



Modification of SnO₂ Electron Transport Layer in Perovskite Solar Cells

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Abstract: Rapid development of the device performance of organic-inorganic lead halide perovskite solar cells (PSCs) are emerging as a promising photovoltaic technology. Current world-record efficiency of PSCs is based on tin oxide (SnO₂) electron transport layers (ETLs), which are capable of being processed at low temperatures and possess high carrier mobilities with appropriate energy-band alignment and high optical transmittance. Modification of SnO₂ has been intensely investigated by various approaches to tailor its conductivity, band alignment, defects, morphology, and interface properties. This review article organizes recent developments of modifying SnO₂ ETLs to PSC advancement using surface and bulk modifications, while concentrating on photovoltaic (PV) device performance and long-term stability. Future outlooks for SnO₂ ETLs in PSC research and obstacles remaining for commercialization are also discussed.

Keywords: metal-halide perovskite; photovoltaics; solar-cell materials; tin-oxide-electron- transport layers



Citation: Park, H.H. Modification of SnO₂ Electron Transport Layer in Perovskite Solar Cells. *Nanomaterials* 2022, 12, 4326. https://doi.org/ 10.3390/nano12234326

Academic Editor: Alessandro Pecchia

Received: 13 November 2022 Accepted: 2 December 2022 Published: 5 December 2022

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1. Introduction

Solar energy is one of the most plentiful energy resources accessible to humankind. Among the various PV technologies, currently monocrystalline-silicon-solar cells dominate the PV market due to its high PCE of 26.1% and high working stability, but suffers from cost-intensive production cost of the highly purified monocrystalline silicon. The low production cost and rapid increase in unit-cell efficiency of organic-inorganic PSCs, which is currently 25.7% [1], enables it to compete with silicon-solar cells. Organometallic- halide perovskites are based on the chemical formula of ABX_3 , where *A* is organic or metal cations, such as methylammonium (CH₃NH₃⁺ (MA⁺)), formamidinium ((NH₂)₂CH⁺ (FA⁺)), Rb⁺, or Cs⁺, *B* is metal ions, such as Pb²⁺ or Sn²⁺, and *X* is halogen ions, such as I⁻, Br⁻, or Cl⁻. Organometallic-halide perovskites possess features of an ideal absorber material, including high absorption coefficients (~10⁻⁴ cm⁻¹), long carrier-diffusion lengths (>1 μ m), ambipolar-charge-transport capabilities, and low exciton-binding energy (20–50 meV), [2].

A typical *n-i-p* PSC device structure consists of glass/transparent conducting oxide (TCO)/n-type ETL/perovskite absorber/*p*-type hole transport layer (HTL)/metal contact. The bottom TCO is usually fluorine-doped tin oxide (FTO) or indium tin oxide (ITO), and the top metal contact is typically gold (Au), silver (Ag), or aluminum (Al). For a typical *p-i-n* PSC device, the structure consists of glass/TCO/HTL/perovskite/ETL/top metal contact.

Among the various layers in PSCs, the ETL plays a key role in photovoltaic performance and the charge dynamics. Traditionally, mesoporous titanium dioxide (mp-TiO₂) was used as the ETL in *n-i-p* structured devices with 2,2',7,7'-tetrakis-(N,N-di-4methoxyphenylamino)-9,9'-spirobifluorene (spiro-OMeTAD) or poly[bis(4-phenyl)(2,5,6trimethylphenyl)amine] (PTAA) as the HTL. However, high-temperature sintering is required for the mp-TiO₂ to enhance the crystallinity and remove organic material in the TiO₂ paste. Furthermore, there is a charge barrier at the TiO₂/perovskite interface, leading to inefficient charge transfer and a large charge accumulation at the interface. Other organic materials, including fullerene and its derivatives, have also been used as ETLs in PSCs [3,4]. However, such organic-conducting materials have unreliable stability against light, thermal, and environmental factors. Other low-temperature processed metal oxides, such as tin oxide (SnO₂) [5], zinc oxide (ZnO) [6,7], tungsten oxide (WO₃) [8], indium oxide (In₂O₃) [9], niobium oxide (Nb₂O₅) [10], cerium oxide (CeO_x) [11], Zn₂SO₄ [12], BaSnO₃ [13], SrTiO₃ [14], and cadmium sulfide (CdS) [15] have also been explored. ZnO can be processed at low temperatures, but the -OH residue on the ZnO surface causes to decompose the perovskite layer leading to environmentally unstable devices. The high toxicity of cadmium becomes a concern regarding to CdS. In addition, the low bandgap of CdS (2.4 eV) causes current loss in the UV range.

Compared to the traditional *mp*-TiO₂ ETL in PSCs, SnO₂ can be fabricated at lower temperatures, which expands its possible applications to flexible substrates. SnO₂ also has a more favorable band alignment in PSCs compared to TiO₂, as the conduction-band minimum is lower than that of TiO₂, which induces higher efficiency of charge injection. It also possesses good electrical conductivity and high optical transmittance [16,17]. Furthermore, the larger bandgap of SnO₂ compared to TiO₂ makes it less vulnerable to UV light. Thus, the device stability can be improved by suppressed UV-related photochemical reaction. Some drawbacks of SnO₂ are the bulk and surface defects in the pristine films, such as surface-adsorbed hydroxyl groups, uncoordinated Sn⁴⁺, and oxygen vacancies, which deteriorate electronic properties and capture electrons, degrading the stability and efficiency of PSCs. Such drawbacks of SnO₂ can be alleviated by modifying the bulk or surface of the film, which will be discussed in this review.

Suitable ETL materials should (i) have a favorable energy-band alignment with the absorber layer for efficient electron transfer from the perovskite to ETL, (ii) exhibit high transparency to minimize optical losses, (iii) possess a wide optical bandgap so that there will be no contribution as a second absorber layer and can also benefit the photochemical reaction, as the wide bandgap will prevent reaction with high-energy radiation, such as UV-light, which is key for the device stability, (iv) have a high conductivity for high fill factors and low series resistance, (v) exhibit appropriate hydrophobic behavior to tolerate long-term exposure to humidity, (vi) be environmentally friendly, and (vii) have low fabrications and materials costs [17–21].

The modification of SnO₂ has been investigated by various institutions and has contributed to enhancing the PV performance and device stability of PSCs. In this review, the recent contributions of SnO₂ ETLs in PSCs are organized based on photovoltaic performance and stability. Section 2 will cover modification of SnO₂ ETLs in PSCs using elemental doping, insertion of metal-oxide layers, ionic compounds, carbon materials, and organic molecules. Section 2 will also discuss the long-term stability of the modified SnO₂ ETL-based PSCs. Development in the device efficiency and stability are organized in Tables 1–9, respectively. Section 3 will summarize the SnO₂ modification approaches and discuss future outlooks for commercialization.

ETL	Method	Device Stack	J _{SC} (mA/cm ²)	V _{OC} (V)	FF (%)	η (%)	Institute, Year [Ref.]
Ta:SnO ₂	Chemical Bath Deposition	ITO/ETL/MAPbI3/Spiro-OMeTAD/Au	$21.7 \rightarrow 22.8$	1.16 ightarrow 1.16	$77.7 \rightarrow 78.6$	19.5 ightarrow 20.8	Fudan, 2019 [22]
Bilayer F:SnO ₂	Spin Coating	FTO/ETL/(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} /Spiro- OMeTAD/Au	$21.7 \rightarrow 22.9$	$1.03 \rightarrow 1.13$	$72.3 \rightarrow 78.1$	16.3 ightarrow 20.2	Huazhong UST, 2018 [23]
Li:SnO ₂	Spin Coating	ITO/ETL/MAPbI3/Spiro-OMeTAD/Au	$22.0 \rightarrow 23.3$	$1.08 \rightarrow 1.11$	$64.2 \rightarrow 70.7$	$15.3 \rightarrow 18.2$	KIST, 2016 [24]
Nb:SnO ₂	Spin Coating	FTO/ETL/(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} /Spiro- OMeTAD/Au	$21.7 \rightarrow 22.4$	$1.06 \rightarrow 1.08$	$65.9 \rightarrow 72.7$	$15.1 \rightarrow 17.6$	Shaanxi Normal U., 2017 [25]
Y:SnO ₂	Hydrothermal Growth	FTO/ETL/MAPbI ₃ /Spiro-OMeTAD/Au	$19.3 \rightarrow 22.6$	$1.05 \rightarrow 1.08$	$66.0 \rightarrow 71.0$	13.4 ightarrow 17.3	Wuhan U. & Toledo, 2017 [26]
Sb:SnO ₂	Spin Coating	ITO/ETL/MAPbI ₃ /Spiro-OMeTAD/Au	$22.3 \rightarrow 22.6$	$1.01 \rightarrow 1.06$	69.6 ightarrow 72.0	$15.7 \rightarrow 17.2$	UNL, 2016 [27]
Ga:SnO ₂	Spin Coating	AZO/ETL/CsFAMAPb(Br,I)3/Spiro- OMeTAD/Au	$22.0 \rightarrow 22.8$	1.00 ightarrow 1.07	57.0 ightarrow 70.0	12.5 ightarrow 17.0	Adolphe Merkle Inst. & HZB, 2018 [28]
Mg:SnO ₂	Spin Coating	FTO/ETL/MAPbI ₃ /Spiro-OMeTAD/Au	17.4 ightarrow 21.4	0.94 ightarrow 1.00	$50.0 \rightarrow 70.8$	$8.2 \rightarrow 15.2$	Wuhan U., 2016 [29]
Al:SnO ₂	Spin Coating	FTO/ETL/MAPbI ₃ /Spiro-OMeTAD/Au	$16.8 \rightarrow 19.4$	$1.00 \rightarrow 1.03$	$53.0 \rightarrow 58.0$	9.0 ightarrow 12.1	UESTC, 2017 [30]

Table 1. Summary of perovskite-solar cells based on elemental doping of SnO₂ ETL.

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ETL	Method	Device Stack	J _{SC} (mA/cm ²)	V _{OC} (V)	FF (%)	η (%)	Institute, Year [Ref.]
In ₂ O ₃ /SnO ₂	Spin Coating	ITO/ETL/MAFAPbICl/spiro- OMeTAD/Au	$24.3 \rightarrow 24.5$	1.13 ightarrow 1.16	78.1 ightarrow 81.2	$21.4 \rightarrow 23.1$	Nankai, 2020 [31]
$SnO_2/Eu:WO_x$	Spin Coating	FTO/ETL/CsFAMAPbIBr/spiro- OMeTAD/Eu:WO _x /Au	$23.3 \rightarrow 24.0$	$1.11 \rightarrow 1.16$	$73.4 \rightarrow 79.4$	19.0 ightarrow 22.1	Jilin, 2021 [32]
TiO ₂ /SnO ₂	Potentiostatic Anodization, Spin Coating	FTO/ETL/MAFAPbBrI/spiro- OMeTAD/Ag	$22.1 \rightarrow 22.9$	1.14 ightarrow 1.20	75.4 ightarrow 76.4	19.0 ightarrow 21.1	Toronto, POSTECH, 2017 [33]
TiO_2/SnO_2	Spray Pyrolysis, Spin Coating	FTO/ETL/MAPbI3/PTAA/Au	$21.5 \rightarrow 22.6$	$1.10 \rightarrow 1.13$	$69.0 \rightarrow 78.0$	16.4 ightarrow 19.8	EPFL, 2017 [34]
SnO_2/MgO	Spin Coating	ITO/ETL/MAPbI3/spiro-OMeTAD/Au	$21.3 \rightarrow 22.1$	$1.10 \rightarrow 1.13$	$64.9 \rightarrow 75.7$	$15.2 \rightarrow 19.0$	RTV, 2018 [35]
PbO:SnO _{2/} SnO ₂	Spin Coating	FTO/ETL/MAPbI3/spiro-OMeTAD/Au	$20.9 \rightarrow 22.6$	$1.11 \rightarrow 1.10$	$72.9 \rightarrow 75.5$	17.0 ightarrow 18.8	CAS, 2021 [36]
MgO/SnO_2	Spin Coating	FTO/ETL/MAPbI3/spiro-OMeTAD/Au	$21.6 \rightarrow 22.7$	$1.07 \rightarrow 1.10$	$71.0 \rightarrow 73.0$	$16.4 \rightarrow 18.2$	Wuhan, 2017 [37]
SnO_2/TiO_2	Chemical Bath Deposition	FTO/ETL/MAPbI ₃ /spiro-OMeTAD/Ag	$22.2 \rightarrow 22.5$	$0.97 \rightarrow 1.01$	$56.0 \rightarrow 79.0$	$12.0 \rightarrow 18.1$	ECUST, Griffith, 2017 [38]
SnO ₂ /ZnO	Spin Coating	ITO/ETL/CsPbI2Br/spiro- OMeTAD/MoO3/Ag	$14.7 \rightarrow 15.0$	$1.06 \rightarrow 1.23$	75.7 ightarrow 78.8	$11.9 \rightarrow 14.6$	South China UT, 2018 [39]

Table 2. Summary of perovskite-solar cells based on metal oxide modified SnO₂ ETL.

ETL	Method	Device Stack	J _{SC} (mA/cm ²)	V _{OC} (V)	FF (%)	η (%)	Institute, Year [Ref.]
SnO ₂ /RbF	Spin Coating	ITO/ETL/CsMAFAPbIBr/CH ₃ O-PEAI/Spiro- OMeTAD/Au	$24.2 \rightarrow 24.3$	1.20 ightarrow 1.21	$77.4 \rightarrow 79.3$	$22.4 \rightarrow 23.4$	CAS, 2021 [40]
p-SnO ₂ :RbF/m- SnO ₂ /RbF	Spin Coating	ITO/ETL/CsMAFAPbIBrCl/Spiro-OMeTAD/Ag	$23.7 \rightarrow 24.5$	$1.11 \rightarrow 1.15$	77.8 ightarrow 82.1	$20.6 \rightarrow 22.7$	Southwest Petrolium, 2022 [41]
SnO ₂ /4- Imidazoleacetic acid hydrochloride (ImAcHCl)	Spin Coating	FTO/ETL/MA _{0.05} FA _{0.95} Pb(I _{0.95} Br _{0.05}) ₃ /Spiro- OMeTAD/Au	$22.7 \rightarrow 23.1$	1.09 ightarrow 1.15	79.0 ightarrow 79.0	$19.5 \rightarrow 21.0$	SKKU, 2019 [42]
SnO ₂ /KOH	CBD, Spin Coating	FTO/ETL/Cs _{0.05} (FA _{0.85} MA _{0.15}) _{0.95} Pb(I _{0.85} Br _{0.15}) ₃ /Spiro- OMeTAD/Au	$22.5 \rightarrow 22.6$	$1.10 \rightarrow 1.15$	$78.0 \rightarrow 79.0$	19.3 ightarrow 20.5	Wuhan UT, 2018 [43]
SnO_2/Cs_2CO_3	Spin Coating	FTO/ETL/Cs _{0.05} (MA _{0.17} FA _{0.83}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ /Spiro- OMeTAD/Au	$20.7 \rightarrow 23.3$	$1.14 \rightarrow 1.17$	$66.2 \rightarrow 71.4$	$15.6 \rightarrow 19.5$	Shanghai UES, 2021 [44]
SnO ₂ /KCl	Spin Coating	ITO/ETL/MAPbI ₃ /Spiro-OMeTAD/Au	22.0 ightarrow 22.7	1.05 ightarrow 1.06	$77.3 \rightarrow 77.6$	17.8 ightarrow 18.7	UST Beijing, 2020 [45]
$SnO_2/NaCl$	Spin Coating	ITO/ETL/MAPbI ₃ /Spiro-OMeTAD/Au	$22.0 \rightarrow 22.1$	1.05 ightarrow 1.06	$77.3 \rightarrow 79.0$	17.8 ightarrow 18.5	UST Beijing, 2020 [45]
$SnO_2/LiCl$	Spin Coating	ITO/ETL/MAPbI ₃ /Spiro-OMeTAD/Au	22.0 ightarrow 22.5	$1.05 \rightarrow 1.06$	$77.3 \rightarrow 76.9$	17.8 ightarrow 18.3	UST Beijing, 2020 [45]
$SnO_2/RbCl$	Spin Coating	ITO/ETL/MAPbI ₃ /Spiro-OMeTAD/Au	22.0 ightarrow 22.2	1.05 ightarrow 1.04	$77.3 \rightarrow 77.4$	17.8 ightarrow 17.9	UST Beijing, 2020 [45]
$SnO_2/CsCl$	Spin Coating	ITO/ETL/MAPbI ₃ /Spiro-OMeTAD/Au	$22.0 \rightarrow 22.1$	$1.05 \rightarrow 1.05$	$77.3 \rightarrow 76.1$	$17.8 \rightarrow 17.7$	UST Beijing, 2020 [45]

Table 3. Summary of perovskite-solar cells based on surface modification of SnO₂ ETL by ionic compounds.

ETL	Method	Device Stack	J _{SC} (mA/cm ²)	V _{OC} (V)	FF (%)	η (%)	Institute, Year [Ref.]
CoCl ₂ :SnO ₂	Spin Coating	ITO/ETL/MAFAPbIBrCl/Spiro-OMeTAD/Au	$24.2 \rightarrow 24.6$	1.16 ightarrow 1.20	$78.9 \rightarrow 80.8$	$22.2 \rightarrow 23.8$	Nankai, 2021 [46]
Heparin potassium:SnO ₂	Spin Coating	FTO/ETL/Cs _{0.05} MA _{0.10} FA _{0.85} Pb(I _{0.97} Br _{0.03}) ₃ /Spiro- OMeTAD/Au	$24.3 \rightarrow 25.0$	$1.13 \rightarrow 1.16$	$75.4 \rightarrow 79.4$	20.7 ightarrow 23.1	Huazhong UST, 2020 [47]
KCl:SnO ₂	Spin Coating	ITO/ETL/MAFAPbIBr/Spiro-OMeTAD/Au	$24.0 \rightarrow 24.2$	$1.08 \rightarrow 1.14$	77.9 ightarrow 80.7	$20.2 \rightarrow 22.2$	Nanjing, 2020 [48]
Girard's Reagent T (GRT):SnO ₂	Spin Coating	ITO/ETL/Rb _{0.05} (FA _{0.95} MA _{0.05}) _{0.95} PbI _{2.85} Br _{0.15} /Spiro- OMeTAD/Au	$22.6 \rightarrow 22.9$	$1.08 \rightarrow 1.15$	$81.2 \rightarrow 82.3$	$19.8 \rightarrow 21.6$	Chongqing, 2021 [49]
NH ₄ Cl:SnO ₂	Spin Coating	ITO/ETL/MAFAPbIBr/Spiro-OMeTAD/Au	$23.2 \rightarrow 24.3$	$1.10 \rightarrow 1.15$	$73.5 \rightarrow 76.8$	$18.7 \rightarrow 21.4$	Soochow, 2019 [50]
Potassium sodium tartrate (PSTA):SnO ₂	Spin Coating	ITO/ETL/MA _{0.85} FA _{0.15} PbI ₃ /Spiro-OMeTAD/Ag	$23.5 \rightarrow 24.5$	$1.08 \rightarrow 1.12$	$71.9 \rightarrow 76.9$	18.3 ightarrow 21.1	Jilin Normal, 2021 [51]
Phosphoric acid:SnO ₂	Spin Coating	ITO/ETL/MA _{0.15} FA _{0.85} Pb(I _{0.85} Br _{0.15}) ₃ /Spiro- OMeTAD/Ag	$22.5 \rightarrow 23.2$	1.18 ightarrow 1.17	$73.8 \rightarrow 77.4$	19.7 ightarrow 21.0	CAS, 2019 [52]
Tetramethylammonium hydroxide (TMAH):SnO ₂	Spin Coating	FTO/ETL/MA _{0.25} FA _{0.75} PbI _{2.5} Br _{0.5} /Spiro- OMeTAD/Au	$22.8 \rightarrow 23.3$	$1.13 \rightarrow 1.14$	70.4 ightarrow 77.4	18.1 ightarrow 20.5	Shenzhen, 2018 [53]
CsF:SnO ₂	Spin Coating	FTO/ETL/Cs _{0.05} (MA _{0.15} FA _{0.85}) _{0.95} Pb(I _{0.85} Br _{0.15}) ₃ /4- tert-butyl-D-phenylalanine (D4TBP)/Spiro-OMeTAD/Au	$22.6 \rightarrow 23.2$	1.13 ightarrow 1.16	75.0 ightarrow 76.0	$19.3 \rightarrow 20.5$	KMU, 2020 [54]
(NH ₄) ₂ S:SnO ₂	Spin Coating	ITO/ETL/MAFAPbIBr/Spiro-OMeTAD/Ag	$22.4 \rightarrow 23.0$	1.13 ightarrow 1.15	73.4 ightarrow 76.0	18.7 ightarrow 20.0	CAS, 2019 [55]

Table 4. Summary of perovskite-solar cells based on bulk incorporation of ionic compounds into SnO₂ ETL.

ETL	Method	Device Stack	J _{SC} (mA/cm ²)	V _{OC} (V)	FF (%)	η (%)	Institute, Year [Ref.]
SnO ₂ /fulleropyrrolidine (NMBF-Cl)	Spin Coating	ITO/ETL/MAFAPbIBr/Spiro- OMeTAD/Ag	25.2 ightarrow 26.0	$1.13 \rightarrow 1.12$	$75.0 \rightarrow 77.0$	$21.4 \rightarrow 22.3$	Wuhan UT, 2020 [56]
SnO ₂ /Polystyrene (PS)	Spin Coating	ITO/ETL/MAFAPbIBr/PS/Spiro- OMeTAD/Au	$23.8 \rightarrow 24.0$	$1.09 \rightarrow 1.10$	$74.0 \rightarrow 76.0$	19.3 ightarrow 20.5	CAS, 2019 [57]
SnO ₂ /Graphene quantum dots	Spin Coating	ITO/ETL/MAPbI3/spiro-OMeTAD/Au	22.1 ightarrow 23.1	$1.10 \rightarrow 1.13$	$73.6 \rightarrow 77.8$	$17.9 \rightarrow 20.3$	Zhejiang, 2017 [58]
SnO ₂ /[6,6]-phenyl- C ₆₁ -butyric acid methyl ester (PCBM)	Spin Coating	FTO/ETL/MAPbI ₃ /spiro- OMeTAD/PbS/Au	$22.3 \rightarrow 23.3$	1.13 ightarrow 1.14	$75.0 \rightarrow 74.0$	18.8 ightarrow 19.6	Wuhan, 2017 [59]
SnO ₂ /PCBM	Spin Coating	FTO/ETL/MAPbI ₃ /spiro-OMeTAD/Au	$21.1 \rightarrow 22.6$	$1.09 \rightarrow 1.12$	$71.5 \rightarrow 75.8$	$16.5 \rightarrow 19.1$	Toledo, Wuhan, 2016 [60]
SnO_2/C_{60} -SAM	PEALD, Spin Coating	FTO/ETL/MAPbI ₃ /spiro-OMeTAD/Au	$21.2 \rightarrow 21.4$	1.07 ightarrow 1.13	$75.5 \rightarrow 79.1$	$17.2 \rightarrow 19.0$	Toledo, 2016 [61]
SnO ₂ /[6,6]-phenyl- C ₆₁ -butyric acid (PCBA)	Spin Coating	ITO/ETL/MA _{0.34} FA _{0.66} PbI _{2.85} Br _{0.15} /Spiro- OMeTAD/MoO ₃ /Au	$22.0 \rightarrow 22.2$	1.10 ightarrow 1.10	64.0 ightarrow 76.0	$15.4 \rightarrow 18.6$	Eindhoven, 2019 [62]

Table 5. Summary of perovskite-solar cells based on surface modification of SnO_2 ETL by carbon materials.

ETL	Method	Device Stack	J _{SC} (mA/cm ²)	V _{OC} (V)	FF (%)	η (%)	Institute, Year [Ref.]
Polymeric carbon nitrides (cPCN):SnO ₂	Spin Coating	FTO/ETL/MAFAPbIBr/Spiro- OMeTAD/Ag	23.4 ightarrow 24.9	1.11 ightarrow 1.13	$82.0 \rightarrow 82.5$	$21.3 \rightarrow 23.2$	CAS, 2021 [63]
Nb ₂ C:SnO ₂	Spin Coating	ITO/ETL/Cs _{0.05} MA _{0.07} FA _{0.88} PbI ₃ /Spiro- OMeTAD/MoO ₃ /Au	$24.7 \rightarrow 25.3$	$1.11 \rightarrow 1.14$	$69.1 \rightarrow 79.5$	$19.0 \rightarrow 22.9$	China UPB, 2021 [64]
Carbon quantum dot:SnO ₂	Spin Coating	ITO/ETL/Cs _{0.05} (MA _{0.17} FA _{0.83}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ /Spiro- OMeTAD/MoO ₃ /Au	$23.1 \rightarrow 24.1$	1.07 ightarrow 1.14	77.8 ightarrow 82.9	19.2 ightarrow 22.8	CAS, 2020 [65]
Polyacrylamide (PAM):SnO ₂	Spin Coating	ITO/ETL/MAFAPbIBrCl/Spiro- OMeTAD/Au	$23.2 \rightarrow 24.8$	$1.10 \rightarrow 1.12$	$79.2 \rightarrow 81.1$	$20.2 \rightarrow 22.6$	Guilin UT, CAS, 2022 [66]
g-C ₃ N ₄ :SnO ₂	Spin Coating	ITO/ETL/CsMAFAPbIBr/Spiro- OMeTAD/Au	$23.7 \rightarrow 24.0$	$1.11 \rightarrow 1.12$	$76.2 \rightarrow 78.3$	$20.2 \rightarrow 22.1$	Xian Jiaotong, 2020 [67]
Graphdiyne:SnO ₂	Spin Coating	ITO/ETL/CsMAFAPbIBr/Spiro- OMeTAD/Au	$22.9 \rightarrow 23.3$	$1.13 \rightarrow 1.14$	$74.3 \rightarrow 79.6$	19.2 ightarrow 21.1	UST Beijing, 2020 [68]
Naphthalene diimide graphene:SnO ₂	Spin Coating	ITO/ETL/MA _{0.17} FA _{0.83} PbI _{2.63} Br _{0.37} /Spiro- OMeTAD/Au	$23.2 \rightarrow 22.7$	1.10 ightarrow 1.08	74.6 ightarrow 82.1	19.0 ightarrow 20.2	Huazhong UST, 2018 [69]
Carbon nanodot:SnO ₂	Spin Coating	ITO/ETL/CsMAFAPbIBr/Spiro- OMeTAD/Au	$22.5 \rightarrow 23.1$	1.08 ightarrow 1.10	76.0 ightarrow 79.0	18.5 ightarrow 20.0	UST Beijing, 2019 [70]

Table 6. Summary of perovskite-solar cells based on bulk incorporation of carbon materials into SnO₂ ETL.

ETL	Method	Device Stack	J _{SC} (mA/cm ²)	V _{OC} (V)	FF (%)	η (%)	Institute, Year [Ref.]
KCl:SnO ₂ /BTAC4	Spin Coating	ITO/ETL/Cs _{0.05} (MA _{0.15} FA _{0.85}) _{0.95} Pb(I _{0.85} Br _{0.15}) ₃ /Spiro-OMeTAD/Ag	23.1 ightarrow 24.2	$1.23 \rightarrow 1.25$	$75.0 \rightarrow 76.1$	$21.2 \rightarrow 23.1$	CAS, 2021 [71]
KCl:SnO ₂ /Y6	Spin Coating	ITO/ETL/Cs _{0.05} (MA _{0.15} FA _{0.85}) _{0.95} Pb(I _{0.85} Br _{0.15}) ₃ /Spiro-OMeTAD/Ag	23.1 ightarrow 23.6	$1.23 \rightarrow 1.24$	$75.0 \rightarrow 75.6$	$21.2 \rightarrow 22.1$	CAS, 2021 [71]
SnO ₂ /Si(OCH ₃) ₃ (CH ₂) ₃ I (I-SAM)	Spin Coating, Immerse in solution	ITO/ETL/Cs _{0.05} (FA _{0.85} MA _{0.15}) _{0.95} Pb(I _{0.85} Br _{0.15}) ₃ /Spiro-OMeTAD/Au	$23.0 \rightarrow 23.3$	1.13 ightarrow 1.19	77.4 ightarrow 77.8	$20.2 \rightarrow 21.4$	Brown, 2021 [72]
SnO ₂ /Triphenylphosphine oxide (TPPO)	Spin Coating	ITO/ETL/Cs _{0.05} (FA _{0.85} MA _{0.15}) _{0.95} Pb(I _{0.85} Br _{0.15}) ₃ /Spiro-OMeTAD/Au	$24.4 \rightarrow 24.3$	1.08 ightarrow 1.11	$72.2 \rightarrow 77.0$	19.0 ightarrow 20.7	SUST, 2019 [73]
SnO ₂ /Thiophene-3- acetic acid	Spin Coating	ITO/ETL/MAPbI ₃ /spiro- OMeTAD/MoO ₃ /Ag	$22.3 \rightarrow 23.0$	1.07 ightarrow 1.12	$73.5 \rightarrow 80.1$	17.5 ightarrow 20.6	South China UT, 2021 [74]
SnO ₂ /Aminosulfonic acid	Spin Coating, Immerse in solution	ITO/ETL/Cs _{0.05} (FA _{0.85} MA _{0.15}) _{0.95} Pb(I _{0.85} Br _{0.15}) ₃ /Spiro-OMeTAD/Au	$21.8 \rightarrow 22.8$	$1.12 \rightarrow 1.15$	$74.8 \rightarrow 77.9$	18.2 ightarrow 20.4	Beihang, 2020 [75]
SnO ₂ /p-amino benzenesulfonic acid (ABSA)	Spin Coating	ITO/ETL/MAPbI ₃ /Spiro- OMeTAD/MoO ₃ /Ag	22.4 ightarrow 22.9	1.10 ightarrow 1.13	73.0 ightarrow 78.8	18.0 ightarrow 20.3	South China UT, 2021 [76]
SnO ₂ /Choline chloride	Spin Coating, Immerse in solution	FTO/ETL/MAPbI3/Spiro-OMeTAD/Au	$21.3 \rightarrow 22.8$	1.07 ightarrow 1.15	$73.9 \rightarrow 72.4$	16.8 ightarrow 18.9	Renmin U. China, 2020 [77]
SnO ₂ /4- pyridinecarboxylic acid (PA-SAM)	Spin Coating	ITO/SnO ₂ -SAM/MAPbI ₃ /spiro- OMeTAD/Au	$21.7 \rightarrow 22.0$	1.06 ightarrow 1.10	$74.9 \rightarrow 77.4$	17.2 ightarrow 18.8	UCLA, 2017 [78]
SnO ₂ /Potassium hexylxanthate	Spin Coating	ITO/ETL/MAPbI ₃ /Spiro-OMeTAD/Au	$21.7 \rightarrow 22.6$	$1.03 \rightarrow 1.06$	$73.7 \rightarrow 76.9$	$16.6 \rightarrow 18.4$	Kyushu Tech., 2018 [79]
SnO ₂ /4-cyanobenzoic acid (CBA-SAM)	Spin Coating	ITO/SnO ₂ -SAM/MAPbI ₃ /spiro- OMeTAD/Au	$21.7 \rightarrow 21.7$	$1.06 \rightarrow 1.08$	$74.9 \rightarrow 78.1$	17.2 ightarrow 18.3	UCLA, 2017 [78]
SnO ₂ /benzoic acid (BA-SAM)	Spin Coating	ITO/SnO ₂ -SAM/MAPbI ₃ /spiro- OMeTAD/Au	$21.7 \rightarrow 21.9$	1.06 ightarrow 1.11	$74.9 \rightarrow 74.6$	17.2 ightarrow 18.1	UCLA, 2017 [78]

Table 7. Summary of perovskite-solar cells based on surface modification of SnO₂ ETL by organic molecules.

ETL	Method	Device Stack	J _{SC} (mA/cm ²)	V _{OC} (V)	FF (%)	η (%)	Institute, Year [Ref.]
Poly(ethylene glycol) diacrylate (PEGDA):SnO ₂	Spin Coating	ITO/ETL/FAPbI ₃ /Spiro-OMeTAD/MoO ₃ /Ag	$24.8 \rightarrow 25.3$	$1.09 \rightarrow 1.14$	80.6 ightarrow 81.0	$21.8 \rightarrow 23.3$	CAS, Chongqing, 2021 [80]
2,2,2- trifluoroethanol:SnO ₂ , O ₂ plasma	Spin Coating	ITO/ETL/MAFAPbIBr/Spiro-OMeTAD/Au	$\begin{array}{c} 23.1 \rightarrow 23.9 \rightarrow \\ 24.1 \end{array}$	$\begin{array}{c} 1.10 \rightarrow 1.12 \rightarrow \\ 1.12 \end{array}$	$\begin{array}{c} 75.5 \rightarrow 78.0 \rightarrow \\ 80.2 \end{array}$	$\begin{array}{c} 19.2 \rightarrow 20.9 \rightarrow \\ 21.7 \end{array}$	CAS, 2019 [81]
Ethylene diamine tetraacetic acid (EDTA):SnO ₂	Spin Coating	ITO/ETL/Cs _{0.05} FA _{0.95} PbI ₃ /Spiro-OMeTAD/Au	$22.8 \rightarrow 24.6$	1.10 ightarrow 1.11	$75.5 \rightarrow 79.2$	18.9 ightarrow 21.6	Shaanxi Normal, 2018 [82]
Polyethylene glycol (PEG):SnO ₂	Spin Coating	ITO/ETL/Cs _{0.05} FA _{0.81} MA _{0.14} Pb(I _{0.85} Br _{0.15}) ₃ /Spiro-OMeTAD/Au	$22.6 \rightarrow 22.7$	$1.09 \rightarrow 1.12$	$77.9 \rightarrow 81.9$	$19.2 \rightarrow 20.8$	Peking, 2018 [83]
Polyethylenimine (PEIE):SnO ₂	Spin Coating	ITO/ETL/CsMAFAPbICl/Spiro-OMeTAD/Ag	$22.9 \rightarrow 23.8$	$1.08 \rightarrow 1.14$	$76.0 \rightarrow 76.0$	$18.7 \rightarrow 20.6$	Xidian, 2020 [84]

Table 8. Summary of perovskite-solar cells based on bulk incorporation of organic molecules into SnO₂ ETL.

Table 9. Summary stability of ETL-modified perovskite-solar cells.

ETL	Device Stack	Encapsulated	Conditions	Continuous 1 SUN Illumination?	Duration	η Maintained	Institute, Year [Ref.]
F:SnO ₂	FTO/bilayer F:SnO ₂ /(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} /Spiro-OMeTAD/Au	Y	40–50%, Air, RT	Ν	300 h	>85%	Huazhong UST, 2018 [23]
Nb:SnO ₂	FTO/Nb:SnO ₂ /(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} /Spiro-OMeTAD/Au	Ν	Air, RT	Ν	288 h	90%	Shaanxi Normal U., 2017 [25]
Sb:SnO ₂	ITO/Sb:SnO2/MAPbI3/Spiro-OMeTAD/Au	Ν	Dessicator, RT	Ν	504 h	>95%	UNL, 2016 [27]
Ga:SnO ₂	AZO/Ga:SnO2/CsFAMAPb(Br,I)3/Spiro-OMeTAD/Au	Ν	N_2 , 1 SUN	Y	1000 h	~70%	Adolphe Merkle Inst. & HZB, 2018 [28]
Mg:SnO ₂	FTO/Mg:SnO ₂ /MAPbI ₃ /Spiro-OMeTAD/Au	Ν	<20%, Air	Ν	720 h	>90%	Wuhan U., 2016 [29]
In_2O_3/SnO_2	ITO/ETL/MAFAPbICl/spiro-OMeTAD/Au	Ν	N_2	Ν	1920 h	98%	Nankai, 2020 [31]
		Ν		Y	180 h	91%	
		Ν	75%	Ν	120 h	~80%	
$SnO_2/Eu:WO_x$	FTO/ETL/CsFAMAPbIBr/spiro-OMeTAD/Eu:WO _x /Au	Ν	16–25 °C, 20–30%	Y	500 h	>90%	Jilin, 2021 [32]
		Ν	Ambient	Ν	2000 h	>90%	
TiO_2/SnO_2	FTO/TiO ₂ -SnO ₂ /MAPbI ₃ /PTAA/Au	Ν	~20%, Air	Ν	1200 h	>95%	EPFL, 2017 [34]
SnO_2/MgO	ITO/ETL/MAPbI ₃ /spiro-OMeTAD/Au	Ν	30%	Ν	2568 h	67%	RTV, 2018 [35]
PbO:SnO ₂ /SnO ₂	FTO/ETL/MAPbI ₃ /spiro-OMeTAD/Au		RT, 15%	Ν	1080 h	>90%	CAS, 2021 [36]
SnO_2/ZnO	ITO/ETL/CsPbI2Br/spiro-OMeTAD/MoO3/Ag	Ν	85 °C, N ₂	Ν	300 h	80%	South China UT, 2018 [39]
SnO ₂ /RbF	ITO/ETL/CsMAFAPbIBr/CH ₃ O-PEAI/Spiro-OMeTAD/Au	Ν	White LED light illumination	Ν	200 h	~75%	CAS, 2021 [40]

Table 9. Cont.

ETL	Device Stack	Encapsulated	Conditions	Continuous 1 SUN Illumination?	Duration	η Maintained	Institute, Year [Ref.]
p-SnO ₂ /RbF/m- SnO ₂ /RbF	ITO/ETL/CsMAFAPbIBrCl/Spiro-OMeTAD/Ag	Ν	MPPT	Y	300 h	90%	Southwest Petrolium, 2022 [41]
acid hydrochloride (ImAcHCl)	FTO/ETL/MA _{0.05} FA _{0.95} Pb(I _{0.95} Br _{0.05}) ₃ /Spiro-OMeTAD/Au	Ν	RT, 46–60%	Ν	840 h	94%	SKKU, 2019 [42]
(FTO/ETL/MA _{0.05} FA _{0.95} Pb(I _{0.95} Br _{0.05}) ₃ /PTAA/Au	Ν	85 °C, N ₂	Ν	40 h	90%	SKKU, 2019 [42]
SnO_2/Cs_2CO_3	FTO/ETL/Cs _{0.05} (MA _{0.17} FA _{0.83}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ /Spiro- OMeTAD/Au	Ν	35–45%	Ν	340 h	91%	Shanghai UES, 2021 [44]
SnO ₂ /NaCl	ITO/ETL/MAPbI3/Spiro-OMeTAD/Au	Ν		Ν	960 h	>90%	UST Beijing, 2020 [45]
CoCl ₂ :SnO ₂	ITO/ETL/MAFAPbIBrCl/Spiro-OMeTAD/Au	Ν	N_2	Y	200 h	84%	Nankai, 2021 [46]
		Ν	60 °C, >50%	Ν	100 h	80%	
Heparin potassium:SnO ₂	FTO/ETL/Cs _{0.05} MA _{0.10} FA _{0.85} Pb(I _{0.97} Br _{0.03}) ₃ /Spiro-OMeTAD/Au	Y	60–65 °C	Y	1000 h	~97%	Huazhong UST, 2020 [47]
KCl:SnO ₂	ITO/ETL/MAFAPbIBr/Spiro-OMeTAD/Au	N		Y	120 h	88%	Nanjing, 2020 [48]
Girard's Reagent T (GRT):SnO ₂	ITO/ETL/Rb _{0.05} (FA _{0.95} MA _{0.05}) _{0.95} Pbl _{2.85} Br _{0.15} /Spiro- OMeTAD/Au	Ν	5–10%, RT	Ν	1440 h	96%	Chongqing, 2021 [49]
		Ν	60 °C, N ₂	Ν	720 h	100%	
		Ν	N_2	Y	672 h	59%	
NH ₄ Cl:SnO ₂	ITO/ETL/MAFAPbIBr/Spiro-OMeTAD/Au	Ν	N_2	Ν	1000 h	>95%	Soochow, 2019 [50]
Potassium sodium tartrate (PSTA):SnO ₂	ITO/ETL/MA _{0.85} FA _{0.15} PbI ₃ /Spiro-OMeTAD/Ag	Ν	25 °C, 45%, Air	Ν	1440 h	>95%	Jilin Normal, 2021 [51]
Tetramethylammonium hydroxide (TMAH):SnO ₂	FTO/ETL/MA _{0.25} FA _{0.75} PbI _{2.5} Br _{0.5} /Spiro-OMeTAD/Au	Y	15%	Ν	360 h	97%	Shenzhen, 2018 [53]
CsF:SnO ₂	FTO/ETL/Cs _{0.05} (MA _{0.15} FA _{0.85}) _{0.95} Pb(I _{0.85} Br _{0.15}) ₃ /4-tert-butyl-D-phenylalanine (D4TBP)/Spiro-OMeTAD/Au	Ν	MPPT	Y	800 h	>90%	KMU, 2020 [54]
SnO ₂ /NMBF-Cl	ITO/ETL/MAFAPbIBr/Spiro-OMeTAD/Ag	Ν	25–35 °C, 45–60%, Air	Ν	1000 h	>95%	Wuhan UT, 2020 [56]
SnO ₂ /Polystyrene (PS)	ITO/ETL/MAFAPbIBr/PS/Spiro-OMeTAD/Au	Ν	Air	Ν	2800 h	>90%	CAS, 2019 [57]
		Ν	25 °C, 25%,MPPT	Y	72 h	>90%	
SnO ₂ /GQDs	ITO/ETL/MAPbI ₃ /spiro-OMeTAD/Au	Ν	$N_2 \rightarrow 20-30\%$, Air	Ν	2160 h	>95%	Zhejiang, 2017 [58]
SnO ₂ /PCBM	FTO/ETL/MAPbI3/spiro-OMeTAD/PbS/Au	Ν	Air	Ν	1000 h	~100%	Wuhan, 2017 [59]
SnO_2/C_{60} -SAM	FTO/ETL/MAPbI ₃ /spiro-OMeTAD/Au	Ν	<10%, room light, N ₂	Ν	480 h	> 98%	Toledo, 2016 [61]
Polymeric carbon nitrides (cPCN):SnO ₂	FTO/ETL/MAFAPbIBr/Spiro-OMeTAD/Ag	Ν	N_2	Ν	2880 h	95%	CAS, 2021 [63]
		Ν	25–35%, Air	Ν	2000 h	88%	

Table 9. Cont.

ETL	Device Stack	Encapsulated	Conditions	Continuous 1 SUN Illumination?	Duration	η Maintained	Institute, Year [Ref.]
Nb ₂ C:SnO ₂	ITO/ETL/Cs _{0.05} MA _{0.07} FA _{0.88} PbI ₃ /Spiro-OMeTAD/MoO ₃ /Au	Ν	25 °C, 40–60%	Ν	960 h	98%	China UPB, 2021 [64]
Carbon quantum dot:SnO ₂	ITO/ETL/Cs _{0.05} (MA _{0.17} FA _{0.83}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ /Spiro- OMeTAD/MoO ₃ /Au	Ν	25 °C, 40–60%, Air	Ν	1000 h	96%	CAS, 2020 [65]
Polyacrylamide (PAM):SnO2	ITO/ETL/MAFAPbIBrCl/Spiro-OMeTAD/Au	Ν	45-55%	Ν	1080 h	90%	Guilin UT, CAS, 2022 [66]
g-C ₃ N ₄ :SnO ₂	ITO/ETL/CsMAFAPbIBr/Spiro-OMeTAD/Au	N N	25 °C, 60%, Air 85 °C, 60%, Air	N N	1500 h 75 h	90% 80%	Xian Jiaotong, 2020 [67]
Carbon nanodot:SnO ₂	ITO/ETL/CsMAFAPbIBr/Spiro-OMeTAD/Au	Ν	20 °C, 20–30%, Air, UV	Ν	200 h	90%	UST Beijing, 2019 [70]
		Ν	Dry Air	Ν	1200 h	>90%	
KCl:SnO ₂ /BTAC4	ITO/ETL/Cs _{0.05} (MA _{0.15} FA _{0.85}) _{0.95} Pb(I _{0.85} Br _{0.15}) ₃ /Spiro- OMeTAD/Ag	Ν	35%	Ν	768 h	~90%	CAS, 2021 [71]
KCl:SnO ₂ /Y6		Ν	35%	Ν	768 h	~90%	
SnO ₂ /Si(OCH ₃) ₃ (CH ₂) ₃ I (I-SAM)	ITO/ETL/Cs _{0.05} (FA _{0.85} MA _{0.15}) _{0.95} Pb(I _{0.85} Br _{0.15}) ₃ /Spiro- OMeTAD/Au	Ν	MPPT, N ₂ , RT	Y	1200 h	>90%	Brown, 2021 [72]
SnO ₂ /Thiophene-3-acetic acid	ITO/ETL/MAPbI3/spiro-OMeTAD/MoO3/Ag	Ν	N_2	Ν	1440 h	>90%	South China UT, 2021 [74]
		Ν	85 °C, 70%, Air	Ν	130 h	>80%	
SnO ₂ /Aminosulfonic acid	ITO/ETL/Cs _{0.05} (FA _{0.85} MA _{0.15}) _{0.95} Pb(I _{0.85} Br _{0.15}) ₃ /Spiro- OMeTAD/Au	Ν	25–35%, Air	Ν	1000 h	>80%	Beihang, 2020 [75]
		Ν	60 °C, N ₂	Ν	500 h	>75%	
SnO ₂ /p-amino benzenesulfonic acid (ABSA)	ITO/ETL/MAPbI ₃ /Spiro-OMeTAD/MoO ₃ /Ag	Ν	N ₂	Ν	720 h	57%	South China UT, 2021 [76]
SnO ₂ /Potassium hexylxanthate	ITO/ETL/MAPbI ₃ /Spiro-OMeTAD/Au	Ν	RT	Ν	1680 h	~90%	Kyushu Tech., 2018 [79]
Poly(ethylene glycol) diacrylate (PEGDA):SnO2	ITO/ETL/FAPbI3/Spiro-OMeTAD/MoO3/Ag	Ν	N_2	Y	850 h	>90%	CAS, Chongqing, 2021 [80]
		Ν	30–35%, Air	Ν	1000 h	98%	
2,2,2- trifluoroethanol:SnO ₂ Ethylona diamina	ITO/ETL/MAFAPbIBr/Spiro-OMeTAD/Au	Ν	30-40%	Ν	720 h	>90%	CAS, 2019 [81]
tetraacetic acid (EDTA):SnO ₂	ITO/ETL/Cs _{0.05} FA _{0.95} PbI ₃ /Spiro-OMeTAD/Au	Ν	35%	Ν	2880 h	92%	Shaanxi Normal, 2018 [82]
		Ν	1 SUN	Y	120 h	86%	
Polyethylene glycol (PEG):SnO ₂	ITO/ETL/Cs _{0.05} FA _{0.81} MA _{0.14} Pb(I _{0.85} Br _{0.15}) ₃ /Spiro-OMeTAD/Au	Ν	28–35 °C, 30–80%, Air	Ν	2160 h	>97%	Peking, 2018 [83]
Polyethylenimine (PEIE):SnO ₂	ITO/ETL/MAFAPbI/Spiro-OMeTAD/Ag	Ν	40%	Ν	1680 h	82%	Xidian, 2020 [84]

2. Device Performance and Stability of SnO₂ ETL-Based PSCs

2.1. Elemental Doping

Elemental doping of SnO₂ is a straightforward method to effectively alter the conductivity, defect states, and energy level. SnO₂ can be simply doped by various elements to tune its electrical and chemical properties. SnO₂ is an *n*-type material. The tetravalent-Sn sites can be replaced by cations with low valence states, such as gallium (Ga³⁺), cobalt (Co³⁺), zinc (Zn²⁺), magnesium (Mg²⁺), and lithium (Li⁺) for *p*-type doping, or can be substituted by cations with high valence states, such as antimony (Sb⁵⁺), molybdenum (Mo⁵⁺), tantalum (Ta⁵⁺), and niobium (Nb⁵⁺) for *n*-type doping.

Li et al. reported a significant improvement in conductivity without declining the transmittance by doping SnO₂ with Ta [22]. Ta-doped SnO₂ improved the PCE from 19.5% to 20.9% by improved fill factor (*FF*) and short-circuit current density (J_{SC}), as shown in the illuminated current-density (J-V) curves in Figure 1a. This is due to effective acceleration of electron collection and transfer, and reduction in recombination at the ETL/absorber interface, and shown in the steady state photoluminescence (PL) and time-resolved PL (TRPL) results in Figure 1b,c.

Doping can also be performed by non-metallic elements, such as fluorine (F^-), to replace the oxygen anion sites of SnO₂. X. Gong et al. reported that gradual bilayer replacement of F^- into SnO₂ can decrease the band offset and the ETL/perovskite interface, resulting in increased built-in electric field and enhancing the open-circuit voltage (V_{OC}) [23] from 1.03 to 1.13 V. PSC devices resulted in enhancement of PCE from 16.3% to 20.2%, as shown in Figure 1d. Improved electron-extraction ability is suggested, based on the steady-state PL and TRPL results in Figure 1e,f. Encapsulated devices retained over 85% of its initial efficiency after stored in air at room temperature and 40–50% relative humidity for 300 h.

M. Park et al. reported a solution process to effectively dope SnO₂ with Li at a low processing temperature [24]. Li-doping enhanced the conductivity of SnO₂ and produced a reduction of the conduction-band energy, as shown in Figure 1g, facilitating the transfer of electrons and reduced the charge recombination. This resulted in improved V_{OC} , *FF*, and J_{SC} with a PCE increase of 15.3% to 18.2%, as shown in Figure 1h,i.

Niobium doping of SnO₂ was reported by Ren et al. using a solution-processable low-temperature method [25]. The improvement in PV performance originates from the increased conductivity and improved surface morphology, which lead to enhanced electron extraction and inhibited charge recombination. Unencapsulated devices maintained 90% of its initial PCE after 288 h stored in air at room temperature.

Yttrium (Y³⁺) doping of SnO₂ reported by Yang et al. promotes more homogeneous distribution and well-aligned SnO₂ nanosheet arrays, which leads to improved electron transfer from the absorber to the ETL [26]. Enlarged bandgaps from the Y-doping and a higher conduction-band energy allows improved energy band alignment and reduced the charge recombination at the ETL/absorber interface. This improved the PCE of the PSC from 13.4% to 17.3% by increasing V_{OC} , *FF*, and *J*_{SC}.

Bai et al. reported that Sb:SnO₂ nanocrystals was used to replace the undoped SnO₂ ETL [27]. This shifted the Fermi-energy level upward, which improved the energy- band alignment and reduced charge recombination. Electron = recombination lifetime was longer, and V_{OC} and *FF* increased with less photocurrent hysteresis. PCE values increased from 15.7% to 17.2%. Unsealed devices retained over 95% of its initial efficiency after 504 h stored in a desiccator at room temperature.

Gallium-doped SnO₂ reported by Roose et al. observed decreased trap-state density in the ETL, leading to a reduced recombination rate [28]. V_{OC} and *FF* increased from 1.00 to 1.07 V and 57.0% to 70.0%, respectively, resulting in a PCE enhancement of 12.5% to 17.0%. Unencapsulated devices maintained about 70% of its initial efficiency after 1000 h under continuous 1 SUN illumination in nitrogen (N₂).

Xiong et al. reported Mg-doped SnO₂ as the ETL in PSCs [29]. An optimum-Mg content resulted in uniform, smooth, and dense films with reduced free-electron density,

which suppressed the charge recombination, and increased electron mobility, which enabled fast extraction of electrons, contributing to improved J_{SC} . PCE improved from 8.2% to 15.2% by doping the ETL with Mg. Unencapsulated devices maintained over 90% of its initial PCE after 720 h of storage in air with <20% relative humidity.



Figure 1. (a) Illuminated current density vs. voltage (*J*-*V*) curves under reverse and forward voltage scanning of PSC devices, (b) photoluminescence (PL) spectra, and (c) time-resolved PL (TRPL) spectra of perovskite films on undoped and Ta-doped SnO₂ ETLs. Reproduced from [22] with permission from AIP Publishing, 2019. (d) Illuminated *J*-*V* curves under 1 SUN under reverse and forward voltage scanning of PSC devices, (e) photoluminescence (PL) spectra, and (f) TRPL spectra of perovskite films on undoped and bilayer F-doped SnO₂ ETLs. Reproduced from [23] with permission from American Chemical Society (ACS) Publications, 2018. (g) Energy diagram of FTO, ETLs, and perovskite. Illuminated *J*-*V* curve of PSC based on (h) undoped SnO₂ and (i) Li-doped SnO₂ under 1 SUN. Reproduced from [24] with permission from Elsevier, 2016.

Aluminum doped SnO_2 reported by Chen et al. resulted in increased J_{SC} and FF by using a low-temperature solution-processable method [30]. Doping SnO_2 with Al enhanced the charge transport and electron extraction based on TRPL tests. PSC devices exhibited improved PCE of 9.0% to 12.1%.

2.2. Metal Oxide

Binary layers of SnO₂ with other metal oxides is another approach to modify the ETL in PSCs. This approach leads to tailoring the surface morphology and tunes the energy band alignment. Wang et al. investigated inserting indium oxide (In_2O_3) between ITO and SnO₂, which resulted in reduced trap densities in the perovskite with improved charge transfer and band alignment [31], as shown in Figure 2a. This resulted in higher V_{OC} and *FF* values with a PCE enhancement of 21.4% to 23.1%, as shown in Figure 2b. Unsealed devices retained 98% of its initial efficiency after being stored in N₂ for 1920 h, as shown in Figure 2c, resulting in 91% of its initial PCE after 180 h of continuous 1 SUN illumination and about 80% of its initial PCE after 120 h of exposure to 75% relative humidity.

Europium (Eu) doped tungsten-oxide (WO_x) nanorods were inserted between the perovskite and SnO₂ layer by Chen et al. [32], which contributed to improved crystallinity of the perovskite film and enhanced conductivity and carrier mobility of both the SnO₂ ETL and spiro-OMeTAD HTL. Due to the energy level of the Eu:WO_x nanorods, as shown in Figure 2d, the electron and hole extraction were remarkably boosted at the ETL/absorber and absorber/HTL interface, improving the PV performance, as shown in Figure 2e. Unencapsulated devices retained over 90% of its initial PCE after 500 h of continuous 1 SUN illumination at 16–25 °C and 20–30% relative humidity, and over 90% of its initial PCE after 2000 h of exposure to ambient air, as shown in Figure 2f.

Song et al. investigated inserting an anodized-TiO₂ between the FTO and SnO₂ ETL, which lead to a defect-free physical contact and improved electron extraction [33], as illustrated in Figure 2g. Such bi-layered ETLs resulted in a large change in free energy and moderate electron mobility, as illustrated in Figure 2h. This enhanced the V_{OC} from 1.14 to 1.20 V, which led to an enhanced PCE of 19.0% to 21.1%, as shown in Figure 2i. Similarly, Lee et al. investigated combining a compact TiO₂ between the TCO and SnO₂ ETL, which improved charge collection due to better hole-blocking ability of the TiO₂ underlayer [34]. This resulted in increasing the PCE from 16.4% to 19.8%.

Unencapsulated devices maintained over 95% of its initial PCE after 1200 h of storage in air with 20% relative humidity.

Dagar et al. studied inserting a thin magnesium-oxide (MgO) overlayer on top of SnO₂, which led to more uniform films and reduced interfacial-carrier recombination [35]. This resulted in better stability and enhanced device performance from a PCE of 15.2% to 19.0%. Unsealed devices maintained 67% of its initial PCE after 2568 h in 30% relative humidity.

A bilayer of lead oxide (PbO) doped-SnO₂ with undoped SnO₂ was investigated by Bi et al. [36], which improved the shunt resistance and enhanced the *FF* from 72.9% to 75.5% and PCE from 17.0% to 18.8%. Devices maintained over 90% of its initial efficiency after 1080 h at room temperature with 15% relative humidity.

Ultrathin MgO was also inserted between FTO and SnO₂ ETL in PSCs by Ma et al., which resulted in enhanced electron transporting and hole-blocking properties [37]. Due to MgO passivation, less FTO-surface defects were observed along with a smoother surface and suppressed carrier recombination. The PCE increased from 16.4% to 18.2%.

Hou et al. studied chemical-bath deposition of a SnO_2/TiO_2 bilayer [38], which facilitates charge separation achieving effective extraction and transport of electrons. Higher electron mobility and suppressed recombination was observed due to the reduced energy barriers and gradual-energy levels, which lead to a PCE enhancement of 12.0% to 18.1%.

Yan et al. reported a bi-layered ETL of SnO_2 and zinc oxide (ZnO), which showed superior electron extraction and a lower charge recombination rate [39]. This resulted in a V_{OC} enhancement of 1.06 to 1.23 V, and a PCE enhancement of 11.9% to 14.6%. Unencapsulated devices retained 80% of its initial efficiency after 300 h in N₂ at 85 °C.



Figure 2. (a) Energy-band diagram of PSC based on In_2O_3/SnO_2 . (b) Illuminated *J-V* curves under 1 SUN for forward- and reverse-voltage scans of In_2O_3 , SnO_2 , and In_2O_3/SnO_2 -based PSC devices. (c) Long-term stability measurements of devices with different ETLs. Reproduced from [31] with permission from Wiley, 2020 (d) Energy-band diagram of each layer in PSCs. (e) Illuminated *J-V* curves under 1 SUN under reverse- and forward-voltage scanning of PSC devices with different ETLs. (f) Long-term stability measurements of PSCs with different ETLs in the ambient. Reproduced from [32] with permission from Elsevier, 2021. (g) Schematic illustration of bilayered TiO₂/SnO₂ ETLs with large change in free energy (ΔG) and moderate electron mobility (μ_e). (i) Illuminated *J-V* curves under 1 SUN for various ETLs. Reproduced from [33] with permission from ACS Publications, 2017.

2.3. Ionic Compounds

2.3.1. Surface Modification by Ionic Compounds

Adding ionic compounds into the SnO_2 solution or applying it to the surface the SnO_2 are some other cost-effective approaches to modifying the SnO_2 ETL. Compared to organic molecules and carbon materials, ionic compounds are usually more stable and lower in cost.

Zhuang et al. looked into the modification of SnO₂ by using rubidium fluoride (Rb) by using two different methods: (i) adding RbF into the SnO₂ solution and (ii) inserting RbF at the SnO₂/perovskite interface [40]. Adding RbF to the SnO₂ bulk resulted in improved electron mobility, while adding RbF to the surface of SnO₂ resulted in inhibited ion migration and reduced carrier recombination due to the Rb⁺ cations escaping into the bulk perovskite. This led to increased V_{OC} with PCE of over 23%, as shown in Figure 3a with negligible hysteresis. A stronger steady-state PL intensity of the RbF-treated SnO₂ corresponds to improved perovskite-film quality, as shown in Figure 3b. Based on the TRPL results in Figure 3c, a shorter fast decay (τ_1) indicates enhanced electron extraction, while the longer slow decay (τ_2) corresponds to decreased defects/traps and improved perovskite-film quality. Unencapsulated PSCs maintained about 75% of its initial PCE after 200 h of exposure to white LED light illumination.

Chen et al. studied the combined effect of doping planar-SnO₂ (p-SnO₂) with different concentrations of RbF and depositing RbF onto the mesoporous SnO₂ (m-SnO₂) layer [41], resulting in improved PV performance, as shown in Figure 3d. RbF modification increased the conductivity of SnO₂, as shown in Figure 3e, and passivated interfacial traps through F-Sn bonds. Rb⁺ diffused into the perovskite which passivated the perovskite and suppressed ion migration. Unencapsulated devices maintained 90% of its initial PCE after 300 h at the maximum power point (MPP) under 1 SUN illumination, as shown in Figure 3f.

Chen et al. reported surface modification of the SnO_2 by using 4-imidazoleacetic acid hydrochloride (ImAcHCl) [42], as illustrated in Figure 3g. The chloride anion in ImAcHCl improves the crystallinity of the perovskite layer. Modifying SnO_2 with ImAcHCl shifts the conduction and valence bands up, as shown in Figure 3h, suppresses carrier recombination, and enhances carrier lifetime. This results in the enhancement of PCE from 19.5% to 21.0%, as shown in Figure 3i. Unencapsulated-PSC devices retained 95% of its initial PCE after 840 h at room temperature with 46–60% relative humidity. Unencapsulated PSCs based on PTAA maintained 90% of its initial PCE after 40 h of exposure to 85 °C in N₂.

Potassium-hydroxide (KOH) modification of SnO_2 surfaces was investigated by Bu et al., which resulted in suppressed hysteresis and enhanced PV performance with a PCE increase from 19.3% to 20.5% [43]. Potassium cations were shown to passivate the ETL/perovskite interface, facilitate grain growth of the perovskite, and improve stability.

Cesium-carbonate (Cs_2CO_3) post-treatment, studied by Li et al., improves the electrical properties of SnO_2 and passivates the ETL/perovskite interface [44]. Such Cs_2CO_3 modification improves the surface wettability of the ETL and reduces the roughness, resulting in a perovskite film with larger grains. The Cs_2CO_3 post-treatment lowers the work function, reducing electron-hole recombination, and enhancing the electron transfer. Devices retained 91% of its initial efficiency after stored in 35–45% relative humidity for 340 h.

Alkali-metal cations, such as lithium chloride (LiCl), sodium chloride (NaCl), potassium chloride (KCl), rubidium chloride (RbCl), and cesium chloride (CsCl), were used to modify the SnO₂ surface [45]. Such modification increases the mobility and reduces the trap density of states of SnO₂. Efficient defect passivation suppresses the recombination at the ETL/absorber interface. Devices based on NaCl-treated SnO₂ maintained over 90% of its initial PCE after 960 h.



Figure 3. (a) Illuminated *J*-*V* curves under 1 SUN for forward- and reverse-voltage scanning of SnO₂ and SnO₂/RbF-based PSC devices. (b) Steady-state PL and (c) TRPL spectra of perovskite films on various ETLs. Reproduced from [40] with permission from Wiley, 2021 (d) Illuminated *J*-*V* curves under 1 SUN for PSCs based on various ETLs. (e) Current vs. voltage (*I*-*V*) characteristic curves for various ETLs with an ITO/ETL/Ag structure. (f) Long-term maximum power point tracking (MPPT) stability measurements of devices with different ETLs under continuous 1 SUN illumination (simulated by LED light). Reproduced from [41] with permission from Elsevier, 2022. (g) Schematic illustration of formation of ImAcHCl-modified SnO₂ ETL. (h) Energy-band diagram of each layer in PSCs. (i) Illuminated *J*-*V* curves under 1 SUN for various ETLs. Reproduced from [42] with permission from Wiley, 2019.

2.3.2. Bulk Incorporation of Ionic Compounds

Cobalt chloride hexahydrate (CoCl₂·6H₂O) was incorporated into SnO₂ by Wang et al. which shows better band alignment, as shown in Figure 4a; it enhanced charge extraction and suppressed interfacial recombination [46]. This enhanced the V_{OC} up to 1.20 V for a perovskite layer with a bandgap of 1.54 eV. PSC devices with a PCE of 23.8% was achieved, as shown in Figure 4b, with enhanced stability maintaining 84% of initial efficiencies after 200 h of continuous light exposure, as shown in Figure 4c.



Figure 4. Cont.



Figure 4. (a) Energy-band levels of each layer in the PSC. (b) Illuminated *J-V* curves under 1 SUN for reverse- and forward-voltage scanning of SnO₂ and CoCl₂:SnO₂-based PSC devices. (c) Stability measurements of devices with various ETLs in N₂ atmosphere under continuous irradiation. Reproduced from [46] with permission from ACS Publications, 2021. (d) Illustration of incorporation of heparin potassium (HP) into the SnO₂ nanocrystal dispersions, resulting in arrangements of ETL nanocrystals, and crystal growth of the perovskite films with and without heparin potassium. (e) Illuminated *J-V* curves under 1 SUN for reverse- and forward-voltage scans of PSCs with and without HP incorporation into SnO₂. (f) Long-term MPPT-stability measurements of devices with different ETLs for 1000 h under continuous 1 SUN illumination. Reproduced from [47] with permission from Wiley, 2020. (g) Illuminated *J-V* curves under 1 SUN for various ETLs. (h) Steady state PL and (i) TRPL spectra for various ETLs. Reproduced from [48] with permission from Wiley, 2020.

The contact between the SnO_2 and perovskite was improved by introducing a biological polymer, heparin potassium, to the SnO_2 [47]. Such bulk incorporation regulated the arrangement of SnO_2 nanocrystals and induced vertically aligned crystal growth of the perovskite, as illustrated in Figure 4d. This improved the PV performance, as shown in Figure 4e. Due to the strengthened interface binding, device-operational stability was enhanced resulting in maintaining 97% of the initial efficiency after 1000 h under 1 SUN illumination at the MPP, as shown in Figure 4f.

Introducing KCl to the SnO₂ ETL passivated both the grain boundaries of the perovskite and the defects at the ETL/absorber interface [48]. The Cl⁻ and K⁺ ions passivate the ETL/absorber contact, while the K⁺ ions in the ETL diffuse into the perovskite layer and passivate the grain boundaries, resulting in enhanced V_{OC} from 1.08 to 1.14 V and increased PCE from 20.2% to 22.2%, as shown in Figure 4g. The stronger steady-state PL intensity with the presence of KCl demonstrates suppressed recombination of the perovskite, as shown in Figure 4h. Based on TRPL results in Figure 4i, the decrease in τ_1 suggests faster electron transfer with the incorporation of KCl, and the increase in τ_2 suggests slower recombination in the perovskite film grown on KCl-incorporated SnO₂. Unsealed devices maintained 88% of its initial PCE after 120 h of continuous 1 SUN illumination.

Girard's Reagent T (GRT) was introduced to the SnO₂ nanoparticles by Bi et al. [49]. The carbonyl group in GRT is anticipated to prevent agglomeration of the SnO₂ nanoparticles. The quaternary-ammonium-chloride salt in GRT is expected to facilitate the crystal growth of the perovskite, and the quaternary-ammonium cation and chloride anion can passivate the defects at the ETL/absorber interface. Such GRT incorporation into SnO₂ resulted in better electrical properties of SnO₂, promoted vertical growth of the perovskite, and reduced interfacial defects at the ETL/perovskite interface, resulting in a PCE enhancement of 19.8% to 21.6%. Unencapsulated devices retained over 99% of its initial efficiency after 720 h at 60 °C, and 59% after 672 h under 1 SUN illumination.

Liu et al. introduced ammonium chloride (NH_4Cl) into SnO_2 , which resulted in PSC devices with negligible hysteresis and improvement in PCE from 18.7% to 21.4% [50]. Such improvement is due to the increased electron mobility, and improved band alignment and

passivation of the ETL/perovskite interface, which also improved the device's stability. Unencapsulated devices stored in N_2 retained over 95% after 1000 h.

Sun et al. incorporated potassium sodium tartrate (PSTA) into the SnO₂ colloidal dispersion [51]. PTSA contains mobile-alkali-metal cations leading to improved uniformity and conductivity, and less defects in SnO₂, which improves the crystallinity of the perovskite film. Sodium and potassium cations can diffuse into the perovskite and passivate the defects at the grain boundaries and surface. This results in PCE enhancement of 18.3% to 21.1% with reduced hysteresis. Device stability improves with unencapsulated devices retaining over 95% of its initial efficiency after 1440 h of exposure to ambient air with 45% relative humidity at 25 °C.

Phosphoric acid was introduced into SnO_2 by Jiang et al. to eliminate dangling bonds on the SnO_2 surface and improve the carrier-collection efficiency [52]. Electron mobility increased by 3 times and surface-trap states reduced, decreasing the electron- transport barriers of SnO_2 . Attributed to the enhanced electron-collection efficacy, the PCE increased from 19.7% to 21.0%.

Tetramethylammonium hydroxide (TMAH) was incorporated into SnO_2 by Huang et al. at low temperatures of 100–150 °C [53]. Such modification of SnO_2 attributed to higher conductivity of SnO_2 and also effectively passivated the grain boundaries of the perovskite film. Improved charge transport between the perovskite and ETL resulted in enhanced efficiencies from 18.1% to 20.5%. Encapsulated devices in 15% relative humidity maintained 97% of its initial PCE after 360 h.

Modification of SnO₂ by introducing cesium fluoride (CsF) into the ETL was investigated by Akin et al., which led to improved optoelectronic properties and rapid extraction of photogenerated electrons [54]. By combining the modification of SnO₂ and inserting zwitterion molecules at the perovskite/HTL interface, a high V_{OC} value of 1.23 V and a PCE value of 20.5% were achieved. Device-operational stability was also improved retaining over 90% of its initial PCE after 800 h under continuous 1 SUN illumination at the MPP.

Ammonium sulfide $[(NH_4)_2S]$ is incorporated in SnO₂ reported by Ai et al., which passivated the surface defects by terminating the Sn-S dangling bonds [55]. The conductivity and electron mobility of SnO₂ are increased, enhancing the electron collection and lowering electron-hole recombination rate. The Sn-S-Pb anchors the perovskite crystals at the ETL/absorber interface, which enhances the stability and electron extraction of the PSC. PCE values increase from 18.7% to 20.0% by using this method.

2.4. Carbon Materials

2.4.1. Surface Modification by Carbon Materials

Insertion of highly conductive carbon material at the ETL/absorber interface can facilitate electron transfer. A smooth ETL surface can also be enabled to impact the growth and nucleation of the perovskite layer on top. In addition, defects at the ETL/absorber interface can be passivated by the carbon material. For example, Wang et al. investigated the application of novel fulleropyrrolidine (NMBF-X, X = H or Cl) monomers and dimers, as shown in Figure 5a, in between the perovskite and ETL [56]. The chlorinated- fullerene dimers resulted in the most efficient PCE of 22.3% with minimal hysteresis, as shown in Figure 5b,c, which stems from the passivation of the NMBF-Cl dimer with the SnO₂ and perovskite simultaneously. After 1000 h, unencapsulated PSC devices exposed to air at 25–35 °C with 45–60% relative humidity retained over 95% of its initial PCE.



Figure 5. (a) Chemical structures of fullerene dimers and monomers. Illuminated *J-V* curves under 1 SUN for reverse- and forward-voltage scans of (b) SnO₂ and SnO₂/PCBM-based, and (c) SnO₂/NMBF-Cl and SnO₂/NMBF-H monomer and dimer-based PSC devices. Reproduced from [56] with permission from Wiley, 2020. (d) Schematic of PSC-device stack based on polystyrene (PS) modified SnO₂ ETL. (e) Stability tests at the MPP under 1 SUN illumination. (f) Long-term stability measurements of devices with inner-PS encapsulation stored in air. Reproduced from [57] with permission from Wiley, 2019. (g) Cross-sectional scanning electron microscopy (SEM) image of device with SnO₂/GQDs ETL. (h) Energy-band levels of device based on SnO₂/GQDs before and after illumination. (i) Illuminated *J-V* curves under 1 SUN for various ETLs. Reproduced from [58] with permission from ACS Publishing, 2017.

Polystyrene (PS) was inserted between the ETL and absorber layer to release residual stress in the absorber during annealing, which attributes to reduced interface defects, less recombination, and lower ion-migration tendencies [57]. PS was also applied on top of the perovskite film for inner-encapsulation, as shown in Figure 5d, which improves the long-term device stability maintaining over 90% or its initial efficiency after 72 h at the MPP under continuous 1 SUN illumination, as shown in Figure 5e. Devices with the PS- inner encapsulation maintained over 90% of its initial efficiency after 2800 h in air, as shown in Figure 5f.

Adding graphene quantum dots (GQDs) to the SnO₂ surface, as shown in Figure 5g, will improve the conductivity and fill the electron traps in SnO₂, which improves the electron extraction and reduces the recombination at the ETL/absorber interface [58]. PSC devices with GQD-treated SnO₂ results in a V_{OC} enhancement of 1.10 to 1.13 V and a PCE enhancement of 17.9% to 20.3% with little hysteresis, as shown in Figure 5h,i. Unencapsulated devices maintain over 95% of its initial efficiency in N₂ after 720 h and then an additional 1440 h in air (20–30% relative humidity).

Zheng et al. reported modifying the SnO_2 ETL surface with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) [59]. By simultaneously inserting PbS above the HTL and spiro-OMeTAD, a PCE of 19.6% was demonstrated with long-term storage stabilities of about 100% retained after exposure to air for 1000 h.

Ke et al. also reported fullerene, PCBM, and modification of the SnO₂ ETL surface, which resulted in an increase in PCE from 16.5% to 19.1% [60]. PCBM promotes enhanced electron transfer, suppressed carrier recombination at the ETL/absorber interface, and passivates both the ETL/absorber interface and the perovskite-grain boundaries.

Plasma-enhanced atomic layer deposition (PEALD) was reported to use a low deposition temperature of 100 °C and still attained high efficiencies by surface modification with passivation by C₆₀-self-assembled monolayer (C₆₀-SAM) [61]. The V_{OC} improved from 1.07 to 1.13 V and *FF* increased from 75.5% to 79.1%, resulting in an efficiency enhancement from 17.2% to 19.0%. Unencapsulated devices maintained over 98% of its initial PCE after 480 h in N₂ with room-light exposure and a relative humidity below 10%.

A comparative study between passivation of SnO₂ by [6,6]-phenyl-C₆₁-butyric acid (PCBA) and PCBM was performed by Wang et al. [62]. Passivation of fullerene-molecules at the SnO₂ surface efficiently decreases the defects and improves the conductivity through enhanced electron mobility. The PCBA modification showed higher passivation efficiency, resulting in a PCE increase from 15.4% to 18.6%.

2.4.2. Bulk Incorporation of Carbon Materials

Highly conductive carbon-based materials incorporated into the SnO_2 can enhance the conductivity of the ETL. For example, polymeric carbon nitrides (cPCNs) were introduced into the SnO_2 nanocrystals by Li et al., which led to electron mobilities three times higher than that of the undoped SnO_2 [63]. Such modification of SnO_2 led to less wettability, reduced grain boundaries from the suppressed heterogeneous nucleation of the perovskite, and improved the band alignment, as shown in Figure 6a. This resulted in negligible hysteresis with a PCE enhancement of 21.3% to 23.2%, as shown in Figure 6b. Unencapsulated devices retained 95% of its initial PCE after 2880 h in N_2 , as shown in Figure 6c.

Niu et al. studied the effect of incorporating Nb₂C MXenes into SnO₂, which led to increased grain growth and increased lattice-spacing facets of SnO₂ [64]. A decrease in the steady-state PL, shown in Figure 6d, demonstrates enhanced photogenerated carrier generation and reduced recombination. Superior crystallinity and effective carrier transport resulted in improved PSC PCE from 19.0% to 22.9%, as shown in Figure 6e. Unencapsulated devices retained 98% of its initial PCE after 960 h in 40–60% relative humidity at 25 °C, as shown in Figure 6f.



Figure 6. (a) Energy-band level of each layer in the PSC. (b) Illuminated *J*-*V* curves under 1 SUN for SnO₂ and cPCN:SnO₂-based devices. (c) Long-term stability measurements of unencapsulated devices in N₂. Reproduced from [63] with permission from Springer, 2021. (d) PL spectra of perovskite film grown on various ETLs. (e) Illuminated *J*-*V* curves under 1 SUN for SnO₂ and Nb₂C:SnO₂-based devices. (f) Long-term stability measurements of devices with different ETLs. Reproduced from [64] with permission from Elsevier, 2021. (g) Illuminated *J*-*V* curves under 1 SUN for reverse and forward scans of SnO₂ and carbon quantum dot:SnO₂-based devices. (h) Long-term stability measurements of unencapsulated devices with different ETLs in ambient dark environment at 25 °C with 40–60% relative humidity. (i) Steady-state PL spectra of perovskite on varying ETLs. Reproduced from [65] with permission from Wiley, 2020.

Red-carbon quantum dots were used to dope solution-processed SnO₂, which resulted in increasing the electron mobility by 20 times [65]. The enhanced electron mobility also showed to help passivate the traps and defects at the ETL/perovskite interface and promote growth of highly crystalline perovskite. Efficiencies improved from 19.2% to 22.8% through improvement of J_{SC} , V_{OC} , and FF, as shown in Figure 6g. Unencapsulated devices maintained 96% of its initial PCE after 1000 h in air with 40–60% relative humidity at 25 °C, as shown in Figure 6h. Reduced steady-state PL intensity of the perovskites grown on the SnO_2 doped with red-carbon quantum dots suggest improved photogenerated-carrier generation and suppressed recombination, as shown in Figure 6i.

A water-soluble nonionic polymer, polyacrylamide (PAM), is introduced into SnO_2 be Dong et al., which improves the electron mobility, wettability, and uniformity of SnO_2 [66]. Defects in the perovskite is also reduced and grain size is increased from the PAM addition into SnO_2 . Band alignment at the ETL/perovskite interface is also improved, resulting in a PCE enhancement from 20.2% to 22.6%. Unencapsulated devices maintained 90% of its initial efficiency after 1080 h of exposure to 45%–55% humidity.

Graphitic carbon nitride (g-C₃N₄) quantum dots were added to SnO₂ and applied to PSC devices by Chen et al. [67]. The oxygen-vacancy-reduced trap centers were effectively eliminated and bulk and interface-electron transport were promoted. The high conductivity and suitable energy band alignment of g-C₃N₄-treated SnO₂ led to a PCE improvement of 20.2% to 22.1%. Unencapsulated-PSC devices retained 90% of its initial efficiency after 1500 h in air with 60% relative humidity at 25 °C, and 80% of its initial efficiency after 75 h in air with 60% relative humidity at 85 °C.

Zhang et al. incorporated graphdiyne into SnO₂, which led to improved electron mobility [68]. The enhanced hydrophobicity inhibits heterogeneous-perovskite nucleation, attributing to the reduced grain boundaries and less defect density. The ETL/absorber interface is also improved from passivation of the Pb-I anti-site defects. This results in a PCE increase of 19.2% to 21.1%.

Zhao et al. introduced naphthalene-diimide graphene into nanocrystal SnO₂ [69]. Such modification increases the surface hydrophobicity of SnO₂ and forms a van-der-Waals interaction at the ETL/perovskite interface. Enhanced *FF* values from 74.6% to 82.1% are attributed to the enhanced electron mobility and electron-extraction efficiency, and reduced carrier recombination. PCE improves from 19.0% to 20.2%.

Carbon nanodots by a hydrothermal process were incorporated into SnO_2 by Wang et al. using a simple solution process [70]. Incorporation of carbon nanodots into SnO_2 reduced the density of trap-states and increased the electron mobility of SnO_2 , resulting in a PCE of 20.0% with negligible hysteresis. As carbon materials exhibit high conductivity, incorporation of a carbon material into the ETL can enhance its charge transport and conductivity. Carbon materials can also passivate defects, improving the stability and efficiency of PSCs. Unencapsulated PSCs maintained 90% of its initial efficiency after 200 h of UV exposure in air with 20–30% relative humidity at 20 °C.

2.5. Organic Molecules

2.5.1. Surface Modification by Organic Molecules

Modification of SnO₂ by organic molecules can passivate defects at the ETL surface and improve the electrical properties and transport at the interface. The ETL and absorber layer can be chemically bridged by the organic molecule enhancing the interfacial-electron transfer. For example, Lou et al. investigated the introduction of π -conjugated *n*-type small organic molecules (BTAC4 and Y6) onto the surface of KCl-doped SnO₂ ETL [71], as illustrated in Figure 7a, which yields less trap states, suppressed carrier recombination, and improved electron transport and extraction. Band alignment improves with the modification, as shown in Figure 7b. Applying BTAC4 and Y6 to the surface of SnO₂ results in an enhanced PCE from 21.2% to 23.1% and 22.1%, respectively, as shown in Figure 7c. Unencapsulated devices maintained about 90% of its initial efficiency after 768 h in air with 35% relative humidity.



Figure 7. (a) Illustration of mechanism of oxygen-vacancy-defect passivation of Y6 and BTAC4. (b) Energy-level diagrams of each layer in the PSC. (c) Illuminated *J-V* curves under 1 SUN for reverse and forward scans of SnO₂, SnO₂/Y6, and SnO₂/BTAC4-based devices. Reproduced from [71] with permission from Wiley, 2021. (d) Schematic of toughness testing and toughness results with various ETLs. Inset shows illustration of idealized I-SAM. (e) Illuminated *J-V* curves under 1 SUN for reverse and forward scans of SnO₂, SnO₂/H-SAM, and SnO₂/I-SAM based devices. (f) Long-term stability measurements of unencapsulated devices with various ETLs at the MPP in N₂ atmosphere under continuous 1 SUN illumination. Reproduced from [72] with permission from American Association for the Advancement of Science (AAAS), 2021. (g) The relaxed model of a TPPO molecule absorbed on SnO₂ (110) surface. Energy-level band diagrams of ETL/perovskite heterojunction (h) without and (i) with TPPO-surface treatment of SnO₂. Reproduced from [73] with permission from Wiley, 2019.

An iodine-terminated SAM, 3-iodopropyl trimethoxysilane [Si(OCH₃)₃(CH₂)₃I, I-SAM] was applied to the SnO₂ ETL surface in PSCs, which increased the adhesion toughness at the ETL/absorber interface-enhancing mechanical reliability [72], as shown in Figure 7d. This is attributed to the higher toughness and decreased hydroxyl groups at the interface. Without the SAMs treatment, irreversible morphological degradation, such as voids and delamination, was observed at the ETL/perovskite interface for operational stability tested-devices. Treatment with I-SAM on the SnO₂ enhanced the PCE from 20.2% to 21.4% with diminished hysteresis, as shown in Figure 7e. Long-term working stability was also improved, retaining over 90% of its initial efficiency in N₂ with continuous 1 SUN illumination at the MPP for unencapsulated devices for 1200 h, as shown in Figure 7f.

Triphenylphosphine oxide (TPPO) is an air-robust and cost-effective molecule for *n*-type doping of SnO₂ [73], as shown in Figure 7g. Surface modification by TPPO enhanced the conductivity and lowered the work function of SnO₂, as shown in Figure 7h,i. The V_{OC} improved from 1.08 to 1.11 V and PCE improved from 19.0% to 20.7% attributed to the lower recombination rate and faster electron extraction.

Thiophene-based interlayers were adopted to the SnO₂ surface to reduce the energy loss by optimizing the surface-electronic states of SnO₂ and improving the perovskite- film quality [74]. Surface modification of SnO₂ by thiophene-3-acetic acid improved the conductivity and lowered the work function of SnO₂. Ion-defect states at the ETL/perovskite interfaces were passivated by bonding of the under-coordinated Pb²⁺ of MAPbI₃ with the sulfur atoms of the thiophene rings with a lone pair of electrons. *V*_{OC} improved from 1.07 to 1.12 V, and *FF* improved from 73.5% to 80.1%, resulting in a PCE improvement of 17.5% to 20.6%. This resulted in improved device stability retaining over 90% or its initial efficiency after 1440 h in N₂ and over 80% of its initial efficiency after 130 h in air with 70% relative humidity at 85 °C.

Aminosulfonic acid (⁺H₃N-SO₃⁻, SA) is introduced to the surface of SnO₂ [75], and a chemical bridge is formed between the ETL and perovskite through the coordination bond to SnO₂ via -SO₃⁻ anions and electrostatic interactions with the perovskite via -NH₃⁺ cations. Better surface wettability of the SA-treated SnO₂ led to larger grain size of perovskite films. Attributed to the passivated-contact defects, V_{OC} improved from 1.11 to 1.15 V, while barrier-free charge transferred led to improved *FF* and J_{SC} with reduced hysteresis, resulting in a PCE improvement of 18.2% to 20.4%. Unencapsulated devices maintained over 80% of its initial PCE after 1000 h in air of 25–35% relative humidity and over 75% of its initial PCE after 500 h in N₂ at 60 °C.

The organic molecule p-amino benzenesulfonic acid (ABSA) was introduced to the surface of SnO_2 by inactivating the under-coordinated Sn ions [76]. This decreased the energy-band barrier on the surface of SnO_2 , and increased the conductivity and lessens-carrier recombination. This results in a PCE enhancement of 18.0% to 20.3%. Unsealed PSC devices retain 57% of its initial efficiency after 720 h in N₂.

A plant-photosynthesis promoter, choline chloride, was introduced to the surface of SnO_2 by a simple molecular self-assembly method [77]. Such modification reduces the oxygen vacancies of SnO_2 , while the Cl ions form strong Pb-Cl bonds with the uncoordinated Pb ions in the MAPbI₃. This passivates the defects at the ETL/absorber interface and reduces carrier recombination, improving the V_{OC} from 1.07 to 1.15 V. PCE is improved from 16.8% to 18.9%.

Zuo et al. investigated various SAMs, such as 4-pyridinescarboxylic acid (PA-SAM), 4-cyanobenzoic acid (CBA-SAM), and benzoic acid (BA-SAM), and applied them to the surface of SnO₂ [78]. Proper interfacial interactions were shown to decrease trap- state density and enhance interfacial-charge transfer. Among the various SAMs, application of PA-SAM resulted in the highest efficiency enhancement of 17.2% to 18.8%, with a V_{OC} enhancement from 1.06 to 1.10 V. This is due to improved electronic coupling and suppressed interfacial traps. Charge transfer at the ETL/absorber interface improved from the lowered work function.

Wang et al. reported interfacial-sulfur functionalization anchoring of SnO_2 by using potassium hexylxanthate to modify the surface of SnO_2 [79]. This approach effectively passivated the charge traps and suppressed carrier recombination at the interface by sulfur functionalization of the SnO_2 surface. Functionalized-sulfur atoms can also coordinate with the under-coordinated Pb²⁺ ions at the interface. Such strategy resulted in improved device efficiencies of 16.6% to 18.4%. Unsealed devices maintained about 90% of its initial PCE after 1680 h at room temperature.

2.5.2. Bulk Incorporation of Organic Molecules

Incorporation of organic molecules possessing versatile functional groups into SnO₂ improves the dispersion of colloids, enhances the electrical properties, and passivates the defects in SnO₂. For example, Xiong et al. introduced poly(ethylene glycol) diacrylate (PEGDA), as shown in Figure 8a, into the SnO₂ dispersion to prevent aggregations [80], which resulted in more uniform film and well-matched band-energy alignment with the perovskite. PEGDA-modified SnO₂ also attributed to passivating the defects at the ETL/absorber interface, as shown in Figure 8b,c. This showed a PCE improvement from 21.8% to 23.3%, with a V_{OC} improvement of 1.09 to 1.14 V. Unencapsulated-PSC devices maintained over 90% of its initial PCE after 850 h in N₂ under 1 SUN illumination and 98% of its initial efficiency after 1000 h in air with 30–35% humidity.

Luan et al. incorporated 2,2,2-trifluoroethanol (TFE) into the SnO₂ ETL [81], as shown in Figure 8d, which showed enhanced electron mobility and optimized energy- band alignment. The modified SnO₂ exhibits a very smooth surface, which attributed to the less trap density at the ETL/absorber interface and inside the perovskite film, leading to lessened carrier recombination. With the addition of oxygen-plasma treatments PCE values of 21.7% were achieved with *FF* over 80%, as shown in Figure 8e. Unencapsulated devices maintained over 90% of its initial efficiency after 720 h in 30–40% relative humidity, as shown in Figure 8f.



Figure 8. Cont.



Figure 8. (a) Molecular structure of PEGDA. Cross-sectional SEM images of the perovskite on (b) undoped SnO₂ and (c) SnO₂ doped with PEGDA. Reproduced from [80] with permission from ACS Publications, 2021. (d) Cross-sectional SEM image of PSC device with SnO₂ doped with 2,2,2-trifluoroethanol (T-SnO₂). (e) Illuminated *J*-*V* curves under 1 SUN for forward and reverse scans of SnO₂ and T-SnO₂ based devices. (f) Long-term stability measurements of unencapsulated devices in air with 30–40% relative humidity for SnO₂, T-SnO₂, and oxygen plasma-treated T-SnO₂ (p-T-SnO₂) as ETLs. Reproduced from [81] with permission from Cell Press, 2019. (g) Fermi levels of EDTA, SnO₂, and EDTA:SnO₂ relative to the conduction band of the perovskite layer. (h) Illuminated *J*-*V* curves of PSC devices with various ETLs. (i) Long-term stability measurements of unencapsulated devices for with different ETLs under 1 SUN illumination. Reproduced from [82] with permission from Springer Nature, 2018.

Ethylene diamine tetraacetic acid (EDTA) was incorporated into the SnO_2 ETL by Yang et al. [82]. Electron transfer is facilitated due to the optimized energy-band alignment, as shown in Figure 8g, and enhanced electron mobility of the modified SnO_2 . Perovskite film grown on the modified SnO_2 also exhibited larger grain size and lower trap density. This led to a PCE enhancement of 18.9% to 21.6%, as shown in Figure 8h. Unencapsulated devices maintained 86% of its initial efficiency after 120 h in continuous 1 SUN illumination, as shown in Figure 8i. The large grain size of the perovskite repressed perovskite degradation at the grain boundaries.

Polyethylene glycol (PEG) introduced into the SnO_2 prevented nanoparticle agglomeration, resulting in a dense and uniform film [83]. Such modification of SnO_2 improved the wettability and enabled pinhole-free perovskite films, demonstrating a PCE enhancement of 19.2% to 20.8%. Unsealed devices retained over 97% of its initial efficiency after 2160 h in air with 30–80% relative humidity at 28–35 °C.

Polyethylenimine (PEIE) was added into SnO_2 by a low-temperature solution process [84]. Such doping of SnO_2 resulted in optimized band alignment, larger built-in potential, improved electron transport and extraction, and mitigated charge recombination. Unencapsulated devices retained 82% of its initial efficiency after1,680 h in 40% relative humidity.

3. Conclusions and Future Directions

In summary, recent progress in modifying the SnO_2 -ETL bulk and surface properties are discussed. SnO_2 has been considered the most promising alternative to TiO_2 , as it has a high electron mobility and conductivity. SnO_2 also possesses a suitable band structure owning a deep conduction band allowing enhanced electron extraction at the ETL/absorber interface. The wide bandgap of SnO_2 allows most of the light to be absorbed by the perovskite-absorber layer and suppresses UV-related photochemical reaction, improving the device stability. SnO_2 can also be processed at a lower temperature than TiO_2 allowing for flexible applications to be possible. Despite the many advantages of SnO_2 , there are drawbacks, such as defects in the surface and bulk of the pristine films, deteriorating its electronic properties. Such drawbacks can be alleviated by the various surface-modification and bulk-incorporation methods discussed in this review.

Surface-modification and bulk-incorporation methods are discussed as strategies, including elemental doping, metal-oxides bilayers, incorporation of ionic compounds, carbon materials, and organic molecules. Among the five main aspects of modifying the ETL, bulk and surface modification using ionic compounds are generally lower in cost and more stable than carbon materials and organic molecules. Bilayer-metal-oxide approaches are simple and straightforward; however, an additional fabrication step and additional fabrication step, so bulk incorporation may be considered more fabrication-friendly. Various modification at the surface or the bulk can lead to improved morphology, conductivity, and band alignment of SnO₂, resulting in improved electron-transport capabilities and reduced carrier recombination. Modification of the surface properties of SnO₂ can also lead to improved quality and crystallinity of the perovskite absorber and reduced interfacial defects at the ETL/absorber interface, attributing to improved PV device performance and stability.

Although such modification approaches of SnO_2 have demonstrated enhanced device performance and stability, there still requires improvement in the operational stability of the PSCs at the MPP under continuous 1 SUN illumination. There have been many reports on the long-term stability of devices exposed to elevated temperatures and high relative humidity conditions. However, there are a few reports on the MPP tracking under continuous 1 SUN illumination which are working conditions of the PSCs, and is an important evaluation of the long-term operational stability of PSCs. Such longterm working-stability evaluation methods will help create a better understanding of the mechanisms for improved working stability and will be critical for future directions for commercialization. Another important factor to consider for future directions will be the scalability of the modification approaches for the SnO₂ ETL, since developing methods compatible with large-area substrates will be essential for commercialization.

Perovskite-tandem applications, with lower bandgap absorbers, such as silicon, Cu(In,Ga)Se₂, and tin-related absorbers [85–91], below wider bandgap perovskite-based solar cells, are also future steps to commercialization [92]. Thus, depending on the bottom-solar cell, there may be limitations in fabrication methods or temperature process of the ETL in the tandem configurations. Especially, tandem devices with flexible substrates will have a limitation on the process temperature of the layers in the top solar cell.

Funding: This work was supported financially by the Korea Research Institute of Chemical Technology (KRICT), Republic of Korea (SS2222-20), from the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade Industry and Energy (MOTIE), Republic of Korea (no. 20203040010320), and was also supported by the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (2022K1A4A8A02079724).

Conflicts of Interest: The author declares no conflict of interest.

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