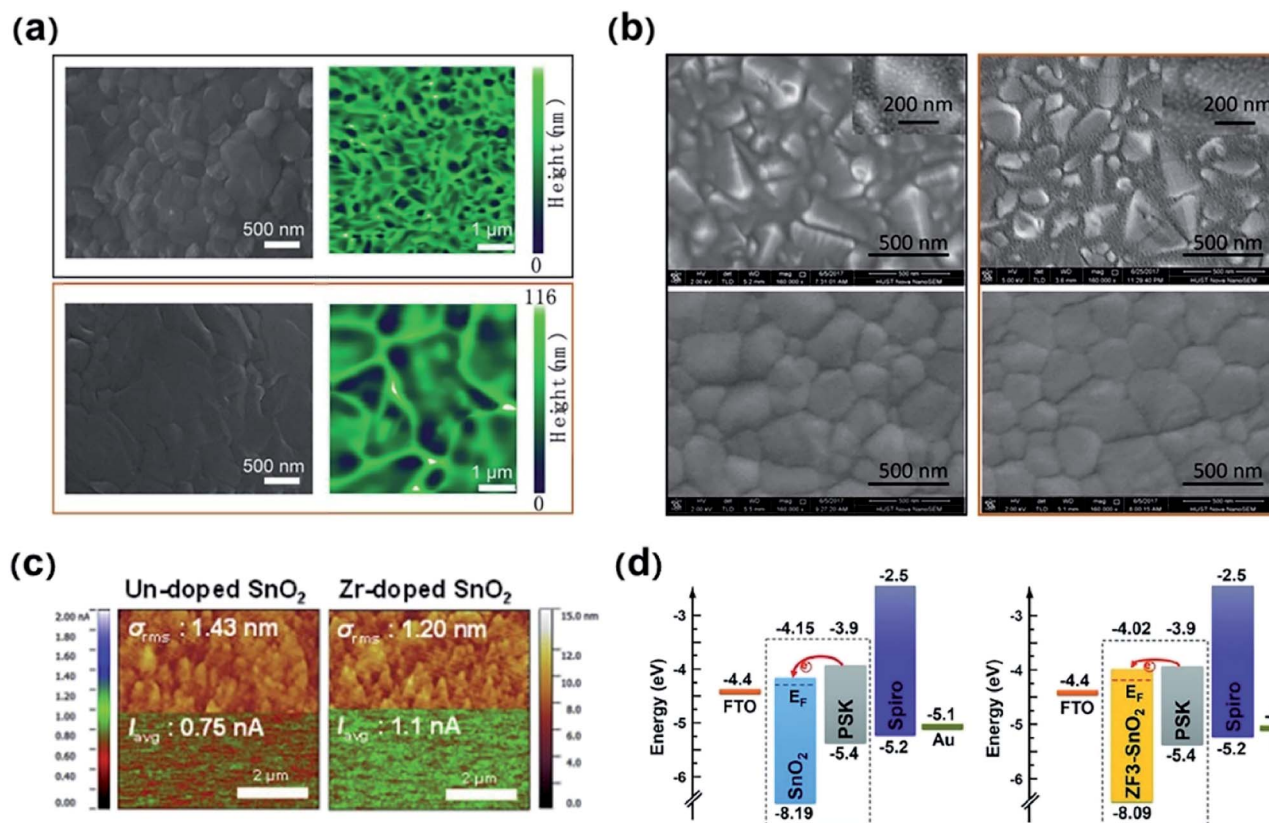


Fig. 8 (a) Top view SEM images and AFM images of perovskite films on (up) FTO/ SnO_2 and (down) FTO/ $\text{SnO}_2\text{-Cl}$. Reproduced with permission.²⁰⁵ Copyright 2020, Royal Society of Chemistry. (b) SEM images of (left) SnO_2 and its perovskite (right) F: SnO_2 and its perovskite. Reproduced with permission.²⁰⁷ Copyright 2020, ACS Publishing Group. (c and a) AFM and c-AFM images (bottom) of SnO_2 NPs thin films with and without Zr-doping. Reproduced with permission.²²⁶ Copyright 2019, Elsevier. (d) Schematic of the energy level arrangement for the pristine SnO_2 device and the Zn/F doped- SnO_2 device. Reproduced with permission.²³⁴ Copyright 2020, Wiley-VCH.

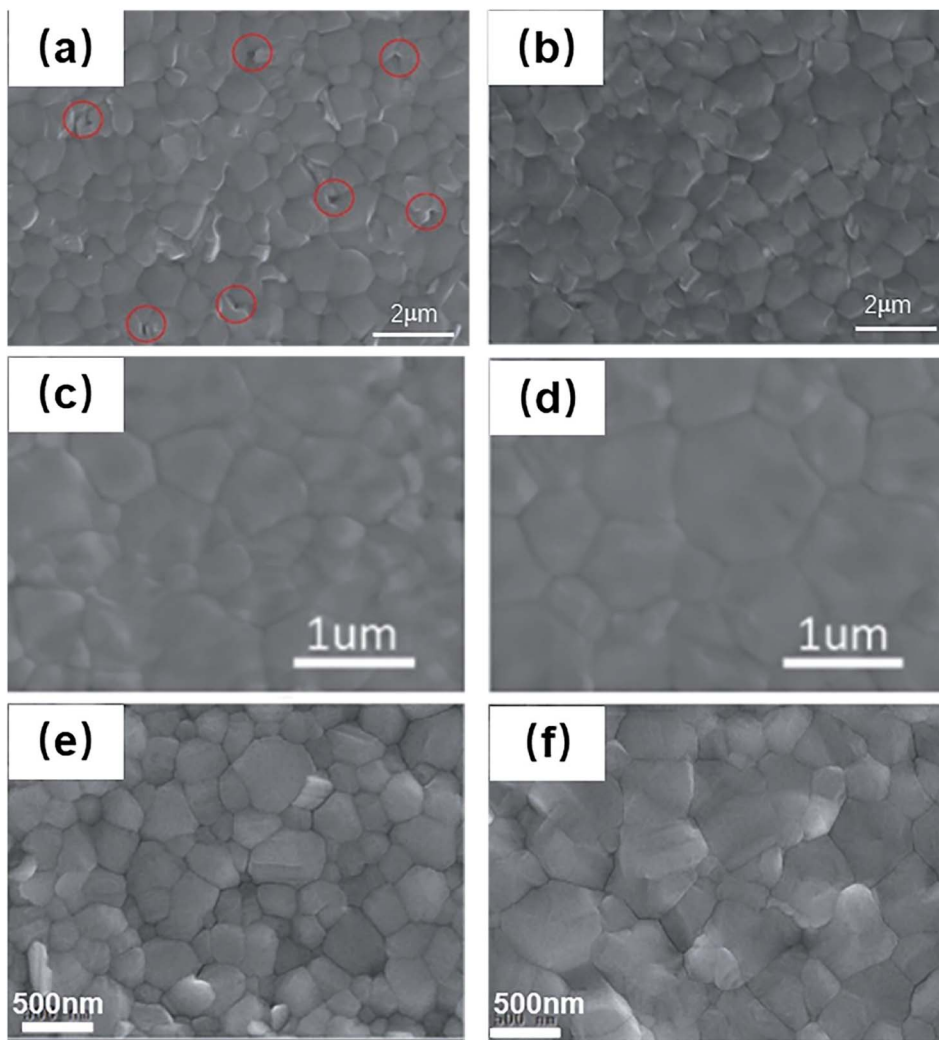


Fig. 9 Top-view SEM images of perovskite films deposited on SnO₂ and SnO₂/metal oxide ETLs. (a) SnO₂ and (b) In₂O₃/SnO₂. Reproduced with permission.²⁴⁵ Copyright 2020, Wiley-VCH. (c) SnO₂; (d) WO_x/SnO₂. Reproduced with permission.²⁴⁶ Copyright 2019, Elsevier B.V. (e) P-SnO₂; (f) B-SnO₂. Reproduced with permission.²⁴⁷ Copyright 2021, Wiley-VCH.

performance. Bilayer ETLs based on SnO₂ films combined with a thin layer of metal oxide (*i.e.* TiO₂,^{235,236} Al₂O₃,^{214,237} Ga₂O₃,²³⁸ ZnO,^{239–242} SnO₂^{122,221} and ZnTiO₃²⁴³) or organic transporting materials (PCBM and C₆₀) are used to suppress the interface and bulk defects and charge recombination.

4.2.1 SnO₂/metal oxide ETLs. In n-i-p PSC devices, bilayers of metal oxide composite structures are massively used as ETLs. For example, considering the advantages of the high electron mobility of SnO₂ ($\approx 10^{-3}$ cm² V⁻¹ s⁻¹) compared with that of TiO₂ ($\approx 10^{-5}$ cm² V⁻¹ s⁻¹) and the high reproducibility of TiO₂ ETLs, Mali and co-workers selected SnO₂ coated c-TiO₂ bilayer ETLs. Owing to its high conductivity, SnO₂ occupied the defect sites, which can suppress the surface traps of the TiO₂ film, leading to efficient electron extraction from the perovskite absorber. Meanwhile, the high mobility of the SnO₂ interfacial layer played a role in maintaining the charge balance of the PSC.²⁴⁴

Wang and co-workers reported a convenient low-temperature process to prepare an In₂O₃/SnO₂ bilayer as the

ETL (Fig. 9a and b). The introduction of In₂O₃ was beneficial to the formation of smooth, dense, and low-defect-density perovskite films. Besides, the CB of In₂O₃ was lower than that of Sn-doped In₂O₃ (ITO), facilitating the charge transfer at the interface between perovskite and the ETL, thus reducing the V_{oc} loss. The device with a PCE of over 23% was achieved, and a high V_{oc} of 1.17 V was obtained with the potential loss (0.36 V). Additionally, the PSC retained 97.5% initial PCE after 80 days in a N₂ atmosphere without encapsulation and maintained 91% of its original PCE after 180 h under 1 AM illumination.²⁴⁵

Wang and co-workers proposed an amorphous WO_x/SnO₂ hybrid ETL to effectively block holes through the defects of the SnO₂ film to ITO, thereby promoting the charge extraction and reducing the electron-hole recombination at the interface (Fig. 9c and d). Moreover, due to the appropriate energy-level alignment and high conductivity, they also obtained better electron transfer channels. In contrast to flexible PSCs with a single SnO₂ ETL, the PSCs with an amorphous WO_x/SnO₂

hybrid ETL showed a better PCE of 20.52%. Moreover, the WO_x/SnO_2 preparation process was at a temperature below 150 °C.²⁴⁶

Ye and co-workers proposed a bilayer ETL consisting of two different SnO_2 films at a low temperature (70 °C), combined with various amounts of NH_4Cl as additives (Fig. 9e and f). The novel SnO_2 bilayer tuned the bandgap alignment at the SnO_2 /perovskite interface and reduced strain in the perovskite film growth, which resulted in negligible carrier recombination, high conductivity, and low voltage loss. Finally, the best device with a doped SnO_2 bilayer ETL achieved a photovoltaic performance of 21.75% and strongly increased the V_{oc} up to 1.21 V with negligible hysteresis.²⁴⁷

4.2.2 SnO_2 /fullerene derivative ETLs. Fullerene and its derivatives with efficient charge extraction are commonly used as the ETL in p-i-n planar PSCs, including C_{60} and phenyl- C_{61} -butyric acid methyl ester (PC_{61}BM).^{157,248–257} Owing to the drawbacks of SnO_2 in inefficient charge extraction and interfacial charge recombination, many researchers have tried to deposit the SnO_2 film combined with fullerenes or its derivatives as a bilayer to eliminate the issues in achieving efficient and stable PSCs.

Tian and co-workers used 2,5-diphenyl- C_{60} -fulleropyrrolidine (DPC_{60}) to passivate the defects on the SnO_2 film surface, forming a $\text{SnO}_2/\text{DPC}_{60}$ bilayer structure as the ETL in PSCs (Fig. 10a, b and c). DPC_{60} can reduce charge

recombination in the interface of SnO_2 /perovskite and offer an appropriate band edge alignment, which led to electron transfer from the perovskite absorber to the FTO electrode. As a result, this reveals that electron extraction can be improved *via* modification on the perovskite/ SnO_2 interface with (DPC_{60}). The PCE of 20.4% was obtained for PSCs based on the $\text{SnO}_2/\text{DPC}_{60}$ bilayer, which was higher than that of 18.8% PSCs based on a single SnO_2 film.²⁵⁸

Later on, Raiford and co-workers reported an ultrathin (2 nm) layer of polyethyleneimine ethoxylate (PEIE) to functionalize the surface of C_{60} for the subsequent preparation of SnO_2 by ALD as an electron contact bilayer for p-i-n PSCs. They first used Auger electron spectroscopy (AES) mapping to shed light on the effect of PEIE on SnO_2 nucleation in C_{60} . Through a series of testing conditions in the air atmosphere with simultaneous stressors of heat and illumination, improved nucleation contributed to more stable PSCs. These devices got a high initial PCE of 18.5% with 40% improvement in stability over devices with $\text{C}_{60}/\text{SnO}_2$ contacts without modification with PEIE following a continuous operation at 60 °C unencapsulated in the ambient environment for 250 h.²⁵⁹

In recent, Palmstrom and co-workers investigated the impacts of SnO_2 on the perovskite film and explored the role of C_{60} as an organic electron extractor at the interface. Furthermore, they offered strategies to remove the C_{60} layer at the perovskite/ SnO_2

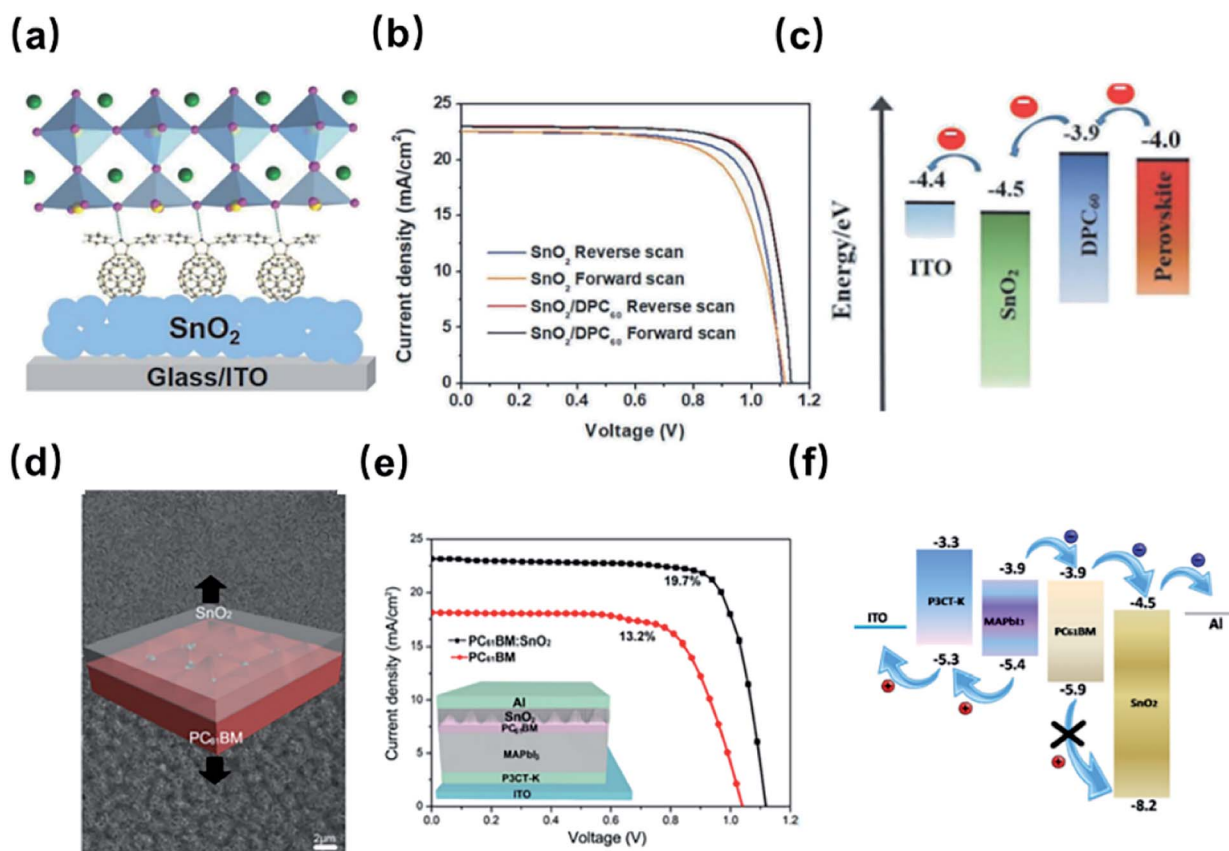


Fig. 10 (a and d) Illustrations of the interfacial treatment. (b and e) Forward and reverse scan J - V curves of devices with and without interfacial modification. (c and f) Energy band diagram of PSCs; (a–c) Reproduced with permission.²⁵⁸ Copyright 2020, Wiley-VCH. (d–f) Reproduced with permission.²⁶⁵ Copyright 2018, ACS Publishing Group.

interface.²⁶⁰ Organic extraction layers reduced the mechanical strength and endowed the perovskite/C₆₀ interface with mechanical defects in PSCs.^{261,262} Owing to the high fabrication cost and poor mechanical stability of C₆₀, PCBM is desirable to reduce the need for the organic layer in future devices.

In addition to regular PSCs, SnO₂ is used in inverted PSCs as bilayers with organic transport materials, which preserve efficient electron transport and improve ambient stability. Zhu *et al.* first used the hydrothermal method to create highly crystalline SnO₂ nanocrystals (NCs) that could be used as an efficient ETL in conjunction with C₆₀. The best device, owing to its high crystallinity and hydrophobicity, achieves a high PCE of 18.8% and retains more than 90% of its initial PCE after 30 days of storage in an ambient environment with >70% relative humidity.¹²⁷ Similarly, Liu used HClO₄ to control crystallization during the SnO₂ deposition process. Based on the SnO₂/C₆₀ bilayer, the unencapsulated inverted PSCs had a champion PCE of more than 16% and retained more than 80% of its initial PCE value after 90 days (>2100 h) of storage in an air atmosphere.²⁶³ Luo *et al.* reported carbon nanotube films coated with SnO₂ (SnO₂@CSCNT) as ETL in the application of inverted CH₃NH₃-PbI₃/NiO PSCs and achieved the best PCE of 14.3% with better stability under a high humidity, thermal stress, or continuous light soaking condition.²⁶⁴

Wang and colleagues used a PC₆₁BM:SnO₂ bilayer as the ETL in inverted PSCs and achieved a high PCE of 19.7% (Fig. 10d, e and f). The device with the PC₆₁BM:SnO₂ bilayer outperformed the device based on a single PC₆₁BM ETL by 49.0%. The SEM revealed smooth and compact PC₆₁BM:SnO₂ layers with minor pinholes and cracks, promoting electron transfer and reducing charge recombination. Furthermore, the device's stability was improved over the PC₆₁BM-only device (Table 3).²⁶⁵

4.3 Interface modification

Although SnO₂ has excellent optoelectronic properties, defects or traps appear in SnO₂ films because of improper deposition methods, which will become the center of carrier recombination, resulting in decreased PCE. UV treatment is a common way to remove surface impurities or residuals, suppress the oxygen vacancies, and facilitate surface wettability for perovskite film growth.^{102,266–269} To improve the film quality, reduce the surface defects, and facilitate interfacial contact, many researchers introduced a series of materials to passivate interfacial defects and promote the conductivity of the SnO₂ film, which are all very significant to achieve an efficient and stable PSC device,

including ammonium salts, quantum dots, self-assembled monolayers, 2D materials, and carbon materials.

4.3.1 Ammonium salts. Despite its high electron mobility, SnO₂ ETL deposited at a low temperature suffers from poor film crystallinity and large defect density, which usually reduce the PSC efficiency. Ammonium salts are introduced for SnO₂ surface modification to reduce the interfacial defects.^{97,247,270,271}

Chen and co-workers introduced Girard's Reagent T (GRT) into the SnO₂ NP colloidal solution and obtained a high efficiency of 21.63% with free hysteresis. The AFM and contact angle test results showed better roughness and wettability for the SnO₂ film with GRT modification due to the chemical interaction between GRT and SnO₂ NPs (Fig. 11a and b). As a result, the quality of perovskite films with GRT modification was also improved. Many holes could be effectively eliminated in the perovskite film compared with the control ones. The vertically oriented large grains were across the whole cross-section, which confirmed that GRT modification is beneficial to the SnO₂ NP dispersion and the interfacial contact between the ETL and the perovskite layer.⁹⁷

Jung and co-workers used ammonium fluoride (NH₄F) to modify the SnO₂ surface to eliminate trap sites and change the Fermi level of SnO₂ thin films (Fig. 11c and d). They suggested that an ammonium cation in NH₄F generated ammonia gas and water vapor due to the reaction with hydroxyls on the SnO₂ surface. Besides, fluoride anions would get inserted into the trap sites, resulting in an adjustment of the energy level. PSCs with treated SnO₂ achieved a champion performance of 23.2%.²⁷²

Huang *et al.* showed that the addition of the IL tetramethylammonium hydroxide N(CH₃)₄OH (TMAH) to the SnO₂ nanoparticle suspension to form a stable and homogeneous suspension could result in a better SnO₂ ETL with lower defect density and higher conductivity for a better FF (Fig. 11e and f).²⁷³ As a result, TMAH-SnO₂-based PSCs showed a higher PCE (20.28%) than that of non-treated SnO₂-based PSCs (18.14%). Ethylenediaminetetraacetic acid (EDTA) is introduced onto SnO₂ to increase the electron mobility of the ETLs, resulting in a PCE of 21.60% and a certified PCE reaching 21.52%.²⁷⁴

4.3.2 Quantum dots (QDs). The quantum dots (QDs) had a tunable bandgap together with the quantum confinement and edge effects, which were novel promising zero-dimensional materials to decorate the SnO₂ surface to promote the electron conduction of SnO₂.^{103,275}

Chen and co-workers developed a SnO₂/graphitic carbon nitride quantum dot (g-C₃N₄ QD) nanocomposite (G-SnO₂) as

Table 3 Representative PSCs based on bilayer ETLs

| Bilayer | Deposition method | J_{SC} (mA cm ⁻²) | V_{oc} (V) | FF (%) | PCE (%) | Ref. |
|--|----------------------------|---------------------------------|--------------|--------|---------|------|
| SnO ₂ /In ₂ O ₃ | Spin-coating | 24.45 | 1.17 | 87.09 | 23.24 | 245 |
| SnO ₂ /a-WO _x | Vacuum thermal evaporation | 23.01 | 1.11 | 80.34 | 20.52 | 246 |
| L-SnO ₂ /H-SnO ₂ | Spin-coating | 23.6 | 1.21 | 76.2 | 21.75 | 247 |
| SnO ₂ /DPC ₆₀ | Spin-coating | 23 | 1.14 | 77.7 | 20.4 | 258 |
| SnO ₂ /C ₆₀ with PEIE | Vacuum thermal evaporation | 19.66 | 1.154 | 81.8 | 18.5 | 259 |
| SnO ₂ /PC ₆₁ BM | Spin-coating | 23.15 | 1.12 | 76 | 19.7 | 265 |

the functional ETL to accurately control the interfacial charge dynamics of efficient n-i-p planar PSCs (Fig. 12a, b and c). The $g\text{-C}_3\text{N}_4$ QDs could suppress the oxygen-vacancy-induced traps and facilitate the interfacial charge transfer by redistributing the electronic density around the neighboring SnO_2 crystal unit, resulting in enhanced electrical properties, appropriate

bandgap matching and high electron conduction. Employing the $\text{SnO}_2/g\text{-C}_3\text{N}_4$ QDs-based ETL, a champion PCE of 22.13% can be obtained with negligible hysteresis and long-term stability.²⁷⁶

Hui and co-workers recently reported carboxylic-acid- and hydroxyl-rich red-carbon quantum dot (RCQ) modified- SnO_2

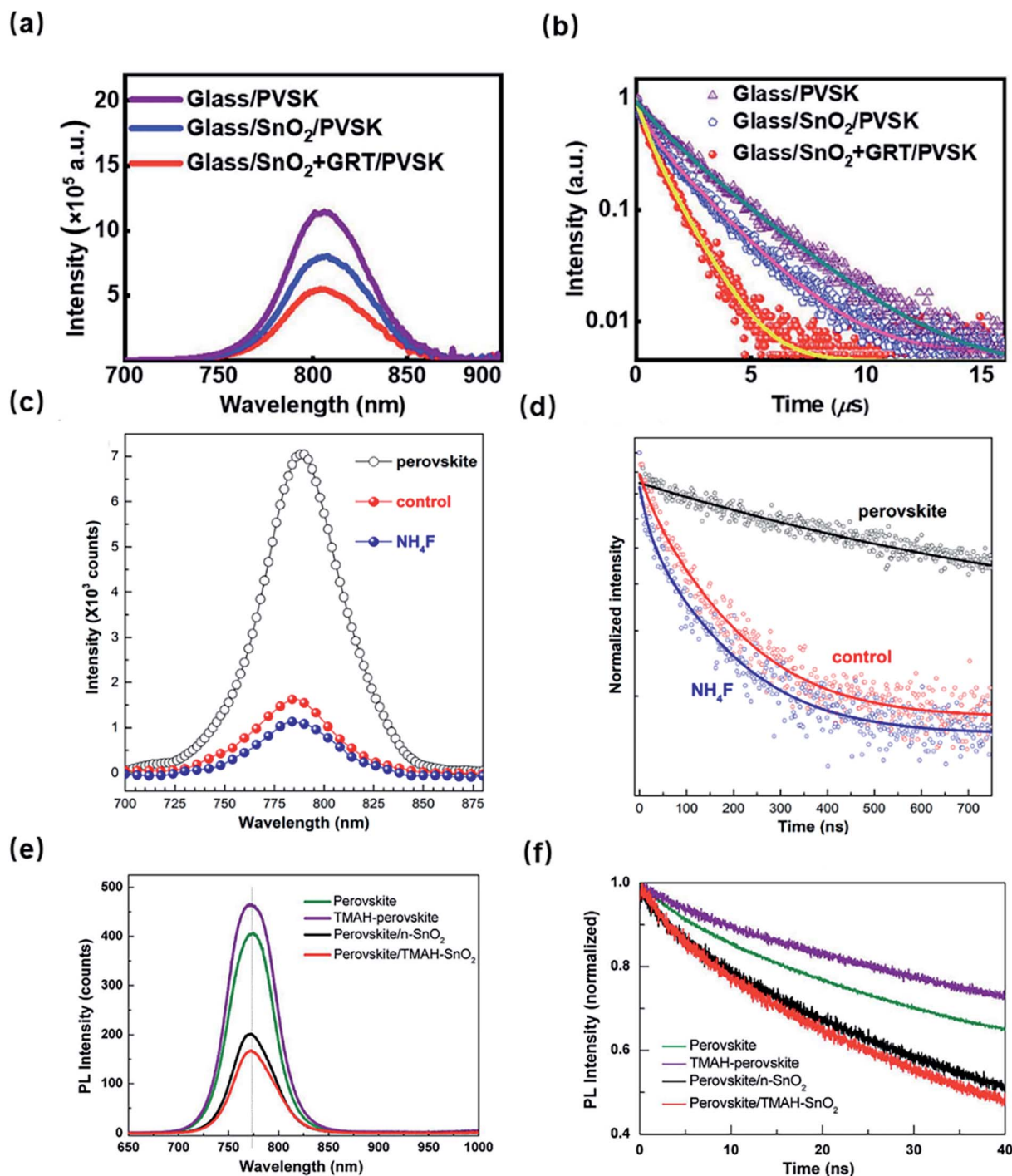


Fig. 11 Steady-state PL spectra of the perovskite film deposited on: (a) SnO_2 and GRT- SnO_2 , (c) SnO_2 and NH_4F - SnO_2 , (e) SnO_2 and TMAH- SnO_2 . Normalized time-resolved PL: (b) SnO_2 and GRT- SnO_2 ETLs, (d) SnO_2 and NH_4F - SnO_2 ETLs, and (f) SnO_2 and TMAH- SnO_2 . (a and b) Reproduced with permission.⁹⁷ Copyright 2021, Royal Society of Chemistry. (c and d) Reproduced with permission.²⁷² Copyright 2020, ACS Publishing Group. (e and f) Reproduced with permission.²⁷³ Copyright 2018, Royal Society of Chemistry.

with a suitable band alignment (Fig. 12d, e and f). The calculated electron mobility of SnO_2 -RCQs by using the space charge-limited current (SCLC) model was increased by 2 orders of magnitudes, resulting in a significant reduction in the conductivity of SnO_2 -RCQs. Simultaneously, the RCQ modified SnO_2 layer not only passivated the ETL/perovskite interface but also facilitated the crystallinity of the perovskite film, with dense and smooth morphology over a large area. This device with modified SnO_2 obtained an outstanding efficiency of 22.77% with negligible hysteresis and showed long-term stability against moisture, maintaining over 95% of the original PCE value after 1000 h storage in an ambient environment.²⁷⁷

Xie and co-workers added graphene quantum dots (GQDs) to the SnO_2 precursor to form a SnO_2 :GQDs layer as the ETL by

a simple spin-coating method (Fig. 12g, h and i). It was found that GQDs effectively promoted electron transport and passivated the electron traps at the interface, which led to improved electron extraction rate and reduced charge accumulation at the ETL/perovskite interface. As a consequence, the best device based on SnO_2 :GQDs ETLs exhibited a PCE of 20.23% and a free hysteresis effect.²⁶⁹

4.3.3 Self-assembled monolayers (SAMs). Like commonly used metal oxides such as TiO_2 , SnO_2 , ZnO , MoO_x , or organic charge transport molecules such as PC_{61}BM and poly(3,4-ethylenedioxy-thiophene)polystyrene (PEDOT:PSS), SnO_2 has hydroxyl groups at the surface of the film, and they cause defects states near the valence band, which can induce a non-radiative recombination at the SnO_2 /perovskite interface.²⁷⁸

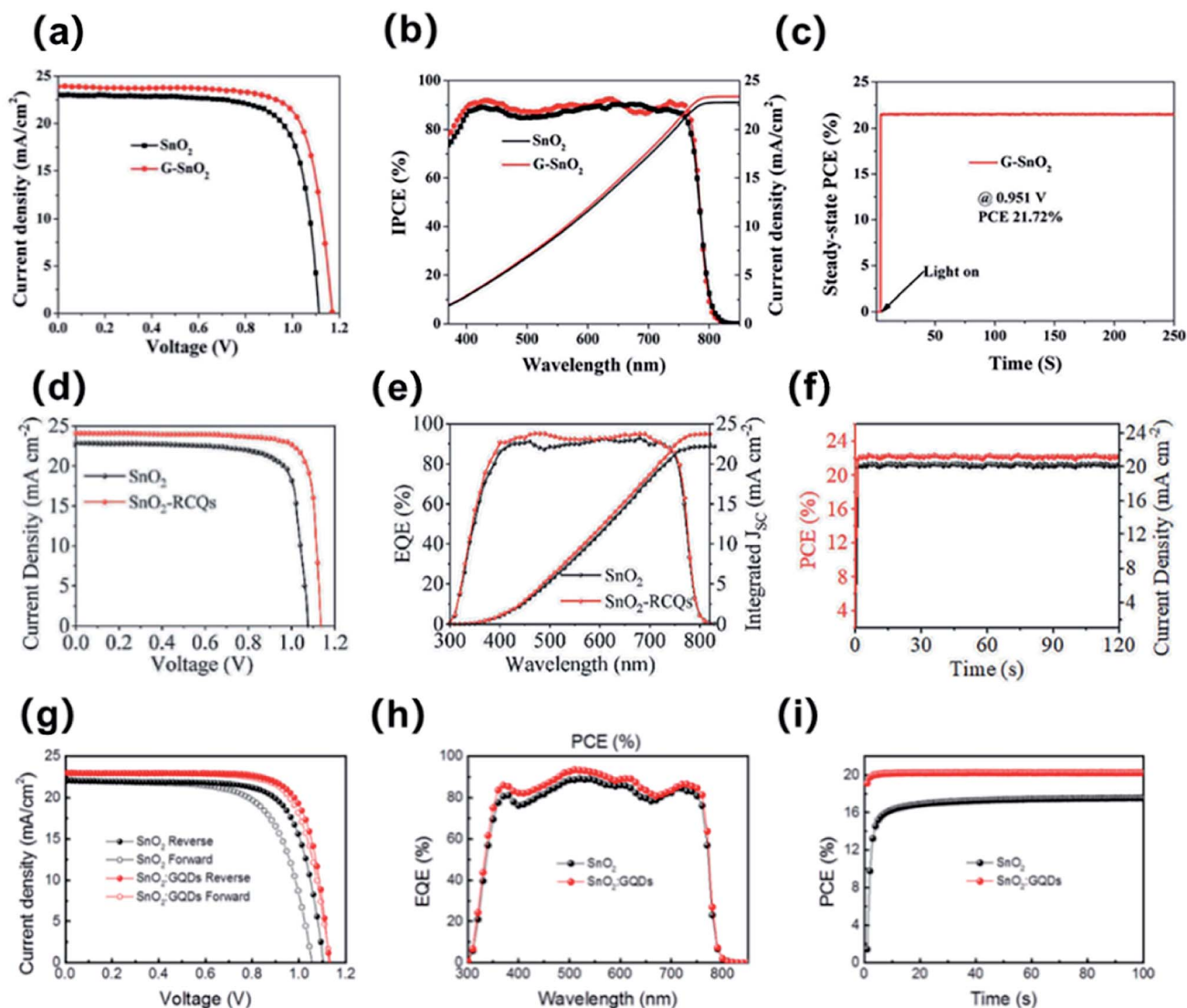


Fig. 12 J - V curves of perovskite solar cells based on (a) pristine and g- C_3N_4 QD-treated SnO_2 ETLs; (d) pristine and RCQ-treated SnO_2 ETLs; (g) pristine and G QD-treated SnO_2 ETLs. The corresponding IPCE spectra of (b) pristine and g- C_3N_4 QD-treated SnO_2 ETLs; (e) pristine and RCQ-treated SnO_2 ETLs; and (h) pristine and GQD-treated SnO_2 ETLs. Steady efficiency at the maximum power point of (c) pristine and g- C_3N_4 QD-treated SnO_2 ETLs; (f) pristine and RCQ-treated SnO_2 ETLs; (i) pristine and GQD-treated SnO_2 ETLs. (a-c) Reproduced with permission.²⁷⁶ Copyright 2020, Royal Society of Chemistry. (d-f) Reproduced with permission.²⁷⁷ Copyright 2020, Wiley-VCH. (g-i) Reproduced with permission.²⁶⁹ Copyright 2017, ACS Publishing Group.

Recently, owing to chemical bonding, self-assembled monolayer (SAM) ordered arrays of organic molecules formed by the spontaneous absorption onto a surface of molecular constituents from a vapor or liquid phase, are introduced to modify the SnO₂ surface, which is beneficial to tuning the energy level, regulating the WF at the surface and promoting the charge collection.^{49,279–283} Besides, SAMs can reduce the vacancies and crystal traps at the perovskite, resulting in high-quality films and improved performance and stability of PSCs.

Yan and co-workers reported a choline chloride SAM on the surface of SnO₂ (chol-SnO₂) by chemically reacting with the perovskite film to eliminate oxygen vacancies at the interface and lengthen the carrier lifetime (Fig. 13a and d). Finally, the device based on SnO₂ modified by choline chloride achieved a champion photovoltaic performance of 18.90% with free-hysteresis and a high V_{oc} (1.145 V).²⁸⁴

Kim and co-workers employed 2-[carbamimidoyl(methyl)amino]acetic acid (creatine), one of the standard amino acids in the human body, on a SnO₂ layer (Fig. 13b and e). Given the chemical structure, creatine can anchor on the surface of SnO₂ by a carboxylic acid functional group and had high polarity, leading to an increase in the charge extraction efficiency. The formamidinium-based perovskite PSC with modified SnO₂ achieved the optimal efficiency of 22.1% and maintained 90% initial performance even after 50 days.²⁸⁵

Anizelli and co-workers performed a systematic study of the application of two special SAMs, ethylphosphonic acid (EPA) and 4-bromobenzoic acid (BBA), onto SnO₂ and the NiO₂ ETL for stability. A series of stability tests of films and devices with and without SAM layers, at a working-condition temperature of 75 °C and continuous illumination, were designed. They demonstrated

a distinct evolution of perovskite thin films with irradiation time by adopting SAMs, and SAMs also generated several changes in the photoelectric parameters of the devices in view of their chemical properties and their combination with the SnO₂ and NiO₂ layers. At last, SAMs exhibited a significant effect on the lifetime of PSCs, extending up to five times that of the device's T50% (time for the efficiency to reach half of its initial value) in some cases.²⁸⁶

Hysteresis and degradation occurring in traditional PSCs structures with SnO₂ as the ETL has not been well understood. Tumen-Ulzii and co-workers modified the SnO₂ surface by a C₆₀ pyrrolidine tris-acid (CPTA) SAM because of the ability to form a strong chemical interaction with the SnO₂ surface (Fig. 13c and f). Furthermore, the SAM can effectively deactivate these hydroxyl groups, which localized the positive ions, leading to the hysteresis and degradation in PSCs. After surface treatment, they obtained free-hysteresis and long-term stability PSCs with no degradation after 1000 h of continuous light incidence.²⁸⁷ Although PCBM or the C₆₀ buffering layer has the merits of suppressing hysteresis behavior and reducing the interfacial charge recombination loss, we do not ignore the drawbacks of difficulties in depositing them. For buffering layers, thermal deposition can precisely control its thickness, but it takes more cost and energy consumption to deposit them in a vacuum environment. On the other hand, solvent orthogonality is required to be solved because the polar solvents used in perovskite precursors like dimethylformamide (DMF) and dimethyl sulphoxide (DMSO) destroy the perovskite crystal structures.

4.3.4 Two-dimensional materials. Recently, two-dimensional (2D) materials such as graphene, MXenes, and metal sulfides have been commonly introduced into SnO₂ based on PSCs owing to their unique photoelectric

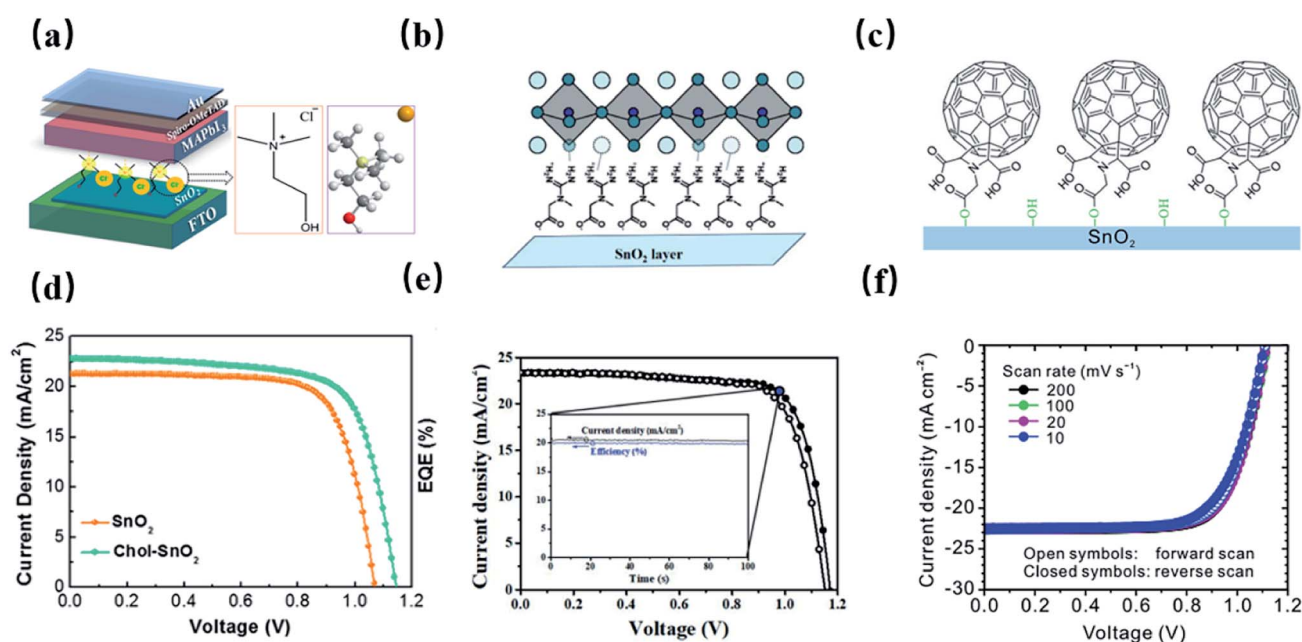


Fig. 13 Schematic illustration of the formation of various self-assembled monolayers adhering to SnO₂ layers and J–V curve of devices with different SAM treatments. (a and d) Choline chloride treatment. Reproduced with permission.²⁸⁴ Copyright 2020, ACS Publishing Group. (b and e) 2-[Carbamimidoyl(methyl)amino] acetic acid treatment. Reproduced with permission.²⁸⁵ Copyright 2015, Royal Society of Chemistry. (c and f) C₆₀-pyrrolidine tris-acid treatment. Reproduced with permission.²⁸⁷ Copyright 2020, Nature Publishing Group.

properties.^{72,77,288–291} MXenes are promising 2D materials that process high electron mobility and less light absorption in the visible range. Their general chemical formula is $M_{n+1}X_nT_x$, in which M displays a type of early transition metal, X usually is a carbon and/or a nitrogen atom, and T is the surface termination group (usually oxygen- and/or fluorine-containing groups).^{292–294} Interestingly, the application of MXenes has been reported in PSCs as additives in the perovskite layer and ETLs.^{291,295,296}

Wang and co-workers used $Ti_3C_2T_x$ MXene to increase the conductivity and the charge collection ability of the SnO_2 ETL. The MXene-modified SnO_2 ETL also led to a preferable growth of perovskite films with free defects. Consequently, the PSCs obtained the best photovoltaic performance of 20.65% with minimal hysteresis.²⁹⁰

Yang and co-workers introduced Ti_3C_2 (the most widely studied MXene) nanosheets into SnO_2 precursors to increase the ETL conductivity *via* a low-temperature method (Fig. 14a, b and c). Through optimizing the Ti_3C_2 contents, the device with the perovskite film of $MAPbI_3$ obtained 18.34%, which was much higher than that of only SnO_2 -based PSCs. The enhancement of the PCE can be ascribed to good bandgap alignment, leading to faster charge extraction from the perovskite layer.²⁹¹

Some metal sulfide materials are also good choices to modify the SnO_2 for enhanced electron conductivity. Huang and co-workers spin-coated the 2D TiS_2 layer on the top of SnO_2 as a bilayer ETL (Fig. 14d, e and f). 2D TiS_2 can suppress trap sites of SnO_2 and change the energy level alignment, resulting in improved electron mobility. The highest PCE reached was 21.73% with free hysteresis.²⁸⁸

4.3.5 Carbon materials. Carbon-based materials are suitable charge-transfer materials for commercializing large-scale

PSCs due to low-expense, high electron conduction, especially low-temperature fabrication (100 °C),^{297,298} and similar work function as gold (5.0 and 5.1 eV, respectively).²⁹⁷ Besides, they possess a highly hydrophobic nature, which protect moisture infiltration into the perovskite layer, resulting in long-term stability without encapsulation.²⁹⁹ Nowadays, carbon-based materials including graphene, carbon nanotubes (CNTs), and carbon or graphene nanodots are widely used in PSCs as additives in perovskite precursors, interlayers between ETL or HTL with the perovskite layer and cathode.^{300–305}

Tang and co-workers prepared SnO_2 and carbon nanotubes (CNTs) hybrid ETL (SnO_2 -CNT) by spin-coating method.¹¹⁶ Besides, carbon nanotubes (CNTs) were modified by oxidative treatment and then dispersed well in $SnCl_4 \cdot 5H_2O$ solution (Fig. 15a and b). As a consequence, the best PCE of 20.33% was obtained with negligible hysteresis, which was attributed to the significant increase in the conductivity of SnO_2 films and decrease in the trap-state density of SnO_2 films. Wang and co-workers firstly introduced carbon nanodots (CNDs) into SnO_2 ETLs by a facile solution method. CNDs could effectively reduce the defect density and promote electron mobility in SnO_2 . Finally, the device with ITO/ SnO_2 : CNDs/perovskite/spiro-OMeTAD/Au structure obtained a high power conversion efficiency (PCE) of over 20% with free hysteresis. Additionally, the SnO_2 : CNDs device dropped only 10% of the initial PCE after storage in ambient for 1200 h and showed better UV stability after continuous UV illumination.³⁰⁶

Zhang and co-workers firstly introduced graphdiyne (GDY) as a novel carbon material to optimize the charge collocation process of SnO_2 ETL, tune the growth of perovskite and eliminate interfacial defects towards both perovskite crystallization process and subsequent photovoltaic service duration. Through

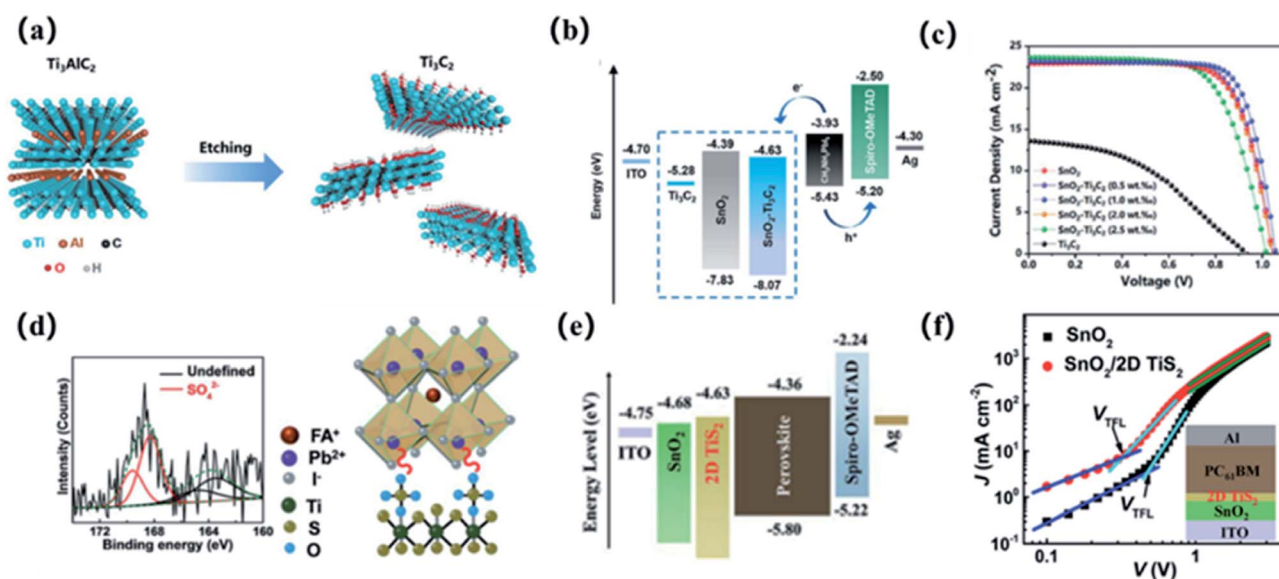


Fig. 14 (a) Schematic diagram of Ti_3C_2 formation. (b and e) Energy level diagram of the components in the semiconductor hybrid perovskite. (c) Backward scan J - V curves of devices with a SnO_2 ETL and with SnO_2 - Ti_3C_2 ETLs at various Ti_3C_2 concentrations. (d) High-resolution XPS spectra of S 2p on the SnO_2 - TiS_2 film; working mechanism of 2D TiS_2 interaction with the perovskite crystal; (f) J - V curves of electron-only devices with the inset illustrating the device structure. (a–c) Reproduced with permission.²⁸⁸ Copyright 2019, Royal Society of Chemistry. (d–f) Reproduced with permission.²⁹¹ Copyright 2019, Royal Society of Chemistry.

the GDY modification, the PCE of over 21% was achieved with 10% improvement together with free hysteresis. It is demonstrated that GDY treated SnO₂ layer improved electron mobility and more facilitated energy level alignment (Fig. 15c and d). Moreover, the improved interfacial hydrophobicity effectively

impeded excess heterogeneous perovskite nucleation, leading to the higher crystal grain size of perovskite, fewer grain boundaries, and decreased trap density.³⁰⁷

Zhao and co-workers treated SnO₂ nanocrystals by chemically modified graphene as ETL for highly efficient and stable

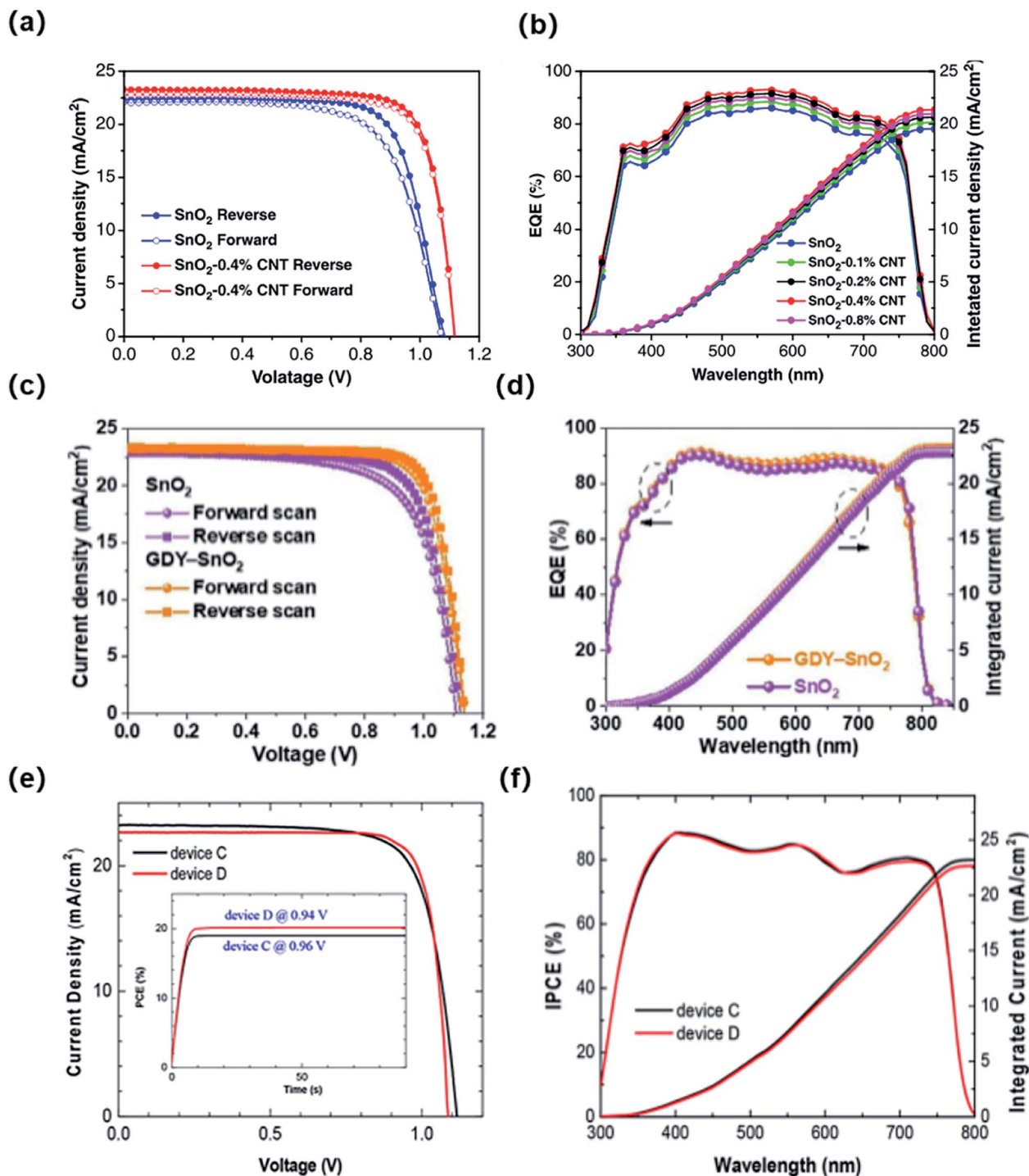


Fig. 15 *J*-*V* curves of (a) SnO₂ and CNT-SnO₂ ETLs; (c) SnO₂ and GDY-SnO₂ ETLs; (e) SnO₂ and graphene-SnO₂ ETLs. EQE spectra of (b) SnO₂ and CNT-SnO₂ ETLs. (d) SnO₂ and GDY-SnO₂ ETLs. (f) SnO₂ and graphene-SnO₂ ETLs. (a and b) Reproduced with permission.¹¹⁶ Copyright 2020, Wiley-VCH. (c and d) Reproduced with permission.³⁰⁷ Copyright 2020, Wiley-VCH. (e and f) Reproduced with permission.³⁰⁸ Copyright 2018, ACS Publishing Group.

PSC (Fig. 15e and f). Besides, they also reported a creative strategy to disperse graphene in an aqueous solution that can preserve any residue on the SnO₂ film. Finally, the best device showed a PCE of over 20% with a high fill factor of up to 82%, which resulted from the enhanced conductivity (Table 4).³⁰⁸

5. Hysteresis and stability

The severe hysteresis and inferiority in the stability of PSCs under operation conditions are urgent challenges that quietly inhibit the PSCs from being used in the commercialization of laboratory products.

5.1 Hysteresis suppression

The presence and behavior of hysteresis, the difference in the I - V curve from the reverse scan (open-circuit to short-circuit) and the forward scan (short-circuit to open-circuit), is a fundamental problem in the perovskite solar cell field. This results in obstacles to the progress of the actual performance of the devices in operation. Compared with devices with an n-i-p structure with a scaffold and an inverted p-i-n structure with a fullerene ETL, PSCs with the regular planar structure show much more evidence of the hysteresis effect.

Although the reasons for the appearance of hysteresis in PSCs are not evident, energy defects at the interfaces, the grain boundary in the perovskite film, and capacitive and ferroelectric polarization possibly affect the hysteresis behavior.^{309–312} Recently, it seems that hysteresis is induced by ion migration, which caused charge accumulation, unbalanced charge mobility, defects or traps in the instinct of perovskites and perovskite/ETL interfaces.^{313–317} As mentioned above, various types of device structures exhibited different hysteresis behaviors. The contact between the perovskite and charge transport layers is the main factor within these other structures, suggesting that the contact could also influence the hysteresis.³¹⁸

Compared with many other metal oxides as ETLs, SnO₂ has the merits of a more bottomless conduction band, higher

conductivity, and electron mobility, which is beneficial to charge transfer from perovskite to ETL low charge accumulation at the interface. To date, devices based on the SnO₂ ETL in planar PSCs show a little hysteresis effect than many common metal oxides as ETLs, especially the TiO₂ ETL.³¹⁹ For PSCs with n-i-p planar structures, SnO₂ is an ideal electron transport material as the ETL to almost solve the hysteresis problem. As previously mentioned, SnO₂ combined with doped elements,³²⁰ bilayers,^{247,321,322} and interfacial engineering^{323,324} can retard the formation of the defect states, which improve the carrier transport performance, leading to negligible hysteresis in the device.

Tumen-Ulzii and co-workers treated the SnO₂ surface with a self-assembled monolayer and achieved a hysteresis-free PCE over 18% (Fig. 16). It was found that hydroxyl groups existing at the SnO₂ surface induced positive ion localization, resulting in hysteresis and degradation. Interestingly, a self-assembled monolayer of a fullerene derivative (CPTA-SAM) can effectively deactivate these surface -OH groups. The temperature and scan speed can affect the hysteresis. Besides, with temperature increase or scan speed decrease, more significant hysteresis is apparent in J - V curves. PSCs with CPTA-SAM treatment significantly reduced the J - V hysteresis of PSCs at different scan speeds in contrast to devices without CPTA-SAM treatment. Furthermore, negligible hysteresis was observed in PSCs with the CPTA-SAM even at a high temperature of 60 °C.²⁸⁷

Ye and co-workers spin-coated KCl and NaCl on the SnO₂ surface to suppress the hysteresis in flexible PSCs.³²⁵ The KCl and NaCl treatments effectively improve the power output of flexible PSCs. However, devices with NaCl modification showed a profound hysteresis effect in J - V curves. It suggested that the hysteresis relied strongly on alkali metals. With the increase of the ionic radius of alkali metal ions from Li⁺ to K⁺ and then to Cs⁺, the hysteresis effect first gradually decreased and disappeared, and then appeared again and increased, which was strongly related to the trapping density.^{326,327} In addition, it can reduce the device hysteresis to use a suitable SnO₂ fabrication process such as ALD, CBD, *etc.*

Table 4 Representative PSCs with interface modification

| | Passivation materials | J_{sc} (mA cm ⁻²) | V_{oc} (V) | FF (%) | PCE (%) | Ref. |
|------------------|---|---------------------------------|--------------|--------|---------|------|
| Ammonium salts | Girard's reagent T | 22.92 | 1.146 | 82.3 | 21.63 | 97 |
| Ammonium salts | NH ₄ F | 24.60 | 1.16 | 81.4 | 23.2 | 272 |
| Ammonium salts | N(CH ₃) ₄ OH | 22.51 | 1.14 | 79 | 20.28 | 273 |
| Ammonium salts | EDTA | 24.57 | 1.11 | 79.2 | 21.6 | 274 |
| QDs | g-C ₃ N ₄ | 23.03 | 1.176 | 78.3 | 22.13 | 276 |
| QDs | RCQ | 24.10 | 1.14 | 83 | 22.77 | 277 |
| QDs | GQD | 23.05 | 1.134 | 77.8 | 20.31 | 269 |
| SAMs | Choline chloride | 22.80 | 1.145 | 72.41 | 18.90 | 284 |
| SAMs | Creatine | 23.4 | 1.19 | 75.9 | 20.8 | 285 |
| 2D materials | Ti ₃ C ₂ T _x | 24.34 | 1.11 | 76.4 | 20.65 | 290 |
| 2D materials | Ti ₃ C ₂ | 23.14 | 1.06 | 75 | 18.34 | 291 |
| 2D materials | TiS ₂ | 24.57 | 1.11 | 79.4 | 21.73 | 288 |
| Carbon materials | CNDs | 23.26 | 1.12 | 78.23 | 20.33 | 116 |
| Carbon materials | CNDs | 23.14 | 1.10 | 79 | 20.03 | 306 |
| Carbon materials | Graphdiyne | 23.32 | 1.137 | 79.62 | 21.11 | 307 |
| Carbon materials | Graphene | 22.66 | 1.084 | 82.1 | 20.16 | 308 |

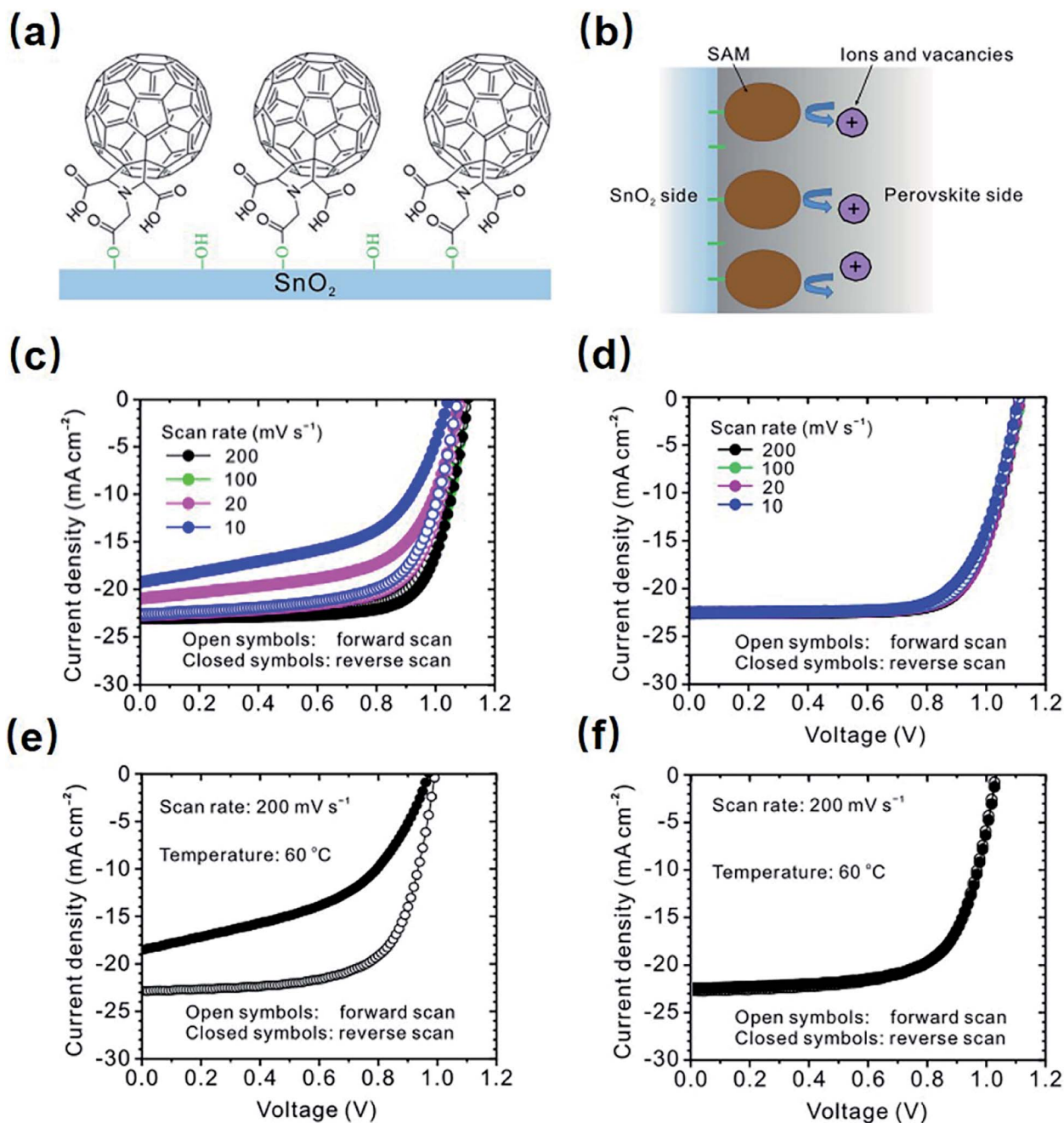


Fig. 16 Positive effect of using a self-assembled monolayer (SAM) on the hysteresis and carrier recombination characteristics in perovskite solar cells. (a) Mixed self-assembled monolayers adhering to the SnO₂ substrates and (b) schematic illustration of reducing localized ionic charges by eliminating –OH groups on the surface; backward and forward scan J - V curves at different scan speeds: (c) untreated devices and (d) devices with SAM treatment; backward and forward scan J - V curves measured at a fast scan rate of 200 mV s⁻¹ at 60 °C: (e) untreated devices and (f) devices with SAM treatment. Reproduced with permission.²⁸⁷ Copyright 2020, Nature Publishing Group.

5.2 Device stability

5.2.1 Ambient stability. SnO₂ is more stable in oxygen and moisture than TiO₂, an ideal alternative to the TiO₂ ETL for device stability.^{188,328,329} Zhang and co-workers found that using poly(vinylpyrrolidone)-doped SnO₂ as the ETL, 88% of its highest PCE is retained even after 41 days of storage without encapsulation.³³⁰ Huang and co-workers also revealed that the SnO₂ ETL modified with polymer ethoxylated polyethylenimine

(PEIE) indicated significant storage device stability, and the device with SnO₂:PEIE ETL preserved 82.1% of its original PCE (PCE_{1/4}, 16.89%) after 70 days of storage.³³¹ Wang and co-workers designed TiO₂/SnO₂ bilayer as the ETL in CsPbI₂Br all-inorganic perovskite, and the devices showed superior photovoltaic properties, particularly excellent phase and thermal stability. After one month of storage in an N₂ environment without any encapsulation, the PCE can retain about 95% of the original efficiency (Fig. 17a and b).³³²

Apart from SnO_2 as ETLs in regular structures, SnO_2 can be introduced as a protecting layer on the top of the perovskite layer or fullerene layer.^{87,127,265,333,334} Wang and co-workers used SnO_2 nanocrystals combined with HClO_4 and HCl treatment as a buffer layer, inserting it into the C_{60}/Ag electrode interface (Fig. 17c and d). The devices with the HClO_4 - SnO_2 ETL without encapsulation increased the PCE up to 16.36% with almost negligible hysteresis and maintained over 80% of their highest PCE after storage in open air for 90 days (>2100 h) and reduced by only about 20% its initial efficiency after 41 h under heating at 85 °C.²⁶³

5.2.2 Light illumination stability. TiO_2 is a common metallic oxide used as the ETL, which induces decomposition of PSC under UV illumination owing to their photocatalytic activity. Due to the efficiency and stability degradation, there is a mass of oxygen vacancies in the TiO_2 lattice, which can be generated by UV illumination.²⁰⁰ The oxygen vacancies cause deep trap states, interacting with molecular oxygen in ambient air, and then cause deep trap sites, which can interact with molecular oxygen in the environment by adsorption, leading to their passivation.^{41,335,336} When deep traps are excited by oxygen desorption, the charge recombination easily occurs at the interface, resulting in a PCE loss. Besides, TiO_2 is able to obtain excess electrons from perovskite because of its high

photochemical activity, which can cause photo-decomposition of the perovskite crystals, particularly in the humid environment.^{337–339}

Liu and co-workers studied the reasons for the degradation process of the perovskite layer deposited on different ETLs (PCBM, TiO_2 , and SnO_2) under strong ultraviolet irradiation. Although the SnO_2 layer reduced light-induced chemical activity in contrast to the TiO_2 layer, the serious decomposition of perovskite observed at the perovskite/ SnO_2 interface, together with the formation of hole structures, decreases the carrier transfer at the interface, owing to the separation of the perovskite absorber from ETLs and thus rapidly decreased the device performance (Fig. 18b).³⁴⁰ Wang and co-workers used carbon nanodots (CNDs) to dope SnO_2 as the ETL and found that SnO_2 :CNDs based PSCs achieved an efficiency over 20% with nearly free hysteresis and maintained over 90% of the initial PCE in a N_2 atmosphere for 1200 h and showed better UV stability under UV illumination for 200 h.³⁰⁶

Similarly, Abate and co-workers reported that Ga doping could improve UV-resistant mesoporous SnO_2 . When SnO_2 and TiO_2 based PSCs were exposed to continuous light illumination for 1000 h, both devices exhibited a rapid decrease to 80% in the first 100 h (Fig. 18a). After this, SnO_2 based PSCs retained

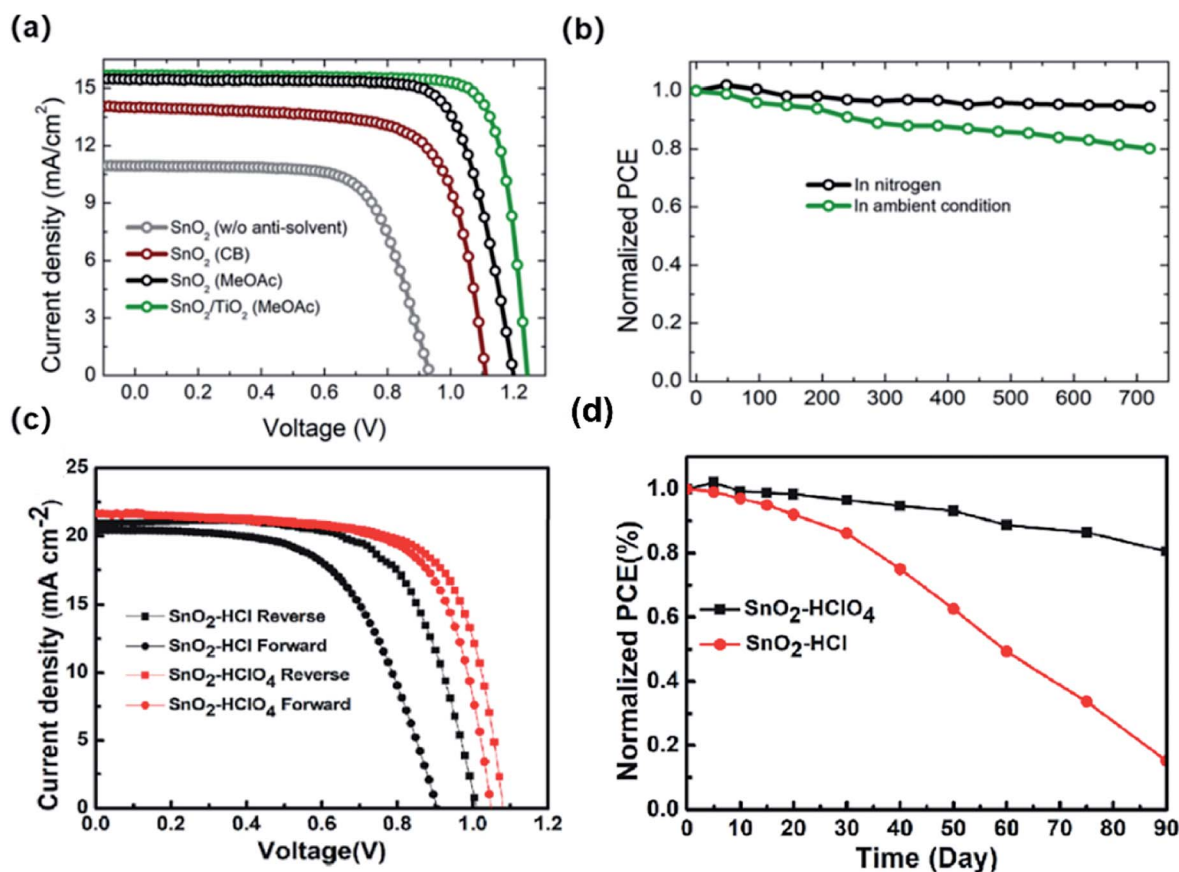


Fig. 17 J - V curves of devices based on (a) SnO_2 and $\text{TiO}_2/\text{SnO}_2$ ETLs and (c) HCl-SnO_2 and $\text{HClO}_4\text{-SnO}_2$ ETLs. Stability test of devices on (b) SnO_2 and $\text{TiO}_2/\text{SnO}_2$ ETLs in an N_2 - filled glovebox and under ambient conditions (@R.T., 20–30% relative humidity) (d) HCl-SnO_2 and $\text{HClO}_4\text{-SnO}_2$ ETLs under the humidity of 55% \pm 10% at 85 °C in open air. (a and b) Reproduced with permission.³³² Copyright 2020, ACS Publishing Group. (c and d) Reproduced with permission.²⁶³ Copyright 2020, Elsevier.

around 70% of the original efficiency up to 1000 h of full-spectrum illumination. In contrast, the normalized PCE of TiO₂ based PSCs dropped rapidly and stabilized only 20% of the initial PCE after illumination.³³⁹

Wang and co-workers introduced a chlorine-rich perovskite interlayer (CIMPI) to modify the SnO₂ ETL/perovskite interface through halide exchange to improve the interfacial charge transfer (Fig. 18c). Encouragingly, the CIMPI-based PSC still maintained over 82% of the initial PCE under UV exposure with a high power of 100 mW cm⁻² after 500 h.³⁴¹

More encouragingly, Gratzel and co-workers designed a bilayer ETL of an amorphous SnO₂ coated TiO₂ scaffold (mp-TiO₂) layer, and they displayed that the devices with a TiO₂/SnO₂ bilayer ETL rendered them more resistant to UV light than devices with only mp-TiO₂ as a single ETL (Fig. 18d).³⁴²

5.2.3 Heat stability. In addition to light and humidity, thermal treatment is also the cause of poor stability problems of perovskite solar cells. The temperature of the cells can increase under exposure to sunlight, resulting in accelerated degradation, especially for MA-based perovskite solar cells.³⁴³ Some strategies were reported, such as designing 2D/3D heterojunctions, using a green antisolvent, interface engineering, and additive engineering for SnO₂-based perovskite solar cells.^{344–350}

Chen and coworkers deposited 4-imidazoleacetic acid hydrochloride (ImACHCl) on the top of the SnO₂ film, leading to a chemical bridge between SnO₂ and perovskite through an ester bond with SnO₂ (Fig. 19a). As a result, ImACHCl could improve the perovskite crystallization, suppress the non-radiative recombination, and the promote carrier lifetime. Moreover, an unencapsulated device with ImACHCl-modified SnO₂ retained 90% of its initial after 40 h of aging at 80 °C, while PCE was degraded by 53% for the control device.³⁴⁴

Zhang and coworkers used ethyl acetate (EA) as a green antisolvent to control the perovskite crystallization process, resulting in smooth and dense perovskite films with free pinholes (Fig. 19b). In the ambient atmosphere, the unencapsulated device maintained about 85% of its initial PCE after more than 1900 h of storage. Meanwhile, the device also showed remarkable thermal stability, retaining 81.03% of the original PCE value at 100 °C for 10 h.³⁴⁹

Interface engineering between SnO₂ and the perovskite layer is a common way to improve thermal stability. Tian and coworkers synthesized 2,5-diphenyl C₆₀ fulleropyrrolidine (DPC₆₀) as an interfacial layer between perovskite and SnO₂ in planar perovskite solar cells (PSCs) (Fig. 19c). As a result, PSCs modified with DPC₆₀ obtained a PCE of 20.4% with high reproducibility. Furthermore, the device retained 82% of its initial efficiency after 200 h of 1 sun continuous irradiation and thermal aging (55 ± 5 °C) due to the suppression of heterogeneous nucleation and improvement in the crystallinity of the perovskite film.³⁴⁸ Similarly, Choi and coworkers exhibited a PCE of 21.43% by incorporation of SnO₂ with a zwitterionic compound (3-(1-pyridinio)-1-propane sulfonate), which led to improved PCE and thermal stability (Fig. 19d).³⁴⁵

6. Commercialization and applications

6.1 Flexible perovskite solar cells (FPSCs)

Because of their potential in portable electronics, flexible perovskite solar cells (FPSCs) have sparked widespread research interest. Because of their low-temperature processability, SnO₂ ETLs play a critical role in realizing highly efficient flexible PSCs.^{351–353}

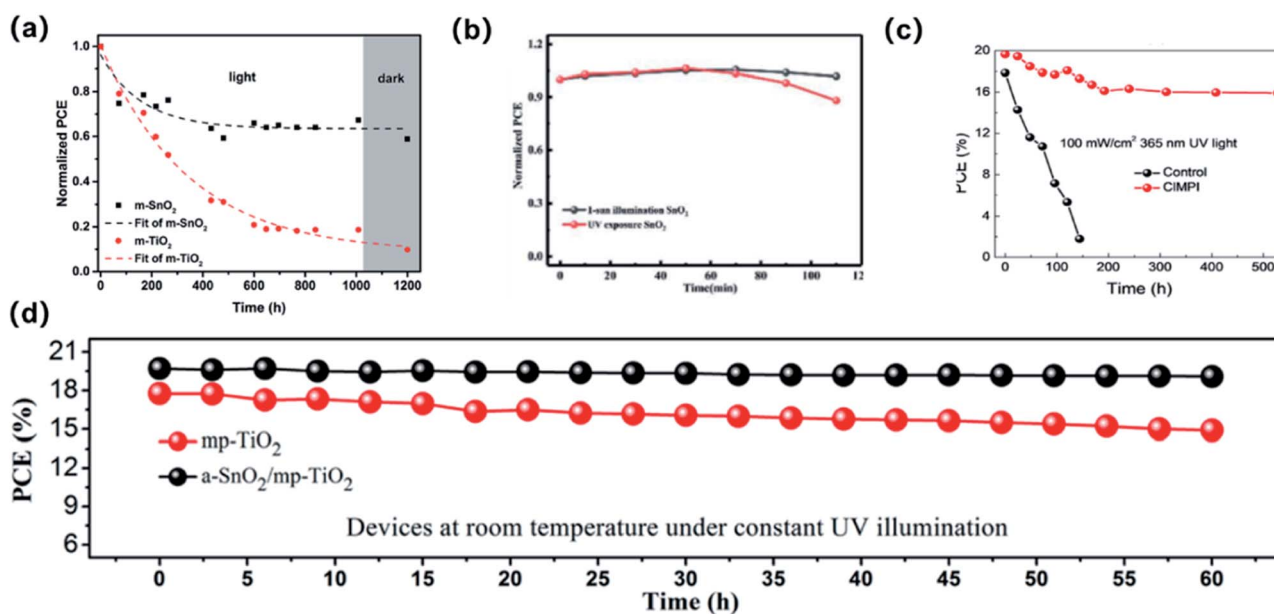


Fig. 18 UV light aging test of devices based on (a) *m*-SnO₂ and *m*-TiO₂ under 100 mW cm⁻² illumination in a N₂ atmosphere; reproduced with permission.³³⁹ Copyright 2018, Royal Society of Chemistry. (b) *mp*-SnO₂ under one sun illumination and UV exposure in a N₂ atmosphere. Reproduced with permission.³⁴⁰ Copyright 2020, Royal Society of Chemistry. (c) CIMPI-SnO₂ reproduced with permission.³⁴¹ Copyright 2019, Elsevier B.V. (d) *mp*-TiO₂ and SnO₂/*mp*-TiO₂. Reproduced with permission.³⁴² Copyright 2018, ACS Publishing Group.

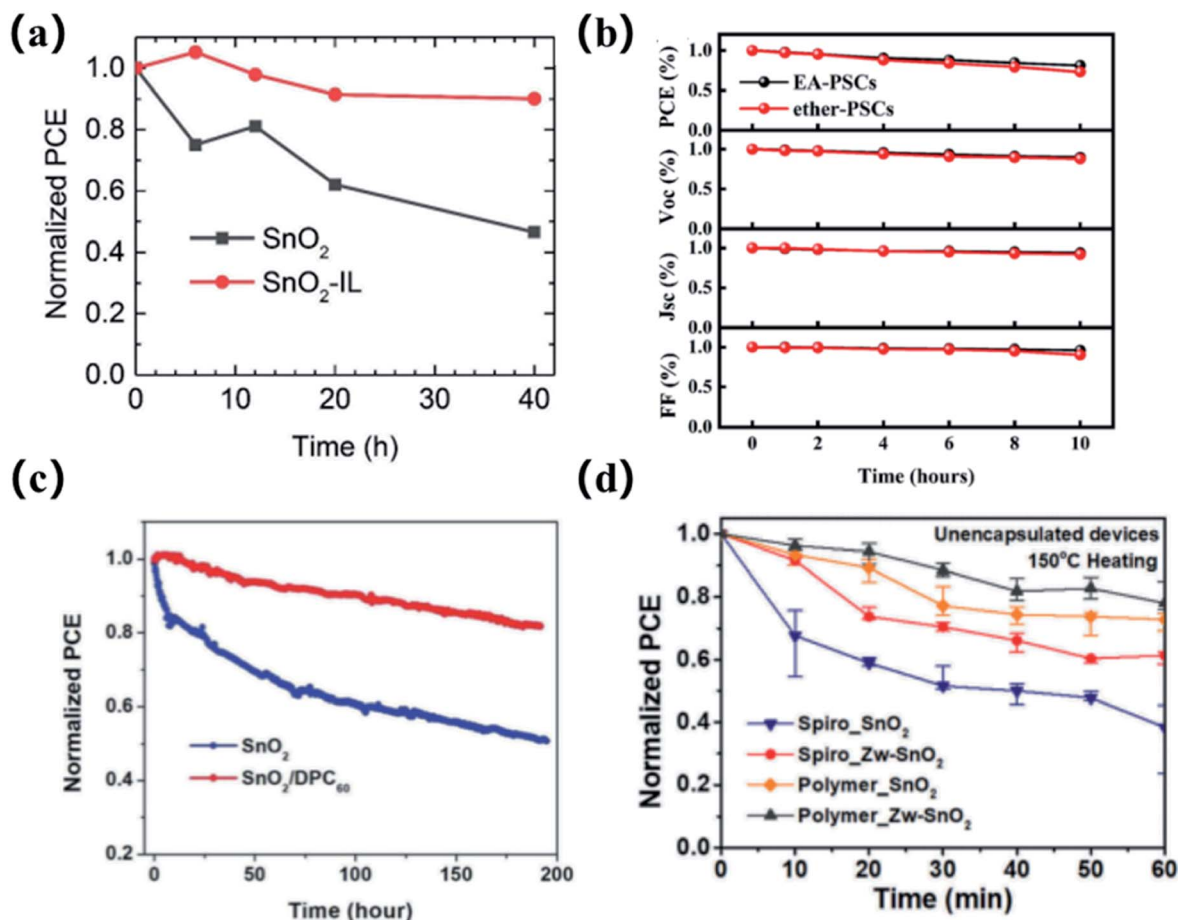


Fig. 19 Device thermal stability of (a) unencapsulated devices at 85 °C in the dark in the glovebox. Reproduced with permission.³⁴⁴ Copyright 2019, Wiley-VCH. (b) Unencapsulated devices at 100 °C in air. Reproduced with permission.³⁴⁹ Copyright 2020, Elsevier. (c) MPP tracking of the unencapsulated devices at (55 ± 5 °C) in a N₂ atmosphere. Reproduced with permission.³⁴⁸ Copyright 2020, Wiley-VCH. (d) Unencapsulated devices at 150 °C in air. Reproduced with permission.³⁴⁵ Copyright 2018, Royal Society of Chemistry.

Zhou *et al.* reported graphene quantum dots (GQDs)/SnO₂ composites (G@SnO₂) as effective ETLs. GQDs can improve SnO₂ electron mobility and coverage. Furthermore, G@SnO₂ has a higher energy level than that of pristine SnO₂, resulting in increased charge transfer and decreased charge recombination. As a result, the flexible PSCs based on G@SnO₂ ETLs achieved a champion PCE of 17.7% with exceptional mechanical durability, retaining more than 91% of the initial PCE value after 500 bending cycles with a bending radius of 7 mm.³⁵⁴

Wang *et al.* reported plasma-enhanced atomic layer deposition (PEALD) for SnO₂ ETLs processed at low temperatures. The PEALD-synthesized SnO₂ is postannealed at 100 °C in the presence of water vapor. Finally, the best flexible PSC demonstrated the highest reported efficiency of 18.36%.¹⁵⁵

Dong *et al.* used ultraviolet ozone (UVO) pretreatment to introduce controlled trace amounts of surface absorbed water on the FTO or ITO for a full-coverage SnO₂ ETL with desirable morphology and crystallinity. It demonstrated optimal hydrolysis–condensation reactions for SnO₂ regrowth. Compared to the control SnO₂ ETL without UVO pretreatment, the rigid and flexible PSC devices with UVO pretreatment achieved high PCEs of up to 20.5% and 17.5%, respectively.³⁵⁵

However, the reported flexible PSCs are almost based on small surface areas to date. It is well known that low-temperature processable SnO₂ provides fundamental support for mass production *via* some scalable fabrication and coating techniques, with enormous potential for practical applications in light, wearable, and portable electronic devices.

6.2 Large-area perovskite solar cells

Large-area fabrication is a critical component in achieving industrial production and commercialization. In general, when the area of the devices is increased to a large scale, the PCE decreases due to the inevitable loss of homogeneity in the films. As a result, various scalable deposition methods and related morphology control strategies for large-area uniform SnO₂ films are developed, determining the performance of large-area flexible PSCs. A solution-based scalable deposition method appears to be promising for preparing large-area SnO₂ films. In the lab, spin-coating is the most commonly used method for producing PSCs; however, it is hard to use it in the large-area fabrication.^{356,357} Other new methods for scalable production include slot-die,¹⁰³ spray-coating,³⁵⁸ CBD,^{359,360} sputtering,^{148,149} and bar coating.³⁶¹

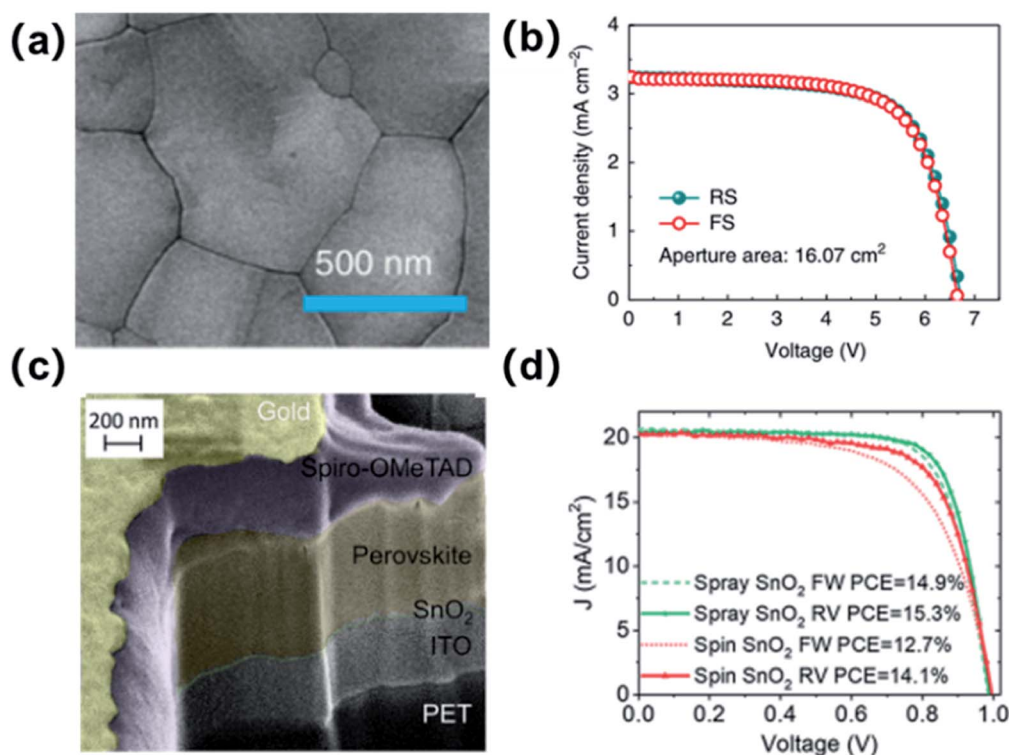


Fig. 20 Top view SEM images of (a) a perovskite film based on SnO_2 fabricated by slot-die coating; (c) the cross-sectional SEM images of a perovskite solar cell based on SnO_2 fabricated by spray-coating; forward/reverse scan J - V curve of (b) the best device based on SnO_2 fabricated by slot-die coating; (d) the best device based on SnO_2 fabricated by spray-coating. (a and b) Reproduced with permission.¹⁰³ Copyright 2020, Nature Publishing Group; (c and d) Reproduced with permission.³⁵⁸ Copyright 2021, ACS Publishing Group.

Bu *et al.* slot-die-coated SnO_2 on $5 \times 6 \text{ cm}^2$ -sized substrates with a potassium interfacial passivation strategy and achieved a 14.89% efficiency (Fig. 20a and b). The results demonstrated that potassium passivation could stabilize SnO_2 colloids, reducing hysteresis in SnO_2 -based devices.¹⁰³ Taheri *et al.* pioneered the concept of combining laser scribing optimization with automated spray-coating of SnO_2 layers for FPSCs (Fig. 20c and d). The method produced uniform and dense SnO_2 ETLs with PCEs of 12% and 10.7% with active areas of 16.84 and 21.2 cm^2 , respectively.³⁵⁸ Qiu *et al.* looked into the effect of an oxidizing environment on the formation of SnO_2 films. As an example, the champion device with an aperture area of 22.8 cm^2 demonstrated a PCE of 12.03%. Currently, the largest SnO_2 -based PSC obtained by CBD deposition was 53.64 cm^2 (active area) on a 100 cm^2 substrate, with a certified PCE of 17.4%.³⁶⁰

The manufacturing cost of SnO_2 films is an important parameter for scalable SnO_2 fabrication. Appropriate deposition methods and raw materials can significantly reduce costs. Instability, on the other hand, can seriously shorten the device's lifespan. As a result, the optimized deposition methods, passivation strategies, and encapsulation have a high potential for scaling up PSCs.

7. Conclusions and outlook

SnO_2 has many merits of direct bandgap, high conductivity, low trap density, and being solution-processable under low-

temperature conditions, which has been regarded as an ideal electron transport material in the field of PSCs. So far, the champion efficiency of SnO_2 ETL-based planar PSCs combined with passivation strategy has been increased to 25.2%, which approached the device with the mesoporous structure.

SnO_2 -based PSCs have distinctive device structures, including planar, mesoporous, distressed, and flexible substrate-based structures. Different testimony techniques for SnO_2 to suit various structures have been reported. Although the annealing temperature is much lower than that of TiO_2 preparation, it is still excessively high to flexible PSCs or inversed structure PSCs. Subsequently, loads of work should be promoted to bring down the process temperature and simplify the process.

Like other metal oxidation, pristine SnO_2 films contain many bulk and surface defects. As previously mentioned SnO_2 combined with doped elements, bilayers, and interfacial engineering can retard the formation of the defect states, which improves the carrier transport performance, leading to negligible hysteresis in the device. To guide the design of an efficient process, we need to fully characterize the types and density of defects that form in SnO_2 and the followed perovskite to gain a fundamental understanding. In addition, standard characterization protocols should be established to properly evaluate the effect of interfacial modifiers on the performance and stability of PSCs. In principle, a molecular library could be found by investigating the effect of functional groups, the

conjugated system, and the substituent of the additives or interfacial modifiers on the passivation capacity. With the research information amassed and distributed in the entire exploration field, we can utilize AI to find the basic standards for choosing the materials and effective processes.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

This work was financially supported by the National Nature Science Foundation of China (21676188).

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