

Solution-Processed Ternary Oxides as Carrier Transport/Injection Layers in Optoelectronics

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With the remarkable progress in solution-processed optoelectronics, high performance is required of the carrier transport/injection layer. Ternary oxides containing a variety of crystal structures, and adjustable composition that results in tunable optical and electrical properties, are one of the promising class of candidates to fulfill the requirements of carrier transport/injection layers for high-performance and stable optoelectronic devices. Solution-processed ternary oxides have seen considerable progress in recent decades, due to their advantages in the quest to design low-cost, high-performance, large-scale, and stable optoelectronic devices. Herein, the recent advances of solution-processed ternary oxides are reviewed. The first section consists of a brief introduction to the topic. In the following section, the fundamentals of the effect of tuning ternary oxide composition are summarized. Section three briefly reviews the synthesis approaches for preparing ternary oxides. Section four discusses the recent progress of solution-processed ternary oxide as carrier transport/injection layer in optoelectronic devices (such as organic solar cells, perovskite solar cells, organic light emitting diodes, etc.). In this section, the impact of controlling ternary oxide composition on device performance and stability is highlighted. Finally, a brief summary and an outlook are given.

1. Introduction

Solution-processed optoelectronic devices have attracted enormous research interest in recent decades, because of their advantages of low cost, simple procedure, and favoring low-temperature and large-scale fabrication.^[1] There has been significant progress in solution-processed optoelectronic devices, including organic solar cells (SCs),^[2] perovskite solar cells (PSCs),^[3] light-emitting diodes (LEDs),^[4] and photodetectors (PDs).^[5] For photovoltaic devices, the efficiency of organic SCs has been continuously increasing. Power conversion efficiency (PCE) of over 16% has recently been achieved in single junction organic SCs.^[6] The hybrid organic–inorganic perovskite materials have risen to stardom due to their extraordinary properties in photovoltaics, achieving impressive progress in

perovskite SCs with a highest PCE of 24.2%.^[7] For other optoelectronic devices, remarkable progress has also been made with solution process techniques.^[4a,b,5,8] These achievements all demonstrate the possibility of realization of low-cost and large-scale optoelectronic devices for practical applications.

The development of high efficiency and good stability of optoelectronic devices are not only ascribed to the evolution of the photoactive layers but also significantly benefited from the advance of the interface layer. Generally, optoelectronic devices are multilayered structures with the photoactive layers sandwiched between two kinds of electrode and their corresponding carrier transport layers (CTLs), namely, hole transport layer (HTL) and electron transport layer (ETL). Solution process for CTLs is the film-formation approach of CTLs with a solvent medium including precursor approach (directly dissolve precursors in a solvent for deposition then converting into metal oxide) and

nanocrystal approach (obtaining metal oxide nanocrystals and then dispersing in a solvent for deposition), which is different to the vacuum deposition techniques (such as thermal evaporation, sputtering, atomic layer deposition, etc.). To achieve cost-effective and large-scale fabrication, it is desirable to deposit all the layers by solution-processed approaches due to its low cost and compatibility to large-scale techniques. Many inorganic and organic materials have been demonstrated as CTL by solution process, such as metal oxides (e.g., ZnO, TiO_x, and NiO_x),^[9] polymers and small molecules (e.g., PEDOT:PSS, PCBM, and C₆₀),^[10] and metal salts (e.g., LiF, and Cs₂CO₃).^[1a,11] There are some impressive and comprehensive reviews to summarize the development of these CTLs.^[1b,12] Metal oxides have been intensively studied due to their unique optical, electrical, and mechanical properties. For instance, metal oxide–based CTL not only favors the formation of Ohmic contact between the photoactive layer and electrodes for effectively extracting (or injecting) charge out of (into) the photoactive layer but also contributes to other functions and performance improvements, such as enhanced light absorption in organic SCs,^[10a,13] stability and ion blocking in perovskite SCs,^[10c,14] and light extraction in LED. Besides, modification on CTL for tuning their properties has been demonstrated as an efficient and effective approach to achieve high-performance optoelectronic devices, such as plasma/ultraviolet-ozone treatment,^[15] nanocomposite,^[10a,16]

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and ion-liquid surface modification.^[17] Since ternary oxides contain the advantages of metal oxides as discussed above and the ability of tuning optical and electrical properties by changing their compositions, they have attracted a great deal of attention in recent years and remarkable progress achieved by wisely choosing ternary oxides and tailoring their chemical composition demonstrates great potential of ternary oxides as highly efficient CTL for optoelectronic devices. In this review, to have a better view on the properties tailoring of ternary oxides, we use a nebulous term of ternary oxide to include metal-doped/modified binary oxide, ternary oxide compound, and mixture of two binary oxides, rather than the only strict ternary oxide compounds themselves.

When it comes to the development of effective ternary oxides to meet the requirements of CTL, two closely related questions need to be addressed: synthesis of ternary oxides and control of their composition. In this review, the discussion will mainly focus on the attractive feature of ternary oxide (tuning electrical and optical properties). Therefore, in Section 2, we will review some fundamentals about how the electrical and optical properties affected by composition change. In Section 3, different synthesis methods to realize tunable ternary oxides will be discussed. In Section 4, the recent progress of ternary oxides as CTL will be discussed in details, especially the influences of their optical and electrical properties on device performances by altering their composition. Finally, some prospects and outlook about preparation and application of ternary oxide CTL will be given.

2. Fundamental Understanding for Tailoring Optical and Electrical Properties of Ternary Oxides

Ideally, qualified CTLs should demonstrate the required electrical and optical features including:^[1b,12c,g] a) suitable band structure for forming Ohmic contact with photoactive layer and corresponding electrode for efficient charge extraction or injection and able to block the counter carrier; b) high enough mobility and conductivity for achieving efficient carrier transport within CTLs to avoid charge accumulation; and c) large enough bandgap for minimum light absorption in the working spectrum range of photoactive layer. In addition, it is also very important for CTLs to have good chemical compatibility and processability (good film-formation ability by solution approach). Chemical compatibility and resistivity is important for preventing the unexpected reaction/interaction between the materials and solvents used in the multilayered device structure including the CTLs, active layers, and electrodes. To meet the requirements of various applications, adjusting the chemical composition of ternary oxide is widely used to tuning the optoelectronic properties. Experimentally, some changes in optoelectronic properties have been observed in many previous reports as summarized in **Table 1**. To promote the development of ternary oxide CTLs, it is certainly worth to review the fundamental understandings on controlling their optical and electrical properties. In this section, the discussion will be divided into three parts of metal-doped/modified binary oxides, ternary oxide compounds, and mixture of two binary oxides, where it is vaguely classified by mole ratio and interaction between two



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metal cations. For the convenience of discussion, the cases with large dopant concentration doped binary oxide are also considered as doping.

2.1. Metal-Doped Binary Oxides

Doping is commonly used to control the optical and electrical properties of binary oxide. Basically, doping can be classified into interstitial doping and substitutional doping according to the lattice site occupied by dopant.^[18] In substitutional doping, carrier concentration primarily depends on the number of

Table 1. Electrical properties and energy levels of ternary oxides.

Oxide formula	Method	Electrical	Note	Energy level		Formula	Electrical	Energy Level		Reference
Cu:NiO _x	combustion	1.25×10^{-3}	a-3			Cu:NiO _x (sol-gel)	7.54×10^{-4}			[24]
Cu:NiO _x	precipitation	3.01×10^{-3} / 1.09×10^{-2}	a-3/c-2			NiO	5.59×10^{-4} / 3.05×10^{-3}			[27f]
Nb:SnO ₂	sol-gel	2.16×10^{-4}	c-2			SnO ₂	1.02×10^{-4}			[21]
Cu:NiO _x	sol-gel	1.21×10^{-3}	a-3				8.34×10^{-4}			[90]
Ga-ZnO	sol-gel	3.27×10^{-3}	b-6			ZnO	7.63×10^{-3}			[20]
Cu:NiO _x	coprecipitation	2.53	c-1			NiO _x	0.12			[27b]
Zn:NiO _x	sol-gel			VB	−5.30 eV			VB	−5.20 eV	[27d]
Cu:NiO _x	coprecipitation	3.01×10^{-3} / 1.09×10^{-2}	a-3/c-2			NiO _x	5.59×10^{-4} / 3.05×10^{-3}			[27f]
Zn _{1-x} Mg _x O	sol-gel	1.1×10^{-4}	c-2	CB	−3.90 eV	ZnO	8.4×10^{-5}	CB	−4.30 eV	[28a]
Zn _{1-x} Mg _x O	nanoparticle	1.79×10^{-3}	c-2	CB	−3.48 eV		1.95×10^{-3}	CB	−3.71 eV	[28b]
Cu ₄ Cr ₁ O	sol-gel			CB	−2.94 eV	Cu ₁ Cr ₄ O		CB	−2.38 eV	[45]
CuGaO ₂	nanoplate	3.6	a-4			as synthesized	0.19			[15b]
ZnO/SnO ₂	nanoparticle	4.3×10^{-3}	c-2			SnO ₂	2.2×10^{-3}			[50]
TiO ₂ /SnO ₂	nanoparticle		CB	CB	−3.91 eV	TiO ₂		CB	−3.80 eV	[51]
Cs:TiO ₂	nanoparticle	1×10^{-4}	c-5	CB	−3.93 eV			CB	−4.30 eV	[54]
Cs _{0.5} MoO ₃	nanoparticle			WF	4.24 eV	MoO ₃		WF	5.35 eV	[55]
CsV ₂ O ₅	nanoparticle			WF	4.15 eV	V ₂ O ₅		WF	5.43 eV	[55]

Note: In the Note column, low case letter denotes the electrical parameter type (unit), number denotes measure method, a-conductivity (S cm^{−1}), b-resistance (Ω cm), c-mobility (cm² V^{−1} s^{−1}); 1-hall effect, 2-space charge limit current, 3-four point probe, 4-conductive atomic force microscopy, 5-charge extraction by linearly increasing voltage, 6-I–V.

created donor (n-type) or acceptor (p-type) sites in the target oxides when substitutional doping creates shallow energy level close to conduction band (n-type) or valence band (p-type). As a result, the conductivity of substitutional doped oxide is mainly determined by doping concentration, and the conductivity of extrinsic semiconductor can be simply represented by equation: $\rho = n \times e \times \mu$; where n represents number density of charge carriers, e is the electric charge of one single proton, and μ denotes the drift mobility of carriers. The intuitive way to improve conductivity of metal oxides is to substitute dominated cations with impurities having comparatively more (for n-type) or less (for p-type) outer electrons to increase the carrier density. Indeed, the moderate amount of impurities can largely enhance the carrier concentration without obstructing carrier transportation. However, high concentration doping is also detrimental to conductivity due to the formation of ionized scattering centers that can contrarily lower the charge drift mobility.^[19] As observed by Thambidurai et al., the resistivity of gallium-doped ZnO decreases as the gallium concentration increases within low range (0–5.03%) and realizes the lowest resistivity of $3.27 \times 10^{-3} \Omega \text{ cm}$.^[20] Since gallium with three outer electrons is used to substitute Zn in ZnO lattice, extra electrons from dopants improve conductivity at lower doping concentration. However, the resistivity increases at over 5.03% gallium concentration because ionized center scattering and phonon scattering from lattice disorder finally reduce the conductivity. In addition, controlling the traps density in CTLs by doping can also improve their mobility. Ren et al. found that niobium n-type doping in

SnO₂ can effectively passivate electron traps.^[21] As their results show, the density of electron traps in pristine SnO₂ can be significantly reduced as the introduction of 0.5% niobium from 2.39×10^{15} to $1.74 \times 10^{15} \text{ cm}^{-3}$, which leads to electron mobility increase from 1.02×10^{-4} to $2.16 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Doping is also conducted in hole transport materials. Taking NiO_x as an example, there are various dopants, such as Li,^[22] and Cs.^[23] Narayan and co-workers have demonstrated Li-doped NiO_x thin film by pulse laser deposition method.^[22a] Substitutional doping of Li cation can gradually reduce electrical resistivity as the doping concentration increases. The minimum resistivity of $0.15 \Omega \text{ cm}$ is achieved when the dopant concentration increases up to 7% while the pristine NiO_x has a high resistivity of $3 \Omega \text{ cm}$. Chen et al. also reported some improvement in conductivity of Cs-doped NiO_x and they gave this credit to higher Ni³⁺/Ni²⁺ ratio in doped nickel oxide.^[23a] Nevertheless, Kim et al. found a detrimental effect on the conductivity after using Cs as dopant for NiO_x.^[23b] The resistivity increases almost two times from initial 8.1×10^4 to $15.2 \times 10^4 \Omega$ after 1% Cs doping. It is important to note that the electrical conductivity of oxide thin film can be strongly affected by film deposition method and condition, structure of nanomaterial, and material composition.^[24] Besides, the valence band upper edge of oxide is typically related to the strong localization 2p states of oxygen.^[25] The p orbit nature and high electronegativity of oxygen lead to a flat energy band, large hole effective mass, and thus cause difficulty for largely improving conductivity by introducing a shallow acceptor.^[26] Rather than using acceptor

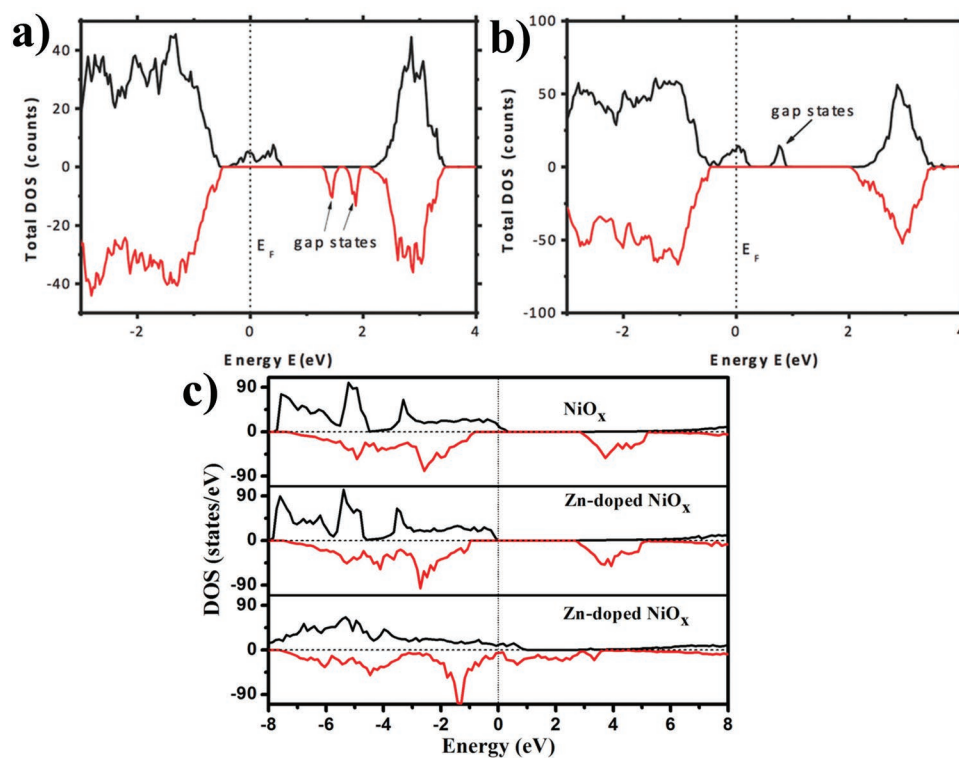


Figure 1. a) The total DOS spectra of undoped NiO; b) the total DOS spectra of Cu-doped NiO. The Fermi level for the calculation is set at zero for the data process. The corresponding gap states are labeled with arrows. Reproduced with permission.^[27b] Copyright 2018, Wiley-VCH. c) Spin-decomposed density of states of a $2 \times 2 \times 2$ NiO_x supercell with a Ni vacancy (the top panel), with one Ni atom replaced by a Zn atom (the middle panel), and the supercell containing a Ni vacancy plus a substituted Zn atom (the bottom panel). Zero energy is set at the Fermi level. The positive and negative scales correspond to the spin-up and spin-down components, respectively. Reproduced with permission.^[27d] Copyright 2018, American Chemical Society.

dopant, Co, Cu, and even Zn were also adopted to dope NiO.^[27] With two-outer-electron dopants, both of Wan et al. and Chen et al. have used density functional theory (DFT) calculation to investigate the spin-decomposed density of states (DOSs) after doping as shown in **Figure 1**.^[27b,d] After introducing the dopant, there are energy states near or above the Fermi level. In Chen's results, there are so-called gap states near the Fermi level which are much closer to Fermi level than that of undoped oxide as shown in **Figure 1a,b**. While in the results of Wan et al., there are some continuous states above Fermi level (**Figure 1c**). Although both of them ascribed the NiO_x property change to the appeared states, the original of these new energy states after doping is not clearly stated.

In addition, doping with metal ion can not only change electrical properties but also tailor the bandgap by shifting conduction band minimum (CBM) and valance band maximum (VBM). There are two typical manners for bandgap tailoring, reconstructing energy states and Burstein–Moss shift. For the former, the interaction or electron orbit coupling of host and dopant cations affects the distribution of energy states. Taking doped ZnO as an example, its bandgap can be significantly adjusted by Mg and Cd doping.^[28] In the Mg:ZnO, the bandgap is widened as Mg concentration increases while it is narrowed down in the Cd:ZnO, which is due to the difference of outer electrons distribution in these two dopants.^[29] Based on the DFT calculation results of Janotti and Van de Walle,^[29] the deformation energy of CBM (a_c) of MgO is much smaller

than that of ZnO while a_c of CdO is larger than that of ZnO. Therefore, Mg doping can reduce the electron affinity and results in upshift of CBM and thus larger bandgap. Cd doping causes the electron affinity increment and results in downshift of CBM and thus bandgap reduction. In these cases, VBM is strongly dependent on the O 2p orbits; therefore, neither Mg nor Cd doping can adjust the VBM of ZnO obviously. But, there are still some differences in change magnitude due to the coupling effect of d orbits and p orbits. In Zn and Cd cations, there are d orbits in similar energy level while Mg cation has no d orbits; it results in larger VBM change by Mg doping. Analogue phenomenon in doped ZnO was also observed by Qiu et al. in their calculation results on the basis of plane-wave density function theory.^[30] As shown in **Figure 2**, the conduction band of Mg:ZnO is gradually dominated by high-energy Mg 3s states rather than Zn 4s states as the Mg dopant concentration increases. Since the VBM of Mg:ZnO does not change obviously, the bandgap is widened upon Mg doping. They also pointed out that the incident interstitial doping of Mg can form shallow acceptor states above Fermi level as shown in **Figure 2d**. Although these shallow states do not affect optical bandgap, it can act as trapping states or recombination center affecting the optoelectronic properties of devices. In addition to doped ZnO, study on tailoring bandgap of SnO₂ is also conducted by Scanlon and Ganose via theoretical calculation.^[31] As shown in **Figure 3**, lead-doped tin oxides (Pb:SnO₂) still maintain the similar band structure with a direct large bandgap. As

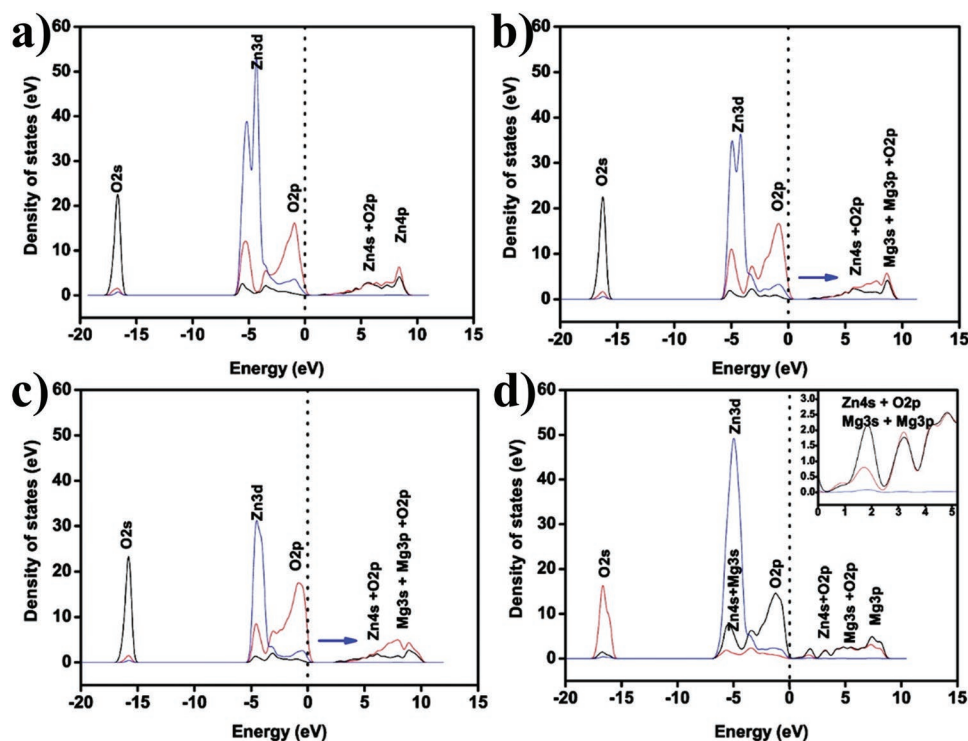


Figure 2. Local density of states for a) pure ZnO, b) $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{O}$, c) $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{O}$, and d) ZnO with 1/8 Mg interstitial doping every ZnO unit cell. The vertical dash line represents the Fermi level. Reproduced with permission.^[30] Copyright 2008, American Chemical Society.

the dopant concentration increases, the CBM shows obvious downward shift, which is ascribed to the formation of low-energy states by the relativistic contraction Pb 6s orbits. From band alignment based on O 1s level, small decrease of VBM is observed in Figure 3c, which is contrary to the predicted result by Pb d-O 2p orbits repulsion. It is speculated to be related to an artefact of simplified alignment model. Another bandgap change model is the Burstein–Moss shift,^[32] which typically happens in highly doped semiconductor. As shown in **Figure 4**, in an intrinsic semiconductor, optical bandgap is typically defined as the offset between VBM and CBM. In n-type doping, free electrons from donors are injected into conduction band. When the number of electrons are over the critical value of Mott carrier density in heavy doped semiconductor,^[33] the CBM states will be fully occupied as shown in Figure 4 middle panel. In this case, photoexcited electrons need extra energy to go to higher unfilled states, resulting in observed blue-shift in absorption spectrum (bandgap widening). As pointed out by Walsh et al,^[32b] bandgap change in highly doped semiconductor is determined by Burstein–Moss effect and renormalization model of mutual exchange and Coulomb interactions between electrons in conduction band.

Consequently, doping is a useful approach to form ternary oxide with controllable electrical and optical properties. However, it is worth to point out that there are still limitations of reported strategies, such as the lack of compatibility, the deep energy levels of dopant for ionization, spontaneous defects of compensation from intrinsic atoms by excessively bending Fermi level, and the tradeoff of decreased transparency under high carrier concentration.^[34]

2.2. Ternary Oxide Compound

A new crystal structure formed with proper amount of two kinds of metal precursors can exhibit favorable optical and electrical properties for optoelectronic applications, which is different from that of the oxide of each of the metal precursors. In this section, the understandings about the impact of ternary oxide compound composition change on their optical and electrical properties are summarized. Since some concepts are applicable to both p- and n-type oxides, we will mainly focus on p-type oxide here.

As mentioned, the conductivity of p-type oxide is strongly related to oxygen ion due to the localized nature of O 2p orbits limiting hole mobility and p-type doping generated hole still in localized O 2p states. To alleviate this problem, it is useful to delocalize O 2p orbits states by orbit hybridization with other ions.^[26,35] It is found that cations with close d shell (d^{10}), semiclose d shell (d^6 and d^3), and lone electron pair (ns^2) are promising to form oxide with decent conductivity and transparency that is favorable for CTL application.^[26a] From the crystal structure point of view, ternary oxides exhibit various crystal structures depending on the molecular composition, such as spinel (AB_2O_4),^[36] perovskite (ABO_3),^[37] and delafossite (ABO_2).^[38] Multiple crystal structures of ternary oxide offer many promising options to develop an approach to lower the localization effect of p orbitals of oxygen. Moreover, spatial estrangement of ions in ternary compound can prevent the direct interaction of close cations that avoid colorization by d–d transition in dense lattice plane,^[39] rendering wide bandgap nature to ternary oxides. Besides, ternary oxide contains two metal

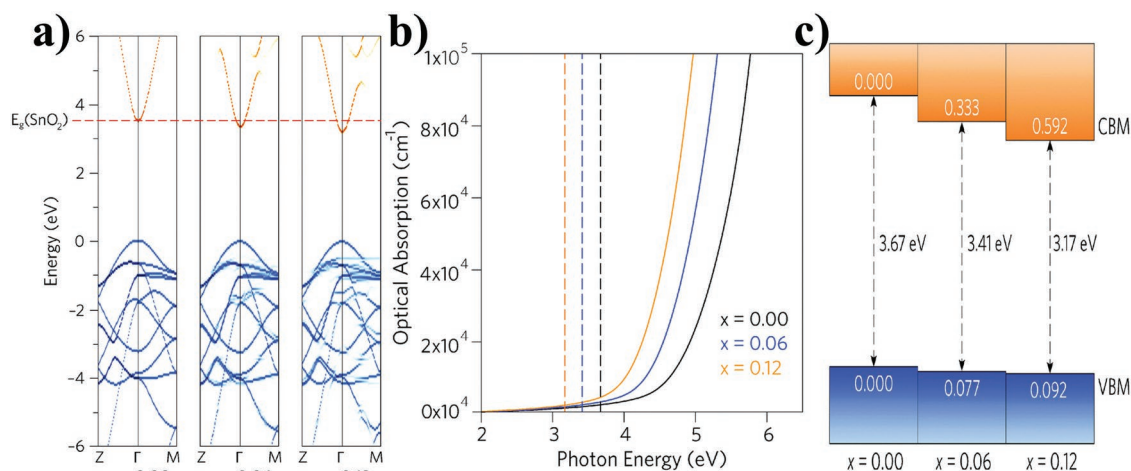


Figure 3. a) The calculated effective band structure for $\text{Sn}_{1-x}\text{Pb}_x\text{O}_2$ where $x = 0.00, 0.06$, and 0.12 . The conduction bands are colored orange whereas the valence bands are shown in blue, with the VBM set to 0 eV in each case. b) Calculated optical absorption spectra for $\text{Sn}_{1-x}\text{Pb}_x\text{O}_2$ where $x = 0.00, 0.06$, and 0.12 . Full lines indicate optical absorption and dashed lines indicate fundamental bandgap. c) Band alignment for $\text{Sn}_{1-x}\text{Pb}_x\text{O}_2$, where $x = 0.00, 0.06$, and 0.12 . All energies are given relative to an O $1s$ state. Reproduced with permission.^[31] Copyright 2016, The Royal Society of Chemistry.

cations in a crystal structure which opens up different varieties of choices of cations and thus a wide range of ternary oxides.

Containing the cation with close d shell, copper-based delafossite (CuMO_2) receives much attention due to the considerable hole conductivity, proper bandgap with high transparency, and low production cost, where M can be trivalent metal, such as Al, Cr, Ga, In, etc. In delafossite structure, Cu cation is coordinated to two oxygen atoms and forms a O–Cu–O bond along c -axis, which makes it an anisotropic conductivity in c -axis and a – b plane.^[40] CuCrO_2 is a large bandgap delafossite with reported superior conductivity (17 S cm^{-1}).^[41] As the nature of copper-based delafossite, the Cu vacancy (ratio of Cu^{2+} to Cu^+),^[42] Cr deficiency,^[43] and excess oxygen^[44] are responsible for the charge origin in CuCrO_2 . Based on this consideration, both electrical and optical properties of CuCrO_2 are expected to be controlled by monitoring Cu(poor)-Cr(poor)-O(rich) fabrication environment without extrinsic modification. Qin et al. have manipulated the proportion of $\text{Cu}_x\text{Cr}_y\text{O}_2$ by mixing different precursor solution of copper acetylacetonate

and chromium acetylacetonate in volume ratio range from 4:1 to 1:4.^[45] Surprisingly, the optical bandgap of $\text{Cu}_x\text{Cr}_y\text{O}_2$ shows high dependence (range from 2.80 to 3.40 eV) on the volume ratio of two precursors that coincide well between the bandgap of mono Cu_xO (2.24 eV) and Cr_yO_2 (3.62 eV). Besides, the work function can also be shifted between 5.1 and 5.26 eV. As inherited characteristic of copper-based delafossite, interstitial oxygen improves the conductivity attributed to enhanced hole density at valence band. Wang et al. modified the work function and VBM of nanoplates to deeper level of 5.38 and 5.49 eV by oxidizing Cu with UV-ozone treatment.^[15b] The conductivity of CuGaO_2 under such modification is dramatically improved to 3.6 S cm^{-1} along with the increment of Cu^{2+} concentration. Meanwhile, since the charge transportation in delafossite is determined by hopping mechanism between the copper to copper valence band, the occupied trivalent cation species would be crucial parameter for electrical conductivity because of spatial estrangement.^[46] Therefore, extra dopant is expected to increase the donor concentration on the M^{3+} sites as reported by others^[46,47] which will not be detailed here.

Apart from the ternary oxide with close d shell, cobalt-based spinel-type ternary oxides are also promising p-type oxides for CTL application due to the hybridization of O $2p$ orbits and semiclosed d shell orbits can also delocalize O $2p$ sates. There are some reports on using cobalt-based ternary oxide as CTL for optoelectronic devices.^[48] Ndione et al. have also investigated the impact of composition change on their optoelectronic properties for organic photovoltaic devices.^[49] By increasing the oxygen pressure during formation of nickel cobalt oxide ($\text{Ni}_x\text{Co}_{3-x}\text{O}_4$) thin films, the composition can be tuned with mole ratio of Ni/Co that varies from 0.43 to 0.7 while oxygen atom mole ratio (O/[Ni+Co]) in the final ternary oxide film increases linearly from 1.98 to 2.68. Interestingly, the work function of these ternary oxides keeps almost unchanged at around 4.7 eV. However, the conductivity shows three orders of variation of magnitude obtaining the highest conductivity of 10.7 S cm^{-1} and the lowest of 0.009 S cm^{-1} at 25 and 200 mTorr

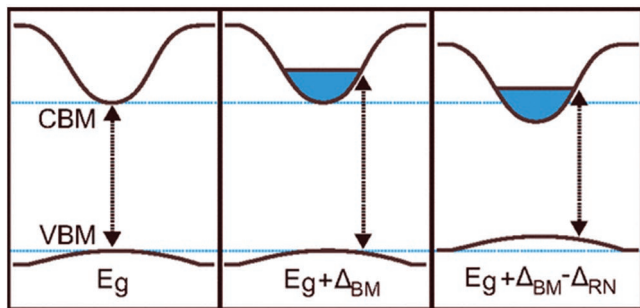


Figure 4. Illustrated effect of charge carriers on the lowest energy transition from the valence to conduction bands (black vertical line) of a highly doped semiconductor where Δ_{BM} is the Burstein–Moss shift and Δ_{RN} represents bandgap renormalization. Note that a positive Δ_{RN} term refers to a bandgap reduction. Reproduced with permission.^[32b] Copyright 2008, American Physical Society.

oxygen pressure, respectively, which is ascribed to oxygen vacancies removal as the oxygen pressure increases.

2.3. Mixture of Two Binary Oxides

For massive commercialization purpose, the CTLs should have high conductivity/mobility, stable chemical/thermal/moisture endurance, high cost-effectiveness, wide bandgap with high transparency, and environmentally friendly features. With the well-developed binary metal oxides, it is intriguing to discover novel composite CTLs for practical application by straightly mixing oxides that are complementary to each other via synergistic effect.

Song et al. have demonstrated ZnO–SnO₂ nanocomposite as CTL with different composition ratios of 5:1, 2:1, 1:1, and 1:2.^[50] As zinc oxide suffers from bad stability under ambient circumstance, the introduction of stable SnO₂ can improve the device durability. While the SnO₂ also possesses deeper conduction band (−4.5 eV), which is not beneficial for charge extraction from photoactive layer. To capture the superiorities from two complementary oxides and suppress the disadvantages at the same time, ingeniously balanced characteristics of ZnO–SnO₂ system were achieved with a precise 89 mol% ZnO. The band levels of ZnO–SnO₂ nanocomposite matched well with photoactive layer and exhibit high transparency with bandgap of 3.3 eV. Meanwhile, the device stability is enhanced by the nanocomposite comparing with the pristine ZnO-based devices. Guo et al. also presented TiO₂–SnO₂ nanocomposite by dispersing SnO₂ into TiO₂ precursor solution.^[51] Since TiO₂ shows relatively higher conduction band level than perovskite layer, the introduction of SnO₂ can offer better band alignment for improving the efficiency of devices. In addition, the hysteresis issue of TiO₂-based device is eliminated because of the better electron extraction ability of SnO₂,^[52] and the device durability is simultaneously improved. There is also a report using a composite of WO_x and TiO_x to demonstrate an efficient CTL with decent properties in both optical and electrical.^[53] Individual WO_x shows low transmittance above 400 nm while higher conductivity and TiO_x show high transmittance with low conductivity. The proper combination offers a better performance in both transmittance and conductivity. As their results show, the small loss in conductivity is paid back by largely increased optical transmission in visible region for improving solar cells efficiency.

3. Synthesis of Ternary Oxides

Metal oxides as a multitudinous class of materials are commonly used in various applications, which led to intensive effort conducted to develop synthesis methods, such as coprecipitation, sol–gel method, hydrothermal/solvothermal, spray pyrolysis, ultrasound-assisted method, pulsed-laser-assisted method and combustion, etc. To prepare metal oxide films for optoelectronic applications, it is not only to synthesize the oxides by different approaches but also to fulfill the requirements of CTLs, which leads to some challenges and also comes with opportunities for development of synthesis methods.

Particularly, the synthesis methods for ternary oxides should exhibit the ability to produce target oxides with controllable chemical composition and properties. This section will summarize some commonly used and newly developed methods for synthesizing ternary oxides or forming ternary oxide films with controllable optoelectronic properties.

3.1. Precursor Approach

In this approach, soluble metal precursors, such as metal salts, metals, or metallo-organic compounds, are dissolved in deionized water or organic solvent. Typically, to prepare ternary oxide film, especially in metal-ion-doped binary oxide, a dopant precursor is added into the precursor solution with desired mole ratio. After depositing on substrate, in situ reaction is generally used to convert the precursor into metal oxide. By this approach, the electrical and optical properties can be controlled by tuning the additive/dopant concentration. It is worth mentioning that the optoelectronic properties change can result from doping and surface modification. Simple procedure and easily forming good-quality thin film make this method frequently employed in preparing CTLs for optoelectronic devices.

To substantially improve conductivity, effective doping needs to be achieved. Recently, cesium has been used as dopant to synthesize ternary oxide CTLs. Kim et al. demonstrate a Cs-doped nickel oxide (Cs:NiO_x) by adding cesium nitrate into nickel nitrate 2-methoxy ethanol precursor solution, following with thermal treatment at 500 °C for 1 h.^[23b] With the high-temperature calcination, successful Cs substitutional doping is confirmed by the peak shift observed in X-ray diffraction (XRD) pattern. While Chen et al. used nickel acetate and cesium acetate as precursors dissolving in isopropanol and ethanolamine mixed solvent. They formed Cs:NiO_x under a lower temperature of 275 °C.^[23a] Apart from using in p-type oxide doping, cesium also functions well as dopant in n-type oxide. By mixing small amount of cesium carbonate (Cs₂CO₃) 2-ethoxyethanol solution into the prepared TiO₂ ethanol solution, Park et al. claimed that Cs-doped TiO₂ thin film was formed after 80 °C thermal treatment on deposited films.^[54] Choy and co-workers also employed cesium carbonate as dopant to intercalate molybdenum oxide (MoO₃) and vanadium oxide (V₂O₅).^[55] By using strong oxidizer (hydrogen peroxide), Cs-doped metal bronze of molybdenum and vanadium can be made under room temperature, which is easy to form the corresponding oxides. Interestingly, by tuning the dopant mole ratio in a large range (from 0:1 to 0.75:1), work function tuning over 1.1 eV has been achieved that allows these intercalated oxides to function as both ETLs and HTLs.

Besides the cesium, niobium (Nb) is also used as n-type dopant in the precursor approach since it contains five valence electrons and can act as donor in some n-type oxides. Ren et al. have demonstrated Nb doped tin oxide (Nb:SnO₂) by adopted niobium ethoxide as precursor. A solution consisting of SnCl₂·2H₂O and desirable amount of niobium ethoxide is deposited on FTO substrate, and Nb:SnO₂ carrier transport layer is obtained after high-temperature annealing (190 °C) in ambient environment. Chen et al. also use niobium ethoxide as precursor and add it into the titanium isopropoxide methanol solution, and precursor film is deposited by spin-coating and

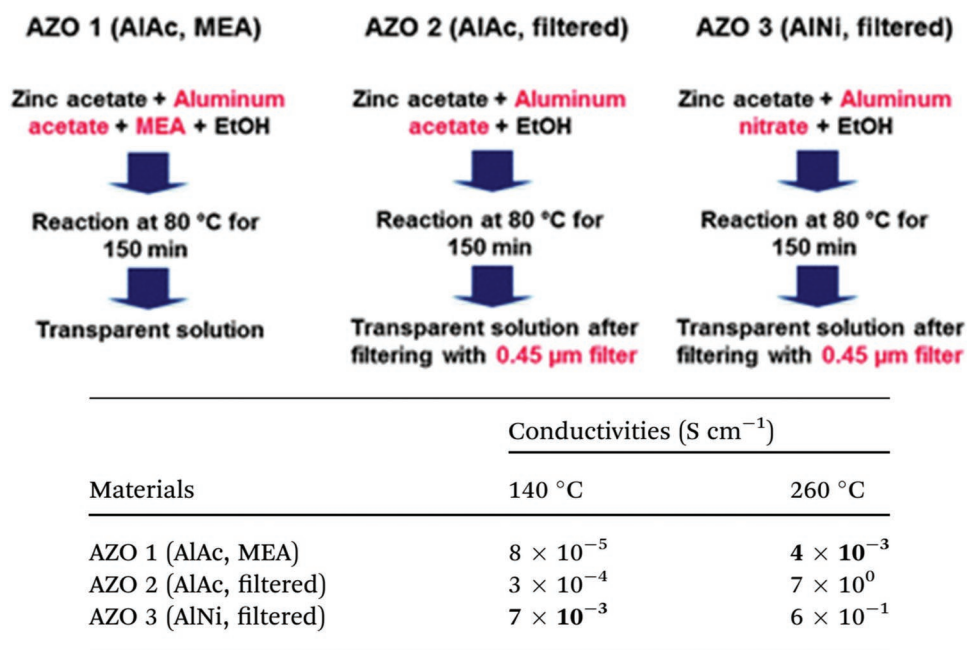


Figure 5. Schemes of the synthesis routes for the three investigated AZO precursor formulations, and the table is: Comparison of conductivity values for layers from different precursors as a function of annealing temperatures: 140 or 260 °C. The samples were annealed in air. The conductivity was measured in a glove box (N₂). Reproduced with permission.^[57] Copyright 2013, Royal Society of Chemistry.

following with 70 °C drying process. Since the precursor film is deposited after photoactive layer, they dropcast water/methanol mix solution on top of the precursor film and then treat at 70 °C to promote the in situ reaction for forming a Nb:TiO₂ thin film. In precursor approach, the selection of in situ reaction methods is important because it needs to consider the compatibility to the adjacent layers. Typically, high temperature (still lower than the tolerance of substrate) and other techniques (combustion reactions^[56]) are just adapted to generate oxides from the precursor when it is deposited on substrate or the adjacent layers are robust. High-temperature treatment is beneficial to the process of doping (instead of surface modification) and improves conductivity that is proven again in the work of Stubhan et al.^[57] Stubhan et al. also investigate the impact of the cases with/without extra additives in different dopant precursors as shown in Figure 5. When additives are used as stabilizer, precursor solution keeps transparent while the precursor solution without additive needs filtering to obtain clear solution. After the same treatment for conversion, the conductivity of samples without additive shows an order of magnitude larger than that with additive. Besides, there is also an order of magnitude difference in conductivity between samples with different dopant precursors as indicated in their results (see table in Figure 5).

In this precursor approach, when comparable amount of two precursors or mismatch of the material crystal phases, a double-phase oxide mixture can form. Wang et al. put two precursors (tungsten ethoxide and niobium ethoxide) into ethanol solution. After treated under 120 °C, two different morphologies of NbO_x and WO_x are clearly observed.^[58] Besides, they also demonstrate a composite CTL of WO_x-TiO_x by the precursor approach. Different amounts of titanium diisopropoxide bis(acetylacetonate) and tungsten trichloride (WCl₃) are used to

prepare precursor solution. An amorphous composite ETL can be deposited with this precursor at a low temperate (at 70 °C or room temperature).^[53]

3.2. Hydrothermal Approach

Ternary oxide nanocrystals typically need high temperature to form a desired material phase due to high formation energy and high energy for ion motion to crystallize, especially for solid state reaction.^[59] Hydrothermal reaction performs in a close system where the temperature and pressure are above the ambient condition, which provides a possibility to synthesize some ternary oxides that have high formation energy or easily decompose to two separated binary oxides. For example, delafossite-type ternary oxide with noble metal (palladium, platinum, and silver) is difficult to synthesize in single step by solid state reaction in open system with high temperature, because these noble metal oxides readily decompose in high temperature. Moreover, high temperature for obtaining some ternary metal oxides is not compatible to the substrates (typically, indium tin oxide (ITO) and fluorine-doped tin oxide (FTO)) used in optoelectronic devices. Therefore, hydrothermal/solvothermal approach is a promising technique for synthesizing ternary oxides.

CuAlO₂, a p-type ternary oxide with delafossite structure, has been synthesized by Ingram et al. via hydrothermal reaction with starting materials of copper oxide, aluminum oxide, and some aluminum metal.^[60] Under condition of 210 °C and NaOH as mineralizer in an autoclave, Cu²⁺ is converted into Cu¹⁺ by aluminum metal reducer and successfully formed delafossite-type CuAlO₂. Comparison of electrical properties between these oxides prepared in low-temperature hydrothermal and

high-temperature solid state method has been made. Their results show that hydrothermal prepared CuAlO_2 exhibits a higher room-temperature conductivity of $\approx 0.2 \text{ S cm}^{-1}$ than that by solid state method ($\approx 0.03 \text{ S cm}^{-1}$), which is ascribed to that low-temperature hydrothermal method (nonequilibrium processes) leads to higher doping/defect levels and thus higher hole concentration. Xiong et al. also use this approach to synthesize a series of delafossite-type ternary metal oxides, such as CuAlO_2 , AgAlO_2 , CuCrO_2 , CuFeO_2 , and CuGaO_2 .^[61] Metal salts ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, AgNO_3 , CuCl , FeCl_2) and alkalines (NaOH or KOH) are used as precursors to form an intermediate then is kept in autoclave at certain temperature to form pure-phase delafossite nanocrystal. In these experiments, reaction temperature, amount of mineralizer, and reaction time are found to be key roles on determining the final products. To lower the reaction time that can last for tens of hours in some cases, microwave-assisted hydrothermal approach was proposed to produce delafossite ternary oxides with a much shorter time. Recently, Wang et al. have utilized microwave to power the hydrothermal reaction to successfully synthesize CuGaO_2 and CuCrO_2 in several hours which is several times shorter than that of conventional heating.^[15b,42b]

In addition to delafossite-type ternary metal oxide, other crystal type ternary oxide can also be synthesized by this approach. Wang et al. have adopted hydrothermal method to prepare perovskite ternary oxide (SrTiO_3).^[62] They use strontium hydroxide octahydrate and titanium-*n*-butoxide as metal source and tetra-*n*-butylammonium hydroxide as the mineralizer to grow perovskite type ternary oxide. When the reaction time increases to 50 h, the byproduct impurity existing in short-reaction-time sample is gradually eliminated and pure phase of perovskite structured SrTiO_3 is obtained. Besides, both Tan et al. and Bera et al. have successfully made Zn_2SnO_4 nanoparticles (NPs) through hydrothermal approach.^[63] By adding tert-butylamine into the mixed water/ethylene glycol precursor solution of zinc chloride and tin chloride, a mixture of zinc and tin tert-butylamine complexes is prepared and it is decomposed to form well-crystallized spinel-structured ternary oxide (Zn_2SnO_4) under hydrothermal condition.

3.3. Coprecipitation and Other Approach

To cater to different applications and fully take advantage of oxide's unique properties, it also needs to explore some different methods for synthesizing advanced metal oxides materials. Other than the methods mentioned above, coprecipitation method and other methods are also adopted to develop ternary oxides.

Recently, both Chen et al. and Yao et al. have demonstrated a copper-doped nickel oxide (Cu:NiO_x) by coprecipitation method.^[27b,f] Referring to previous report,^[9c,64] they perform the reaction in metal salts solution containing nickel nitrate and copper nitrate to form hydroxide intermediate containing desired doping concentration. To obtain nanometer-size oxides, the prepared hydroxide was then calcined at a high temperature of around 270°C . A small change in *d*-spacing of crystal lattice observed in high-resolution transmission electron microscopy (TEM) image by Chen et al. indicates the success of copper

substitutional doping. Besides, Choy and co-workers also adopt coprecipitation method to prepare p-type ternary nickel cobalt oxide (NiCo_2O_4).^[65] By wisely choosing ammonium hydroxide as mineralizer, ultrasmall and well-dispersed ternary oxide particles are obtained by controlling the deamination process. In coprecipitation approach, a hydroxide intermediate is typically obtained from solution with control acidity and this hydroxide intermediate is always directly converted into metal oxide nanoparticles by high-temperature calcination. Fortunately, this high-temperature process is independent to film formation on substrate and post-treatment, which is compatible to low-temperature solution-process fabrication. Moreover, high-temperature calcination is also beneficial to enhance conductivity by removing some small surface ligand and increasing crystallinity.

In optoelectronics application, low-temperature solution-processed CTLs are desirable to achieve low-cost, low-temperature, and flexible device. To lower down synthesis temperature, Seok and co-workers propose a new route to synthesize ternary oxide Zn_2SnO_4 with temperature under 100°C .^[66] In this novel approach, hydrazine (N_2H_4) is used to form a complex with ZnCl_2 , which plays a vital role in achieving low-temperature synthesis as shown in **Figure 6**. By controlling the mole ratio of $\text{N}_2\text{H}_4/\text{Zn}$, there are different reaction routes that can significantly affect the final products. As proposed by Seok and co-workers, in low mole ratio of $\text{N}_2\text{H}_4/\text{Zn}$ (acidic condition), H_2SnO_3 is formed by hydrolysis while Zn source remains in solution with ion format, which results in a final product of SnO_2 . When the ratio of $\text{N}_2\text{H}_4/\text{Zn}$ increases, the complex of Zn-hydrazine is formed and hydrolysis of Sn^{4+} is also prevented (forming $\text{Sn}(\text{OH})_6^{2-}$). When reaction progresses, the Zn-hydrazine complex ($\text{Zn}(\text{N}_2\text{H}_4)_2\text{Cl}_2$) converts into a new zinc ammine hydroxo complex (Zn-N-H-OH) with existence of excess hydrazine. This new complex shows low-energy kinetics of metal-ammine dissociation and the hydroxide condensation/dehydration, which finally leads to the formation of Zn_2SnO_4 with $\text{Sn}(\text{OH})_6^{2-}$ under 100°C . With this low temperature prepared ternary oxide, flexible perovskite SCs are fabricated on ITO coated poly(ethylene 2,6-naphthalate) substrates. With the same goal of achieving low-temperature synthesis, the same group demonstrates a peroxo-complex intermediate method to synthesize perovskite type ternary oxide BaSnO_3 .^[67] A crystalline superoxide-molecular cluster is first prepared by using hydrogen peroxide and ammonium hydroxide to react with corresponding metal salts. The educts of superoxide cluster can be well dispersed for forming thin film and it can convert into perovskite ternary oxide by annealing at only 200°C that is much lower than that of the conventional method. In these two cases, the possibility of forming high-quality ternary oxide CTLs under low temperature is demonstrated via wisely design reaction road.

4. Recent Progress of Solution-Processed Ternary Oxide-Based CTLs

The advantages of solution process have given enough impetus to develop various photoactive materials, which puts the performance of optoelectronics a large step forward. In the past few years, ternary oxides have been developed and demonstrated as efficient interfacial materials and their tunable properties

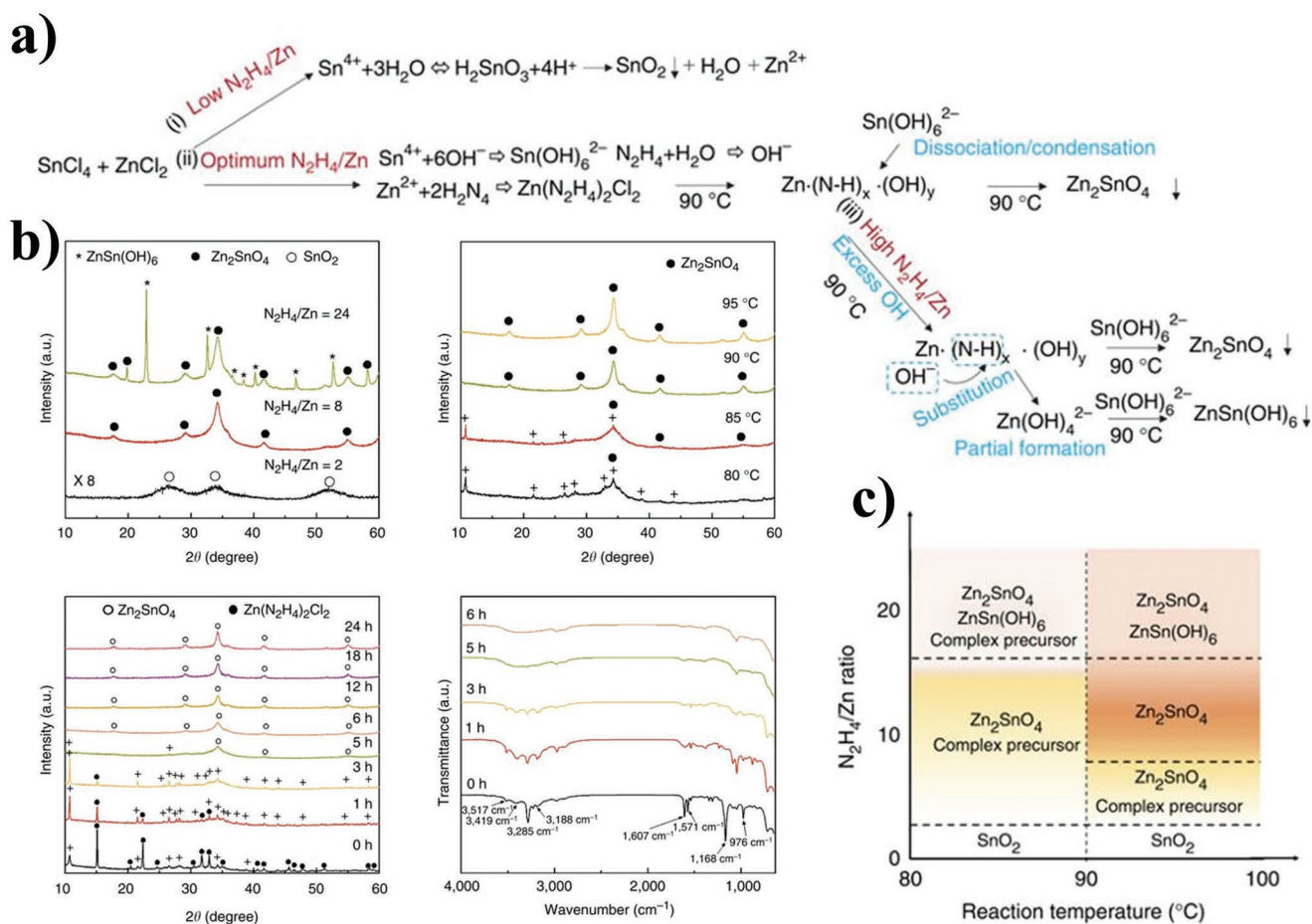


Figure 6. a) Formation mechanism of ZSO NPs in schematic illustration of the formation mechanism of crystalline ZSO NPs via a low-temperature process below 100°C . b) XRD and Fourier transform infrared (FT-IR) of samples obtained with various reaction conditions. Powder X-ray diffractograms (Cu K α radiation) of different $\text{N}_2\text{H}_4/\text{Zn}$ ratios (90°C , 12 h) (up-left), different reaction temperatures ($\text{N}_2\text{H}_4/\text{Zn} = 8$, 12 h) (up-right) and different reaction times (90°C , $\text{N}_2\text{H}_4/\text{Zn} = 8$) (down-left); FT-IR spectra of samples synthesized at different reaction times (90°C , $\text{N}_2\text{H}_4/\text{Zn} = 8$) (down-right), unindexable peaks are denoted as (+). c) Formation map of ZSO with different temperature and hydrazine/Zn ratio. Reproduced with permission.^[66] Copyright 2017, the American Association for the Advancement of Science.

further improve the performance of optoelectronic devices. In this section, we will review their progress in organic SCs, perovskite SCs, and other optoelectronic devices, especially the impact on device performances by tuning optoelectronic properties of ternary oxides.

4.1. Solution-Processed Ternary Oxides as CTLs in Organic SCs

The past two decades have witnessed remarkable progress on organic SCs, which is on account of their advantages of light weight, low cost, flexibility, and solution process ability. Bulk heterojunction is commonly adopted device structure in fabricating organic SCs nowadays.^[68] To form efficient bulk heterojunction, a bicontinuous interpenetration network needs to be constructed by blending donor and acceptor together, which results in undesired direct contact of donor to anode and acceptor to cathode. Therefore, matched and efficient interfacial layers are vital to improve device performance and some work function tunable interlayers have contributed to improvement

on device performances.^[10a,11a,12f,16b,69] Consequently, ternary oxides with high conductivity and tunable properties provide a very promising option as efficient CTLs for developing highly performed and stable organic SCs toward low-cost commercial applications.

Conductivity is considered as one of the vitally important parameters in developing CTLs, which will subsequently affect the process of charge extraction and transport. The conductivity of ternary oxides can be effectively improved by altering their chemical composition to an optimized ratio. For ZnO doping, trivalent element substitution can significantly improve conductivity by providing an extra electron donor to generate a free electron. In some recent works, aluminum-doped ZnO has been reported as CTL to enhance performance of organic SCs by several groups.^[57,70] No surprise, the improved conductivity is obtained after the addition of aluminum because the substitutional Al forms an extra electron donor center. With the improved conductivity of Al:ZnO, reduction in the in-series resistance can be realized for favoring the electron extraction and transport from active layer to the cathode.^[70c,71] It is notable

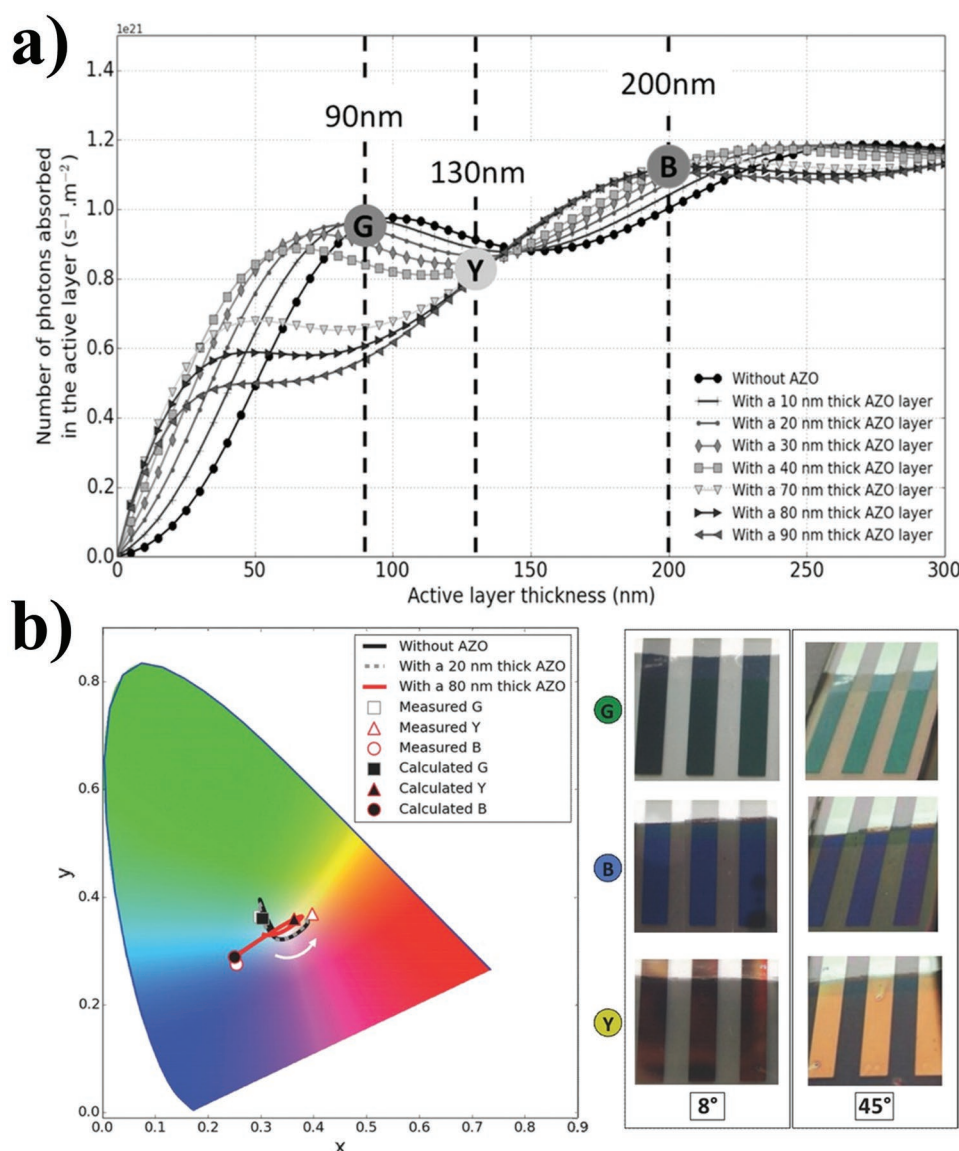


Figure 7. a) Theoretical absorption in the active layer as a function of active layer thickness (B, Y, and G refers to the studied solar cells). Atomic force microscopy (AFM) for $\text{AZO}_{0.8}$ layers with different thickness. b) Predicted color as a function of active layer and $\text{AZO}_{0.8}$ thicknesses (left) and photograph images of the green, blue, and yellow solar cells at 8° and 45° (right). Reproduced with permission.^[70a] Copyright 2015, John Wiley and Sons.

that the Al:ZnO developed by Stubhan et al. exhibits remarkable high conductivity as summarized in the table inserted in Figure 5. An efficient ETL with thickness over 600 nm can be prepared at low temperature (140°C) without significantly drawing down PCE. In addition, Gaceur et al. also report Al:ZnO nanocrystal as efficient ETL without high-temperature annealing.^[70a] With the Al doping, the nanocrystals not only exhibit improved conductivity but also show good film formation for a smooth thin film, which together contribute to a higher PCE of 7.56% compared to that of undoped ZnO of 5.86% in PTB7:PCBM based organic SCs. More importantly, this highly conductive ETL provides more freedom in film thickness which gives an opportunity for designing colored device as shown in Figure 7. Trivalent gallium (Ga) has also been used as dopant in ZnO. Both Thambidurai et al. and Shin

et al. have successfully synthesized Ga:ZnO with reduced film resistance that contributed to performance improvement of organic SCs.^[20,72]

In ternary oxides compounds, conductivity can also be further improved by controlling composition and introducing vacancy and large improvement have been achieved in organic SCs.^[15b,42b] Hsu and co-workers have prepared a delafossite-type HTL (CuGaO_2) by a microwave-assisted hydrothermal approach and they have investigated its application as HTL in normal structured organic SCs.^[15b] A slightly low PCE was obtained with only 0.91% in these devices using as synthesized CuGaO_2 compared to that of control device of 3.59% using PEDOT:PSS. With ultraviolet ozone treatment, the conductivity of the ternary oxide significantly improved from 0.19 to 3.6 S cm^{-1} which is postulated from the oxygen interstitial doping. As

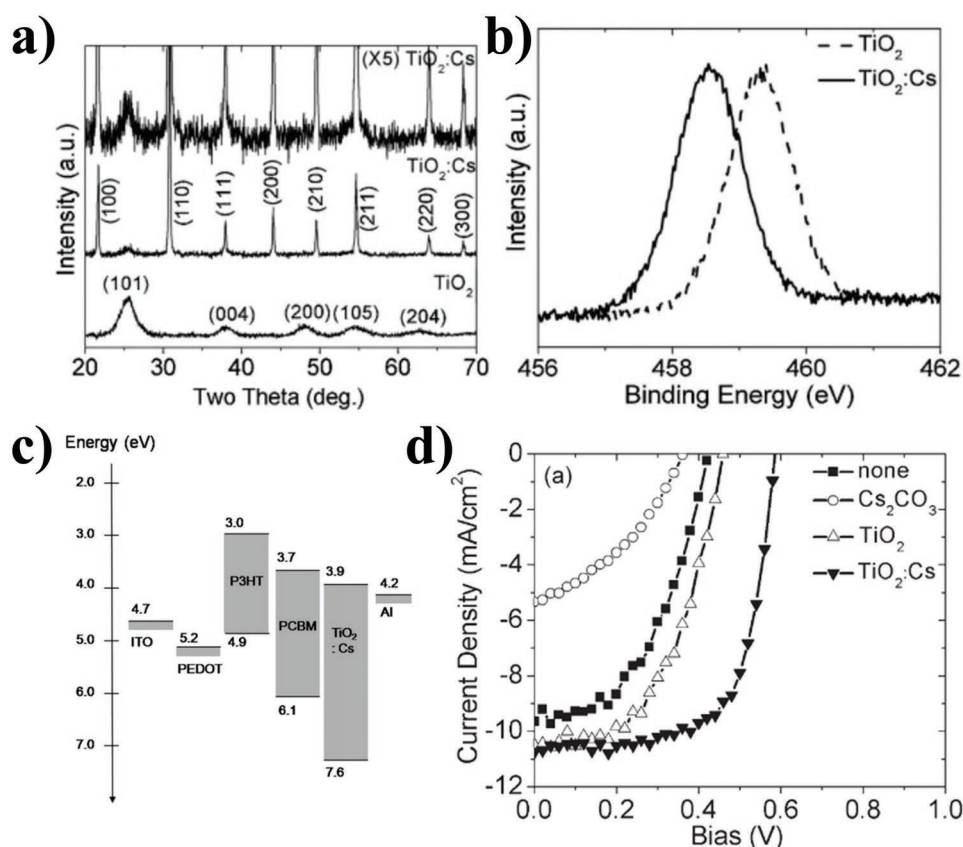


Figure 8. a) X-Ray powder diffraction patterns for TiO_2 (bottom), and $\text{TiO}_2\text{:Cs}$ overview (middle) and zoomed in (top). b) XPS profiles of TiO_2 (dot line) and $\text{TiO}_2\text{:Cs}$ (solid line) samples for Ti peak. c) Corresponding energy level diagram of a device based on a $\text{TiO}_2\text{:Cs}$ interfacial layer. d) J–V characteristics of a P3HT:PCBM based photovoltaic cell with an evaporated Al cathode and different interfacial layers (none; Cs_2CO_3 ; TiO_2 ; $\text{TiO}_2\text{:Cs}$). Reproduced with permission.^[54] Copyright 2009, John Wiley and Sons.

a result, the performance of organic SCs straightly rises to 3.20% in a comparable level to control devices. Besides, the same group also developed small-sized delafossite-type ternary oxide (CuCrO_2).^[42b] With these small-size nanoparticles, much smoother HTL was formed compared with previous CuGaO_2 film and comparable device performance to control devices was achieved on PCDTBT:PC₇₁BM based organic SC devices. In their comparison of two HTLs, it is clear that particle size and thus the film roughness can affect final device performances.

In addition to improve conductivity of ternary oxides, chemical composition change can also contribute to better energy alignment and optical performance for achieving high-performance organic SCs. Alkali metals (Li, Cs) and alkali earth metal (Mg) have also been used as doping elements to prepare efficient ternary oxide CTLs.^[28a,54,73] Yang and co-workers reported a Cs-doped TiO_2 by mixing the solution of Cs_2CO_3 and TiO_2 .^[54] As shown in Figure 8a,b, existence of CsCl is proven by the refraction peaks in XRD pattern that is assigned to the reaction byproduct of residual benzyl chloride and Cs_2CO_3 , and the peak shift in the XPS profile of Ti peak shows the interaction between TiO_2 and Cs_2CO_3 . As a result, the conduction band level of $\text{Cs}:\text{TiO}_2$ decreases to 3.93 eV from the initial value 4.3 eV of undoped TiO_2 . When using this ternary oxide as ETL in P3HT:PCBM based normal structured organic SCs, a preferred band alignment is shown in Figure 8c and a Ohmic

contact is formed between ETL and Al electrode, which significantly facilitates electron transport from active layer to Al electrode comparing with the case of TiO_2 . More importantly, since the open circuit voltage (V_{oc}) is typically determined by the difference of energy level of active layer if there are Ohmic contact in both electrodes,^[69a,74] the reported improvement of V_{oc} may be ascribed to the conduction band level adjustment of ternary oxide and improved conductance of $\text{Cs}:\text{TiO}_2$ based devices, which finally contribute to an overwhelming PCE of 4.2% compared to that of pristine TiO_2 (2.4%) as shown in Figure 8d. Cs doping can not only enhance conductivity and slightly change energy level, but also convert binary oxide hole transport layer into ternary oxide ETL. Recently, Li et al. have achieved a wide-range work function adjustment of over 1.1 eV by controlling the Cs doping ratio in the MoO_3 and V_2O_5 oxides.^[55] As shown in Figure 9a,b, with the concentration of Cs increasing to 0.5, the work functions for both Cs_xMoO_3 and $\text{Cs}_x\text{V}_2\text{O}_5$ have been significantly changed over 1.1 eV and the conduction band and valence band are also affected. By using this intercalated ternary oxide as ETL and corresponding binary oxide as HTL, the current density to voltage characteristics (J–V) gradually become normal from the S-shape as shown in Figure 9c,d, which may result from the variation of work function. Finally, the organic SCs based on PBDTDTT-S-T:PC₇₁BM have achieved comparable performance to previous results,^[75] with PCE of 7.32% and

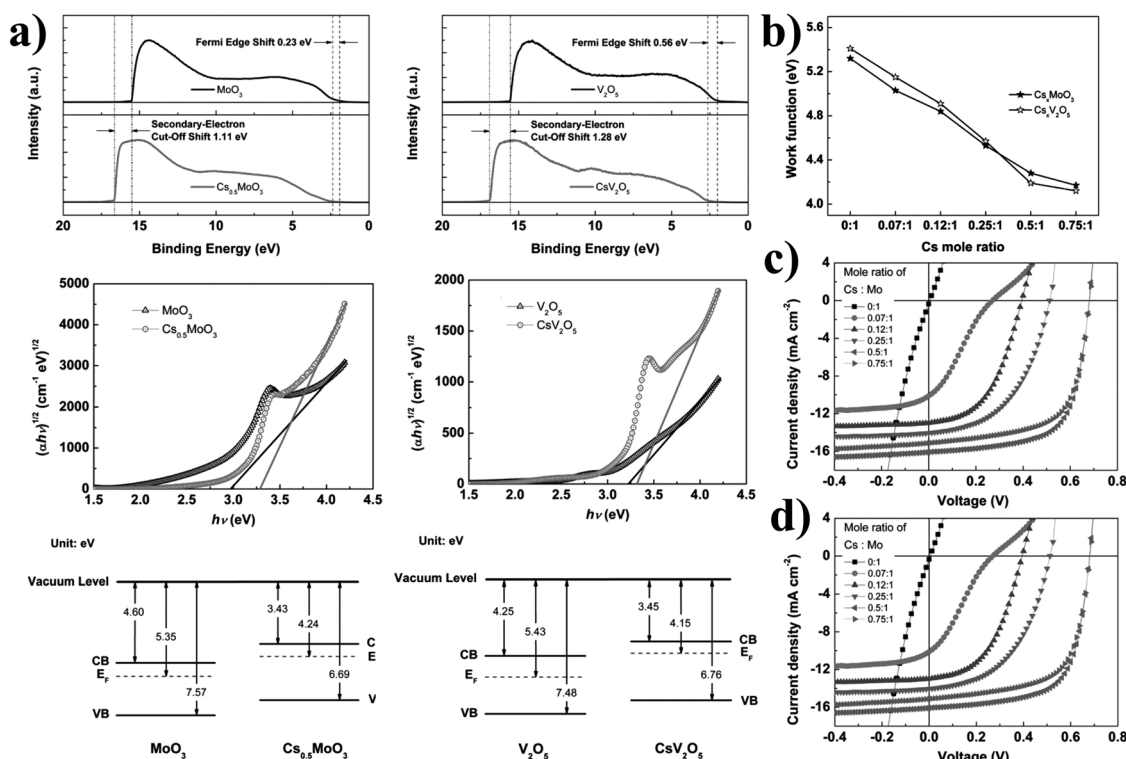


Figure 9. a) Ultraviolet photoelectron spectroscopy (UPS) results of MoO_3 , $\text{Cs}_{0.5}\text{MoO}_3$, V_2O_5 , and CsV_2O_5 (up); optical bandgap (E_{opt}) results from the plot of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) of MoO_3 , $\text{Cs}_{0.5}\text{MoO}_3$, V_2O_5 , and CsV_2O_5 . E_{opt} can be taken from the intersection of extrapolated line with the energy axis, different E_{opt} of MoO_3 , $\text{Cs}_{0.5}\text{MoO}_3$, V_2O_5 , and CsMoO_3 are 2.97, 3.26, 3.23, and 3.31 eV, respectively (middle); detailed energy band structures calculated from the UPS and E_{opt} results of different metal oxides (down). b) The work function variation of Cs intercalated metal oxides with different Cs ratio. c) J–V characteristics of OSCs with MoO_3 as HTL and Cs_xMoO_3 as ETL. d) J–V characteristics of OSCs with V_2O_5 as HTL and CsV_2O_5 as ETL. Reproduced with permission.^[55] Copyright 2014, John Wiley and Sons.

7.49% in normal SC structure, and 6.00% and 6.08% in inverted SC structure for $\text{Cs}_{0.5}\text{MoO}_3$ and CsV_2O_5 , respectively. Apart from wide-range adjustment in work function, doping can also remarkably tune the bandgap of ternary oxide. Zheng and co-workers have demonstrated a large bandgap tunable (3.2–3.7 eV) $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ ternary oxide.^[28a] As shown in Figure 10a,b, the bandgap of this ternary oxide can be continuously enlarged by increasing the Mg content from $x = 0$ to $x = 0.6$. The optical absorption spectra of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ clearly present reduced absorption in ultraviolet region when the bandgap is enlarged. To demonstrate these ternary oxides' application in organic SCs, $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ ETLs are deposited on the ITO substrates. An enhanced transmission is achieved in the ternary oxide-based ETL as shown in Figure 10c, which directly contributes to the substantial enhancement in the absorption. Besides high transmission, slightly increased conductivity is also obtained on the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ ($x < 0.4$) samples. With these ternary oxide-based ETLs, a higher efficiency has been realized with the highest PCE of 7.83% of $\text{Zn}_{0.7}\text{Mg}_{0.3}\text{O}$ compared to that of 7.11% of ZnO .

4.2. Solution-Processed Ternary Oxides as CTLs in Perovskite SCs

Organic–inorganic halide perovskites have been intensively studied new photovoltaic materials, due to their merits in

optical and electrical, such as high absorption coefficient, tunable direct bandgap, low exciton binding energy, and long carrier diffusion length.^[76] The PCE of perovskite SCs has soared to a certified high value over 23%, thanks to many researches that have been conducted on both active and interfacial layers.^[3a,10b,c,64,77] Toward their commercial application, there are still challenges in achieving high PCE and long-term stability. Interfacial layers in perovskite SCs play an important role in achieving high efficiency and long-time stability, due to their multiple potential functions on favorable growth of active layer,^[65,78] effective extraction and transport of carrier,^[64,79] ion blocking,^[80] oxygen/moisture prevention,^[14,77h,81] etc. With these advantages, ternary oxides are promising candidates as highly efficient CTL for realizing highly efficient and stable perovskite SCs.

In order to improve the electrical properties of CTL for largely enhancing the performance of perovskite SCs in efficiency and hysteresis, surface modification and methods were applied to CTLs.^[15a,17,78] Yang et al. and Feng et al. showed that the excellent carrier transport and collection ability of CTLs can significantly enhance device performance with negligible hysteresis.^[82] The strategy of metal-ion doping has also been adopted to promote the charge extraction and transport ability of conventional binary oxide.^[21,22b,23,27f] Recently, Yao et al. have demonstrated a recordable efficiency of inverted mesoporous perovskite solar cells by using copper-doped nickel

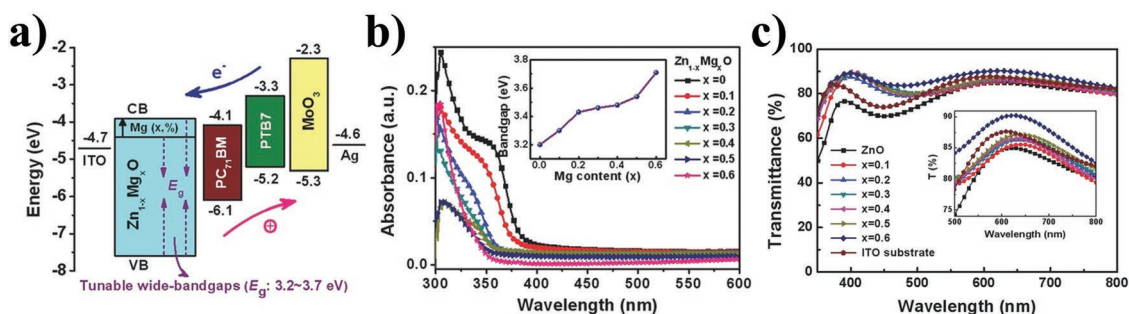


Figure 10. a) Energy levels of the components in the PSCs with various ZMO as the CBL. b) Optical absorption spectra of ZMO films. The inset shows an increase in the bandgap of ZMO films. c) Optical transmission spectra of various ZMO and ZnO films on the ITO-glass substrate. Reproduced with permission.^[28a] Copyright 2014, John Wiley and Sons.

oxide (Cu:NiO_x) as both compact and mesoporous layers.^[27f] Cu:NiO_x nanoparticles prepared by precipitation method with high hole mobility up to $1.09 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are used as mesoporous layer while Cu:NiO_x by sol-gel method is used as compact layer as shown in the Figure 11c. In p-i-n SC structure, perovskite SCs have achieved remarkable PCE of 19.6%, which is ascribed to improved photocurrent and high fill factor (FF). The authors employed steady-state photoluminescence (PL) and time-resolved PL spectra (TRPL) to reveal that the perovskite SC devices with bilayer of Cu:NiO_x show considerably greater PL quenching and shorter decay lifetime than device using undoped NiO_x as shown in Figure 11a,b, indicating enhanced carrier extraction and transport efficiencies. Impressively, with this efficient inorganic bilayer Cu:NiO_x, over 94% and 90% of their initial performance are retained after 1000 h of dark storage and continuous illumination in short-circuit conditions, as shown in Figure 11e. Apart from mesoporous

structure, Cu:NiO_x is also used to achieve high efficiency over 20% and 17% for rigid and flexible devices in planar structured perovskite SCs by Chen et al.^[27b] They pointed out that copper doping slightly narrows the bandgap of nickel oxide from 3.65 to 3.6 eV. However, the introduction of copper in NiO_x can create shallow acceptor level that is likely to increase hole concentration and thus increase conductivity, which finally contributes to enhanced performance comparing with undoped NiO_x. Jen and co-workers also demonstrate the ability of Cu:NiO_x as efficient HTL in perovskite SCs.^[24] A new combustion method for preparing this ternary oxide is proposed. Compared with conventional sol-gel method, this combustion method has a lower process temperature and produces both homogeneous and high-crystallinity film, which enables the low-temperature fabrication of high-efficiency perovskite SCs. Wan et al. introduces a new dopant (Zn) to improve the electrical properties. As indicated by their DFT calculation results (Figure 2c),

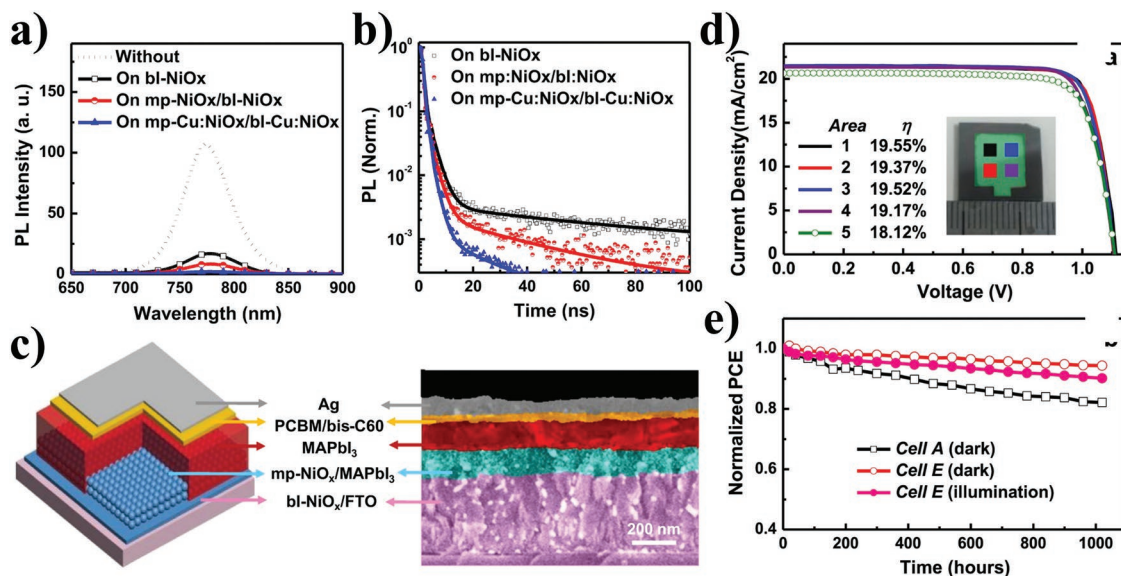


Figure 11. a) PL spectra of the perovskite films deposited on different hole transport layers. b) Time-resolved PL measurements of perovskite films, the solid lines are obtained by fitting the data using a biexponential rate law. c) Device architecture of the inverted mesoporous device and a colored high-resolution cross-sectional scanning electron microscope (SEM) image of a complete solar cell. d) Average efficiency values for a representative Cell E measured from four different spots (Area 1, 2, 3, or 4) with an aperture area of 0.0625 cm² selected from the total active area of 1.08 cm² (Area 5, green). All *J*-*V* curves were recorded in the reverse direction. e) The stability of the cells without sealing, based on planar and mesoporous structures in the dark or under constant light irradiation (AM 1.5G, 100 mW cm⁻², without UV-filter). Cell A with only bi-NiO_x, cell with bi-Cu:NiO_x/mp-Cu:NiO_x, the cells were kept in a dry cabinet (<30% humidity) in the dark and measured in ambient air. Reproduced with permission.^[27f] Copyright 2017, Elsevier Ltd.

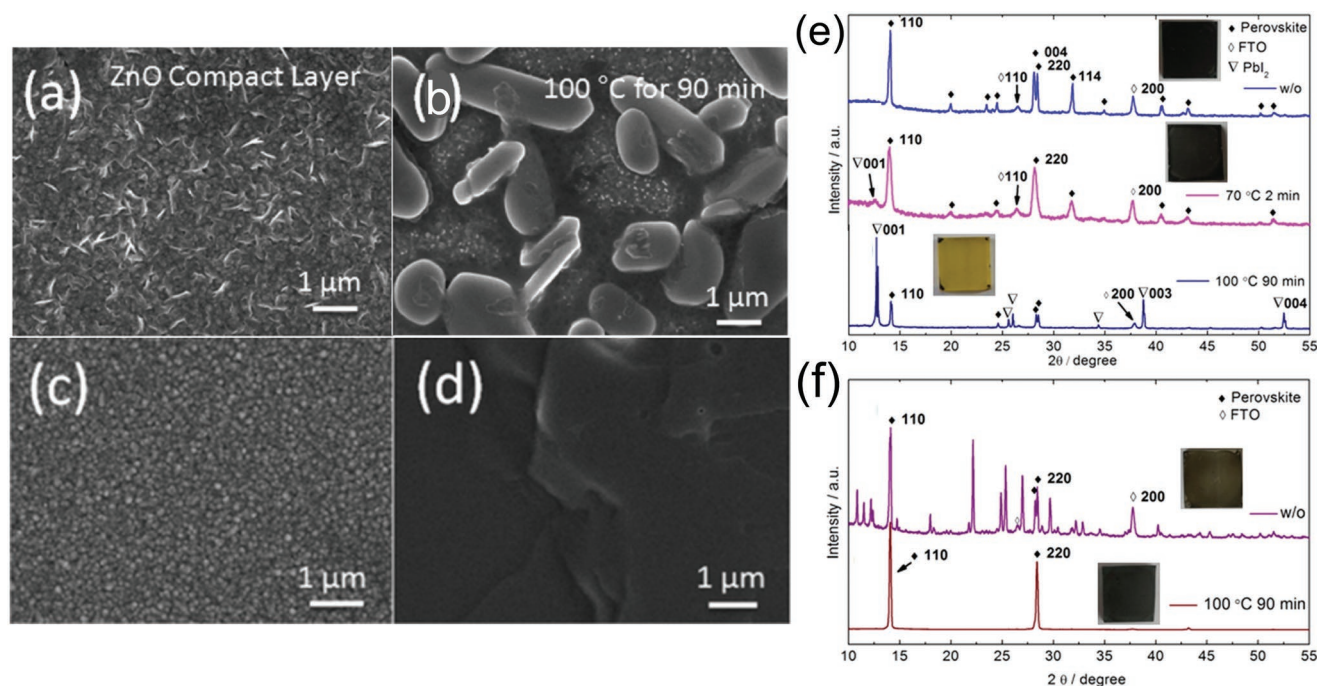


Figure 12. a) SEM images of ZnO electron-transport layer; b) the perovskite layer deposited on ZnO with 100 °C treatment for 90 min; c) SEM images of ternary oxide ETL TiZn₂O₄; d) perovskite film on TiZn₂O₄ layer with 100 °C treatment for 90 min; e) XRD patterns of the perovskite layer on ZnO without and with different heat treatment; and f) XRD patterns of the perovskite layer on ternary oxide TiZn₂O₄ ETL with heat treatment. Insets show the corresponding photographs for the perovskite layer. Reproduced with permission.^[84] Copyright 2016, American Chemical Society.

Zn-ion-doping can induce more electronic states in Fermi level. The conductivity of Zn-doped NiO_x is proven to be enhanced, and perovskite SCs with this ternary oxide as HTL also realize higher PCE of 19.6% than that of undoped ZnO.

In addition to enhancing the PCE by increasing conductivity and suppressing hysteresis, ternary oxides are also reported recently with stability enhancement for perovskite SCs. In previous reports,^[83] perovskite layer can be severely destroyed at the interface of ZnO/perovskite under thermal annealing condition due to the existence of hydroxide group. He and co-workers have demonstrated a TiO₂-ZnO ternary oxide as ETL for perovskite SCs by spraying pyrolysis technique.^[84] Notably, with the introduction of titanium, not only the morphology of the ETL becomes smooth and homogeneous, but also the thermal stability of perovskite deposited on this ETL is significantly enhanced as shown in **Figure 12**. Perovskite on binary oxide (ZnO) is seriously damaged after annealing at 100 °C and the yellow color of lead iodide (PbI₂) is clearly observed, while the perovskite on ternary oxide (TiZn₂O₄) keeps unchanged even after 90 min thermal annealing at 100 °C. With this ternary oxide as ETL, efficient perovskite SCs have been fabricated. They show that adding an extra element to form a ternary oxide can improve the thermal stability. Moreover, ternary oxides with merits of stable and high conductivity can be used to enhance long-term stability.^[77b,85] Zhang et al. have used a p-type delafossite ternary oxide CuGaO₂ as HTL to fabricate highly efficient perovskite SCs in an n-i-p structure as shown in **Figure 13a**. Due to high mobility and favorable energy level of this ternary oxide, an efficient HTL with a thickness as large as 345 nm is deposited atop of perovskite layer and overall PCE

of 18.51% can be achieved in reversed scan. It is worth mentioning that this thick ternary oxide layer can not only achieve high PCE but also remarkably impede the decomposition of perovskite as shown in **Figure 13b–d**. Perovskite SCs with thick CuGaO₂-based HTL maintain most of their original performance after tracking 30 days in ambient environment with 30–55% humidity and room temperature without encapsulation while the control devices decay dramatically to 3% of their PCE within only one week. Recently, another delafossite-type ternary oxide (CuCrO₂) has also been deposited as HTL in an n-i-p structure by Akin et al. Outstanding stability is also achieved by replacing the organic Spiro-OMeTAD HTL with inorganic ternary oxide. Over 80% of initial PCE is retained after storing over 60 days (first 7 days in dry condition and rest 53 days in 40% humidity environment). Since UV radiation can accelerate the decomposition of perovskite, Zhang et al. utilized CuCrO₂ ternary oxide to function as a UV-blocking underlayer in a p-i-n structured perovskite SC.^[86] The bandgap of CuCrO₂ is around 2.9 eV that shows high absorption in UV region (<400 nm) while high transparency in visual region. When compared with NiO_x-based devices, CuCrO₂-based devices show longer photostability under simulated illumination including UV radiation by a xenon lamp as shown in **Figure 14**.

During the fabrication of perovskite SCs, the perovskite crystals typically grow on top of CTL underlayer films. Thus, the properties of the CTLs sometime can affect the perovskite crystallization. Bera et al. find that Zn₂SnO₄ based ETL can facilitate the crystallization of perovskite in a shorter time compared with the conventional TiO_x-based ETL.^[63b] When depositing perovskite layer by one-step method, sharp characteristic peaks of

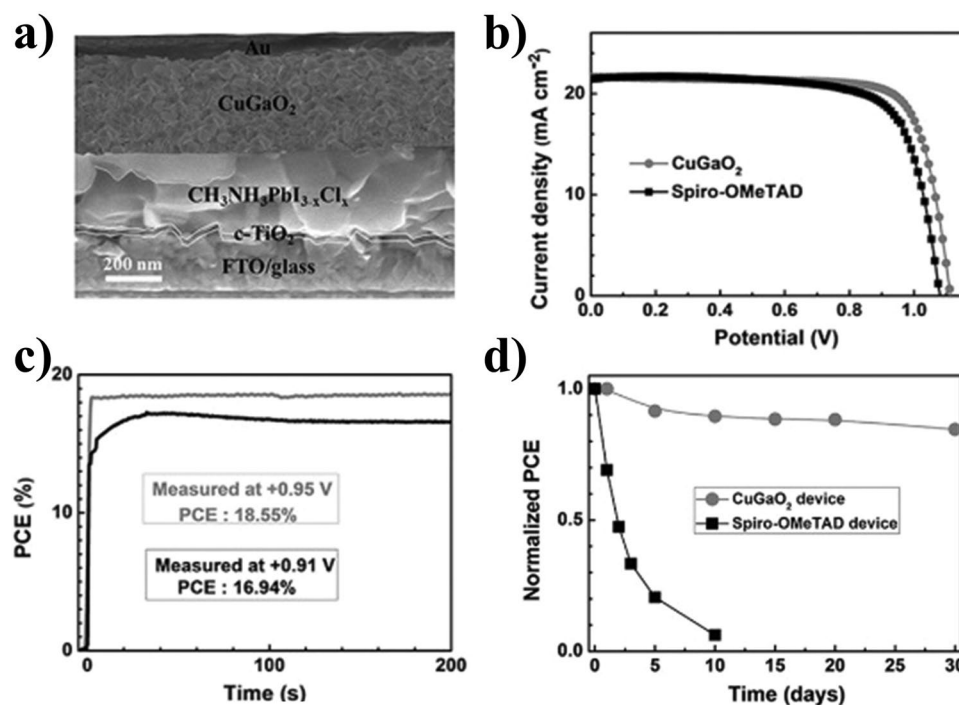


Figure 13. a) The cross-section of perovskite solar cell device; b) current–voltage curves with reverse scan mode for the best-performing devices based on CuGaO₂ and the control device, using a metallic mask with an aperture area of 0.09 cm² at a scan rate of 0.07 V s^{−1}; c) the steady-state power output at the maximum power point for the optimized CuGaO₂-based device and the control device; and d) evolution of normalized PCE for the optimized CuGaO₂-based device and the control device measured under ambient environment (30–55% humidity, *T* = 25 °C). Reproduced with permission.^[85a] Copyright 2016, John Wiley and Sons.

perovskite crystals can be detected from samples on Zn₂SnO₄-based ETL after only 1 min annealing and complete conversion needs only 10 min as shown in Figure 15a,b. While it needs 1 h to complete the formation of perovskite on TiO_x-based ETL. Ouyang et al. also find that the under layer of HTL has significant impact on the grain size of the perovskite as shown in the Figure 15c–f. The grain size of perovskite deposited on spinel-type ternary oxide (NiCo₂O₄) has an average of about 400 nm. In contrast, the average size of grain on PEDOT:PSS is less than 300 nm. This crystal size enlargement is assigned to the hydrophobicity difference between the ternary oxide and PEDOT:PSS.

4.3. Solution-Processed Ternary Oxides as Carrier Injection Layers and CTLs in Other Optoelectronic Devices

In past two decades, solution-processed optoelectronics have gained significant advancement. For achieving low-cost and large-scale fabrication, solution-processed interfacial layers have also been frequently used in various optoelectronic devices. In this part, we will give a brief review on the recent advancement of solution-processed ternary oxides as carrier injection layer (CIL) and CTLs for those optoelectronic devices. Since optoelectronics is a diverse class of photoactive or photo-responding

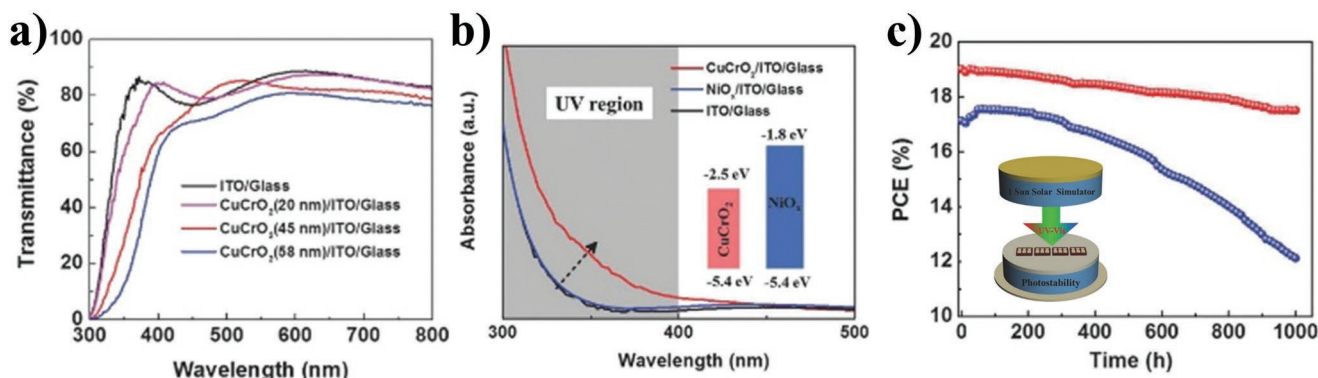


Figure 14. a) The dependence of the optical transmission spectra on the thickness of CuCrO₂ films; b) UV–vis spectra of the CuCrO₂ and NiO_x layer with the optimum thickness, inset shows the energy level, indicating their corresponding optical bandgap; and c) the time evolution of PCE for the unsealed devices based on the CuCrO₂ (red) and NiO_x (blue) as HTLs, inset is photostability study setup under 1 sun solar simulator illumination with a xenon lamp including UV radiation for both unsealed champion devices. Reproduced with permission.^[86] Copyright 2018, John Wiley and Sons.

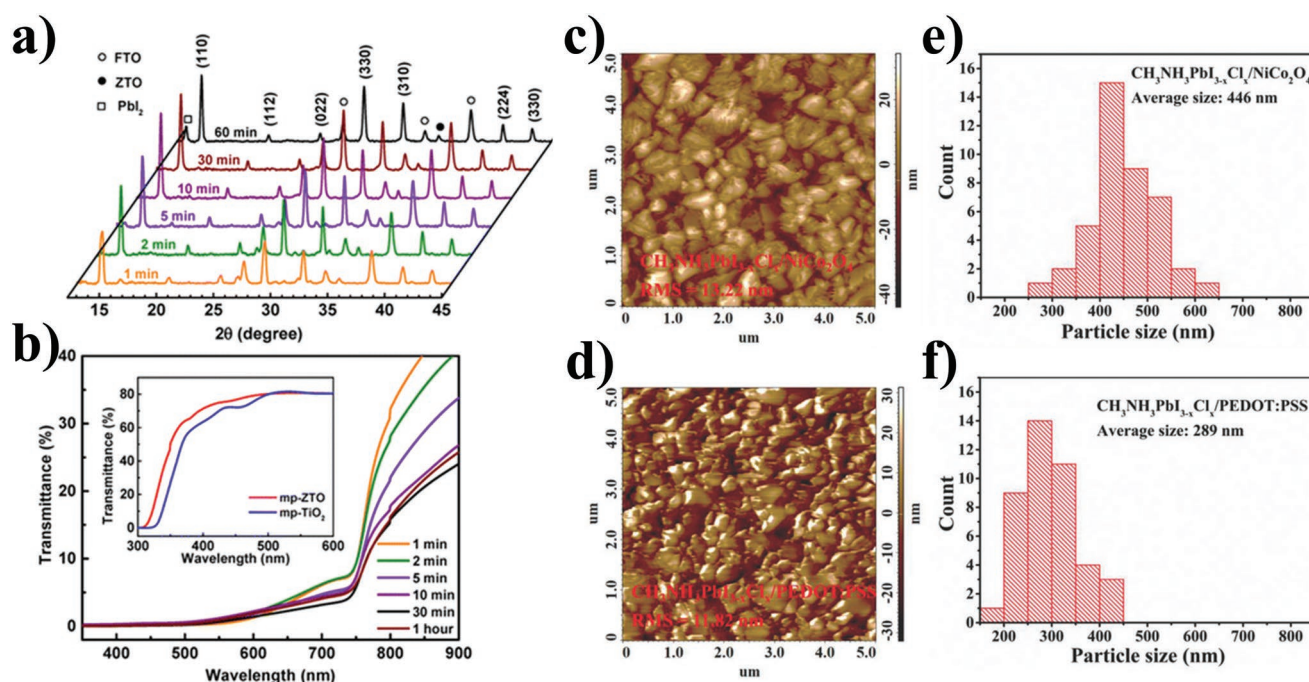


Figure 15. Evolution of crystallization and structure of the perovskite film on ZTO during annealing at 100 °C, a) XRD patterns; and b) transmission spectra. Inset of panel (b) presents the transmittance spectra of mp-ZTO and mp-TiO₂ layers; a,b) Reproduced with permission.^[63b] Copyright 2015, American Chemical Society. AFM images of CH₃NH₃PbI_{3-x}Cl_x, c) on NiCo₂O₄; d) on PEDOT:PSS; and size distribution histogram of perovskites, e) on NiCo₂O₄; and f) on PEDOT:PSS; c–f) Reproduced with permission.^[65] Copyright 2018, John Wiley and Sons.

devices, including light emitting diodes, photodetectors, and other solar energy conversion devices, we will only focus on the optoelectronic devices using polymers and perovskites as photoactive materials, such as organic LEDs, perovskite LEDs, and perovskite PDs, while LED and PDs based on other active layer materials (e.g., LED based on Cd-based II–VI or non-Cd-based III–V quantum dot^[87]) will not be included in this section.

For high-performance organic LED, improving charge injection is of great importance under a lower driving voltage.^[88] Insertion of a thin carrier injection layer is one simple way among many effective methods. To achieve effective injection, it required CILs/CTLs with tunable work function to minimize the energy offset between electrodes and CTLs or photoactive layers. Solution-processed ternary oxides with tunable work function and high conductivity have been adopted in the fabrication of organic LEDs and perovskite LEDs. For instance, Jin and co-workers have demonstrated a work function tunable indium-doped ZnO (In:ZnO) nanocrystals for optoelectronic application.^[89] In:ZnO nanocrystals are successfully synthesized by carefully controlling the synthesis parameters, such as mole ratio, addition sequence of precursor, etc., which exhibits a tunable work function in the range from 3.5 to 3.2 eV. With the In:ZnO of 2 at% of doping (work function of 3.2 eV), significantly better performance has been achieved in a Poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT)-based device compared with pristine ZnO, in terms of lower turn-on voltage of 2.2 V, high efficiency (maximum external quantum efficiency (EQE) of 1.0% and maximum current efficiency of 3.2 cd A⁻¹), and higher maximum luminance of over 78 000 cd m⁻² at 8 V as shown in Figure 16. Lower work function of this ternary oxide

is considered as the reason for the enhanced performances. Similarly, Park et al. also utilize doping strategy to achieve better energy alignment by adding Cs₂CO₃ into TiO₂ colloidal solution. The conduction band of the doped TiO₂ is shifted to 3.93 from initial 4.3 eV. In the organic LEDs using green polyfluorene as the emitting material, obvious improvement has been realized with Cs:TiO₂ as interfacial layer, with current efficiency of 11.5 cd A⁻¹, and power efficiency of 14 lm w⁻¹ at a bias of 2.8 V. Apart from charge transport layer, Li et al. also utilized doping strategy to tune the work function of hole injection layer.^[90] Solution-processed copper doped nickel oxide is prepared by a low-temperature combustion method. With the introduction of copper, the work function of NiO_x slightly increases which finally contributes to 11.3% increase of power efficiency in 4,40-bis(N-carbazolyl)-1,10-biphenyl (CBP)-based devices.

Ternary oxide-based CTLs/CILs with important role of not only realizing high performance but also achieving long working lifetime were used in perovskite-based optoelectronics. Yu and co-workers have used Mg-doped ZnO (Mg:ZnO) as an interfacial layer for fabricating perovskite nanocrystal LED.^[91] Their work demonstrates that the air stability of perovskite nanocrystal film can be greatly improved by inserting a thin interfacial layer of decreased surface-oxygen-vacancy Mg:ZnO between perovskite and ZnO. As shown in Figure 17a,b, the photoluminescence intensity of perovskite nanocrystal film on ZnO obviously decreases after storage for 30 days while the perovskite on Mg:ZnO retains most of its original intensity. Thanks to the favorable electronic energy level of Mg:ZnO for a suitable band alignment, 1.9 times enhanced current efficiency and 2 times increased external quantum efficiency are realized

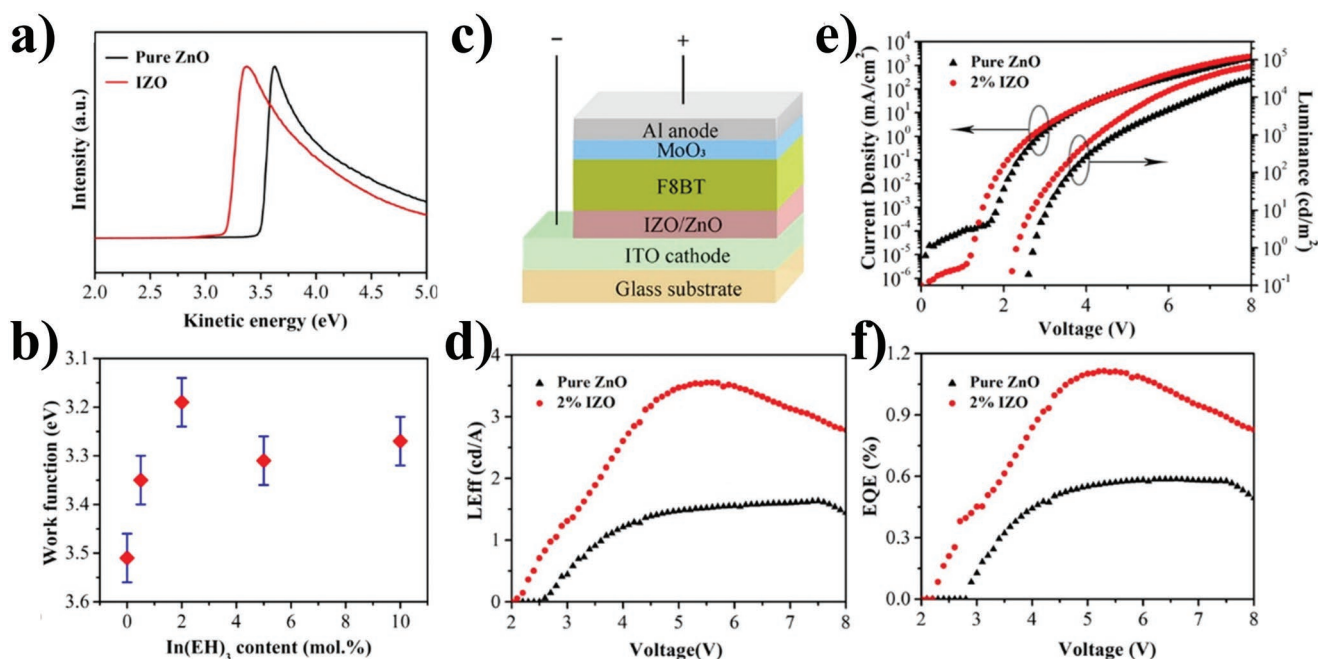


Figure 16. a) UPS spectra showing the normalized secondary electron cutoff. The IZO nanocrystals to prepare this sample are from the 2 mol% $\text{In}(\text{EH})_3$ reaction; b) work function of five samples from reactions starting with 0, 0.5, 2, 5, and 10 mol% $\text{In}(\text{EH})_3$ reactions. The error bar of ± 0.05 eV comes from the overall accuracy of the instrument. c) LEDs device structure; d) current efficiency–V curves; e) J –L–V curves; and f) EQE–V curves. The IZO nanocrystals from the 2 mol% $\text{In}(\text{EH})_3$ reactions were used. Reproduced with permission.^[89] Copyright 2014, American Chemical Society.

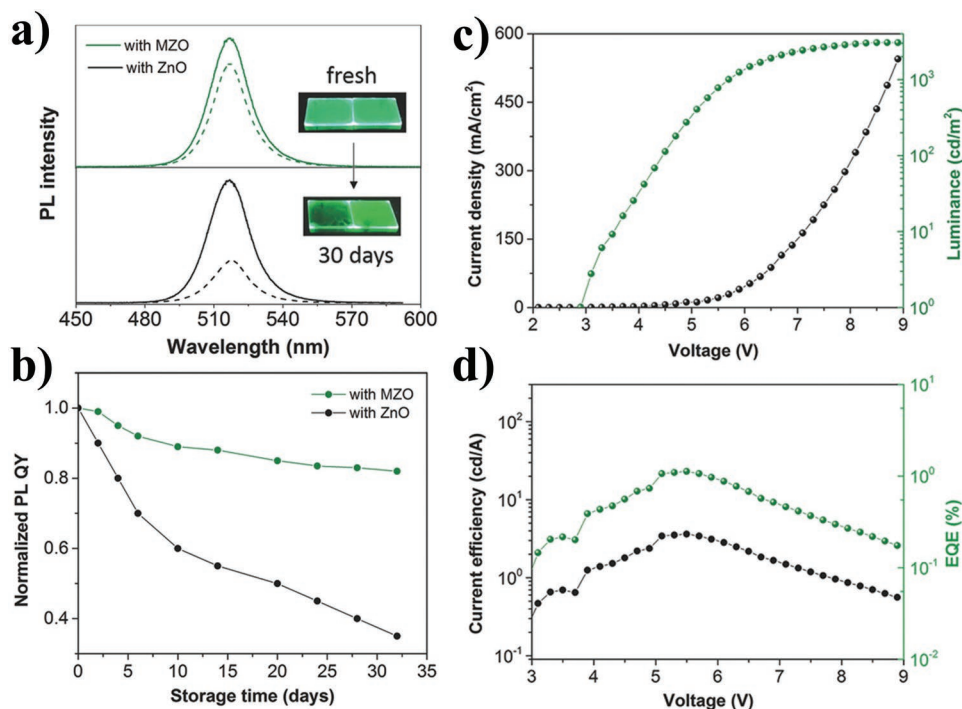


Figure 17. a) Comparison of PL spectra for fresh CsPbBr_3 NC films (solid line) and film stored for 30 days in air (dotted line) when the film was deposited on ZnO (bottom panel) and MZO (upper panel). Inset: photos of the two samples under 365 nm excitation wavelength before and after stored for 30 days; the left is NC film with ZnO, while the right one is NC film with MZO. b) Normalized PL QY evolution of CsPbBr_3 films when deposited on different substrates. c) The variation of current density and luminance as a function of voltage. d) EQE and current efficiency versus voltage for the best-performed LED. Reproduced with permission.^[91] Copyright 2014, American Chemical Society.

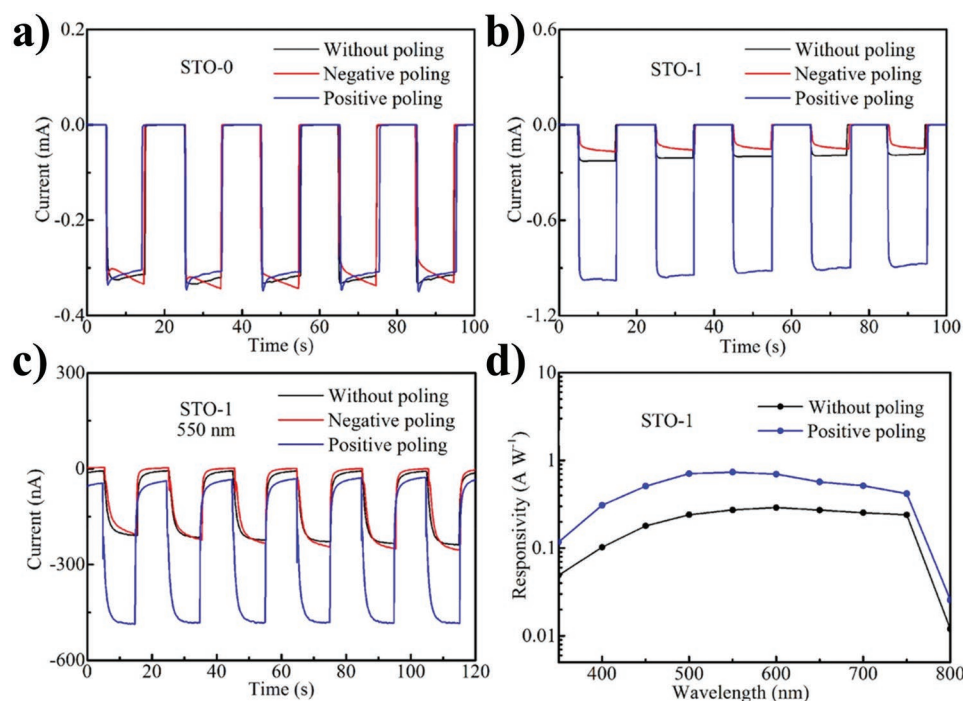


Figure 18. *I*-*t* curves of the as-prepared (black), negatively poled (red), and positively poled (blue) devices under white light illumination at 0 V, a) without SrTiO₃; b) with one layer SrTiO₃ (STO-1). c) *I*-*t* curves of the as-prepared (black), negatively poled (red), and positively poled (blue) STO-1 devices under 550 wavelengths illumination; and d) responsivity of the as-prepared and positively poled STO-1 devices. Reproduced with permission.^[93] Copyright 2018, American Chemical Society.

in perovskite LEDs with luminance of 3059 cd m⁻² as shown in Figure 17c,d. Stable perovskite LEDs are also reported by Shi et al. by using Mg-doped ZnO as carrier injector. They tracked the intensity of unencapsulated perovskite LEDs in ambient environment at different bias voltages (4, 6, and 8 V). Slight decay in emission intensity is observed after testing for 8 h with 10.2%, 13.5%, and 18.2% decay at 4, 6, and 8 V, respectively.

Due to the unique properties, ternary oxide can be also used in PDs exhibiting remarkable performance. Perovskite-type ternary oxide SrTiO₃ is a ferroelectric material with considerable electric polarization and high electron mobility.^[92] Recently, Cao et al. have used this ternary oxide to fabricate high-performance self-powered PDs in a structure of FTO/SrTiO₃/perovskite film/spiro-OMeTA/Ag.^[93] Their results show that the direction of polarized field can largely affect the responsivity and the response speed of devices. As shown in Figure 18a,b, once positive poling is applied, the photocurrent can be significantly enhanced in the SrTiO₃-based PDs while the photocurrent is reduced in negative poling. Under monochromatic light illumination at 0 V, the photocurrent can be strongly enhanced in the PD with SrTiO₃ under positive poling (Figure 18c). PD devices based on SrTiO₃ with positive pooling show higher responsibility than that without poling as shown in Figure 18d and a peak responsivity of 0.73 A W⁻¹ is achieved at the wavelength of 550 nm.

5. Conclusion and Outlook

In this review, some fundamental understandings on tailoring optical and electrical properties and synthesis methods for

ternary oxides are first summarized. Then, we review and discuss the recent application progress of solution-processed ternary oxide-based CTLs/CILs in optoelectronics. Incontestably, solution-processed ternary oxides as CTLs have significantly contributed to the development of solution-processed optoelectronics. However, it still needs more efforts in both theoretical and experimental studies to fully explore their potential for optoelectronic applications. 1) Theoretical study is important to obtain fundamental understanding on the impact on the conductivity and energy level change upon tuning the chemical composition. In practice, it is challenging to obtain continuous and accurate data of an interested parameter without disturbance from other factors, especially in a complicated system. During adjusting the composition of ternary oxide, the film formation can also be affected which shall be carefully and further studied for optimizing element ratio of ternary oxide. Therefore, theoretical calculation (such as DFT) can help to precisely understand the mechanism of their properties changing, even in different cases of ternary oxide (such as interstitial doping and substitutional doping). Meanwhile, theoretical calculation can also provide a clear picture of the density of states in different composition of a specific ternary oxide that gives direct information on energy level and optical bandgap. 2) Synthesis method including precursors, additive, and concentration can remarkably affect the properties of final ternary oxides. To develop an excellent ternary oxide as CTL, it is not enough to only control the chemical composition but also needs a well-developed synthesis method. On the other hand, to apply ternary oxide as efficient CTL for flexible, low-cost, and large-scale devices, it requires that the ternary oxide CTL can be deposited

by solution process techniques at low temperature. Experiment exploration of synthesis methods provides more alternatives to apply ternary oxide-based CTL in practical applications. Consequently, the development of theoretical understanding and experimental synthesis of ternary oxides can provide not only fundamental knowledge on the material but also comprehensive oxide libraries for the full potentials of optoelectronic applications.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

carrier transport/injection layer, metal oxides, optoelectronics, organic solar cells, perovskite solar cells

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- [1] a) F. Wang, Z. A. Tan, Y. Li, *Energy Environ. Sci.* **2015**, *8*, 1059; b) D. Ouyang, Z. F. Huang, W. C. H. Choy, *Adv. Funct. Mater.* **2019**, *29*, 1804660; c) K. Hwang, Y. S. Jung, Y. J. Heo, F. H. Scholes, S. E. Watkins, J. Subbiah, D. J. Jones, D. Y. Kim, D. Vak, *Adv. Mater.* **2015**, *27*, 1241; d) J. H. Kim, S. T. Williams, N. Cho, C. C. Chueh, A. K. Y. Jen, *Adv. Energy Mater.* **2015**, *5*, 1401229; e) C. W. Sele, T. Von Werne, R. H. Friend, H. Sirringhaus, *Adv. Mater.* **2005**, *17*, 997; f) M. Singh, H. M. Haverinen, P. Dhagat, G. E. Jabbour, *Adv. Mater.* **2010**, *22*, 673.
- [2] a) J. You, L. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C. C. Chen, J. Gao, G. Li, Y. Yang, *Nat. Commun.* **2013**, *4*, 1446; b) G. Li, R. Zhu, Y. Yang, *Nat. Photonics* **2012**, *6*, 153; c) S. Li, L. Ye, W. Zhao, S. Zhang, S. Mukherjee, H. Ade, J. Hou, *Adv. Mater.* **2016**, *28*, 9423; d) W. Zhao, S. Li, H. Yao, S. Zhang, Y. Zhang, B. Yang, J. Hou, *J. Am. Chem. Soc.* **2017**, *139*, 7148.
- [3] a) H. Zhang, M. K. Nazeeruddin, W. C. H. Choy, *Adv. Mater.* **2019**, *31*, 1805702; b) J. Huang, Y. Yuan, Y. Shao, Y. Yan, *Nat. Rev. Mater.* **2017**, *2*, 17042; c) J.-P. Correa-Baena, A. Abate, M. Saliba, W. Tress, T. Jesper Jacobsson, M. Grätzel, A. Hagfeldt, *Energy Environ. Sci.* **2017**, *10*, 710.
- [4] a) J. Mao, W. E. I. Sha, H. Zhang, X. Ren, J. Zhuang, V. A. L. Roy, K. S. Wong, W. C. H. Choy, *Adv. Funct. Mater.* **2017**, *27*, 1606525; b) J. Mao, H. Lin, F. Ye, M. Qin, J. M. Burkhartsmeyer, H. Zhang, X. Lu, K. S. Wong, W. C. H. Choy, *ACS Nano* **2018**, *12*, 10486; c) Z. K. Tan, R. S. Moghaddam, M. L. Lai, P. Docampo, R. Higler, F. Deschler, M. Price, A. Sadhanala, L. M. Pazos, D. Credgington, F. Hanusch, T. Bein, H. J. Snaith, R. H. Friend, *Nat. Nanotechnol.* **2014**, *9*, 687.
- [5] H. L. Zhu, Z. Liang, Z. Huo, W. K. Ng, J. Mao, K. S. Wong, W.-J. Yin, W. C. H. Choy, *Adv. Funct. Mater.* **2018**, *28*, 1706068.
- [6] a) B. Fan, D. Zhang, M. Li, W. Zhong, Z. Zeng, L. Ying, F. Huang, Y. Cao, *Sci. China: Chem.* **2019**, *62*, 1; b) Q. An, X. Ma, J. Gao, F. Zhang, *Sci. Bull.* **2019**, *64*, 504.
- [7] Best research-sell efficiencies chart from the National Renewable Energy Laboratory (NREL), <https://www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies-190416.pdf> (accessed: April 2019).
- [8] a) H. L. Zhu, W. C. H. Choy, *Sol. RRL* **2018**, *2*, 1800146; b) L. Dou, Y. M. Yang, J. You, Z. Hong, W.-H. Chang, G. Li, Y. Yang, *Nat. Commun.* **2014**, *5*, 5404; c) V. Adinolfi, O. Ouellette, M. I. Saidaminov, G. Walters, A. L. Abdelhady, O. M. Bakr, E. H. Sargent, *Adv. Mater.* **2016**, *28*, 7264; d) S. Ohisa, T. Takahashi, M. Igarashi, H. Fukuda, T. Hikichi, R. Komatsu, E. Ueki, Y. J. Pu, T. Chiba, J. Kido, *Adv. Funct. Mater.* **2019**, *29*, 1808022.
- [9] a) D. Zhang, W. C. H. Choy, F. Xie, W. E. I. Sha, X. Li, B. Ding, K. Zhang, F. Huang, Y. Cao, *Adv. Funct. Mater.* **2013**, *23*, 4255; b) L. Nian, W. Zhang, N. Zhu, L. Liu, Z. Xie, H. Wu, F. Wurthner, Y. Ma, *J. Am. Chem. Soc.* **2015**, *137*, 6995; c) F. Jiang, W. C. Choy, X. Li, D. Zhang, J. Cheng, *Adv. Mater.* **2015**, *27*, 2930.
- [10] a) Z. Huang, J. Cheng, X. Ren, J. Zhuang, V. A. L. Roy, J. M. Burkhartsmeyer, K. S. Wong, W. C. H. Choy, *Nano Energy* **2018**, *47*, 26; b) H. Zhang, J. Cheng, D. Li, F. Lin, J. Mao, C. Liang, A. K. Jen, M. Grätzel, W. C. Choy, *Adv. Mater.* **2017**, *29*, 1604695; c) Y. Zhao, H. Zhang, X. Ren, H. L. Zhu, Z. Huang, F. Ye, D. Ouyang, K. W. Cheah, A. K. Y. Jen, W. C. H. Choy, *ACS Energy Lett.* **2018**, *3*, 2891.
- [11] a) Z. Yin, J. Wei, Q. Zheng, *Adv. Sci.* **2016**, *3*, 1500362; b) D. Gao, M. G. Helander, Z.-B. Wang, D. P. Puzzo, M. T. Greiner, Z.-H. Lu, *Adv. Mater.* **2010**, *22*, 5404.
- [12] a) J. Meyer, S. Hamwi, M. Kröger, W. Kowalsky, T. Riedl, A. Kahn, *Adv. Mater.* **2012**, *24*, 5408; b) S. Chen, J. R. Manders, S.-W. Tsang, F. So, *J. Mater. Chem.* **2012**, *22*, 24202; c) X. Liang, S. Bai, X. Wang, X. Dai, F. Gao, B. Sun, Z. Ning, Z. Ye, Y. Jin, *Chem. Soc. Rev.* **2017**, *46*, 1730; d) Q. Jiang, X. Zhang, J. You, *Small* **2018**, *14*, 1801154; e) C. Manspeker, S. Venkatesan, A. Zakhidov, K. S. Martirosyan, *Curr. Opin. Chem. Eng.* **2017**, *15*, 1; f) R. Po, C. Carbonera, A. Bernardi, N. Camaioni, *Energy Environ. Sci.* **2011**, *4*, 285; g) H.-L. Yip, A. K. Y. Jen, *Energy Environ. Sci.* **2012**, *5*, 5994.
- [13] J. Gilot, I. Barbu, M. M. Wienk, R. A. J. Janssen, *Appl. Phys. Lett.* **2007**, *91*, 113520.
- [14] R. Fang, S. Wu, W. Chen, Z. Liu, S. Zhang, R. Chen, Y. Yue, L. Deng, Y. B. Cheng, L. Han, W. Chen, *ACS Nano* **2018**, *12*, 2403.
- [15] a) K. Wang, W. Zhao, J. Liu, J. Niu, Y. Liu, X. Ren, J. Feng, Z. Liu, J. Sun, D. Wang, S. F. Liu, *ACS Appl. Mater. Interfaces* **2017**, *9*, 33989; b) J. Wang, V. Ibarra, D. Barrera, L. Xu, Y. J. Lee, J. W. Hsu, *J. Phys. Chem. Lett.* **2015**, *6*, 1071.
- [16] a) J. Cheng, H. Zhang, Y. Zhao, J. Mao, C. Li, S. Zhang, K. S. Wong, J. Hou, W. C. H. Choy, *Adv. Funct. Mater.* **2018**, *28*, 1706403; b) J. Cheng, X. Ren, H. L. Zhu, J. Mao, C. Liang, J. Zhuang, V. A. L. Roy, W. C. H. Choy, *Nano Energy* **2017**, *34*, 76.
- [17] D. Yang, X. Zhou, R. Yang, Z. Yang, W. Yu, X. Wang, C. Li, S. Liu, R. P. H. Chang, *Energy Environ. Sci.* **2016**, *9*, 3071.
- [18] T. Niermann, D. Mai, J. Zenneker, M. Roever, J. Malindretos, A. Rizzi, M. Seibt, *Microsc. Microanal.* **2007**, *13*, 428.
- [19] J. Steinhauser, S. Fay, N. Oliveira, E. Vallat-Sauvain, C. Ballif, *Appl. Phys. Lett.* **2007**, *90*, 142107.
- [20] M. Thambidurai, J. Y. Kim, J. Song, Y. Ko, H.-J. Song, C.-M. Kang, N. Muthukumarasamy, D. Velauthapillai, C. Lee, *J. Mater. Chem. C* **2013**, *1*, 8161.
- [21] X. Ren, D. Yang, Z. Yang, J. Feng, X. Zhu, J. Niu, Y. Liu, W. Zhao, S. F. Liu, *ACS Appl. Mater. Interfaces* **2017**, *9*, 2421.
- [22] a) T. Dutta, P. Gupta, A. Gupta, J. Narayan, *J. Appl. Phys.* **2010**, *108*, 083715; b) M.-A. Park, I. J. Park, S. Park, J. Kim, W. Jo, H. J. Son, J. Y. Kim, *Curr. Appl. Phys.* **2018**, *18*, S55.

- [23] a) W. Chen, F.-Z. Liu, X.-Y. Feng, A. B. Djurišić, W. K. Chan, Z.-B. He, *Adv. Energy Mater.* **2017**, 7, 1700722; b) H.-S. Kim, J.-Y. Seo, H. Xie, M. Lira-Cantu, S. M. Zakeeruddin, M. Grätzel, A. Hagfeldt, *ACS Omega* **2017**, 2, 9074.
- [24] J. W. Jung, C. C. Chueh, A. K. Jen, *Adv. Mater.* **2015**, 27, 7874.
- [25] H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, H. Hosono, *Nature* **1997**, 389, 939.
- [26] a) S. Sheng, G. Fang, C. Li, S. Xu, X. Zhao, *Phys. Status Solidi A* **2006**, 203, 1891; b) G. Hautier, A. Miglio, G. Ceder, G. M. Rignanese, X. Gonze, *Nat. Commun.* **2013**, 4, 2292.
- [27] a) S. C. Chen, T. Y. Kuo, Y. C. Lin, H. C. Lin, *Thin Solid Films* **2011**, 519, 4944; b) W. Chen, Y. Wu, J. Fan, A. B. Djurišić, F. Liu, H. W. Tam, A. Ng, C. Surya, W. K. Chan, D. Wang, Z.-B. He, *Adv. Energy Mater.* **2018**, 8, 1703519; c) A. B. Huang, J. T. Zhu, J. Y. Zheng, Y. Yu, Y. Liu, S. W. Yang, S. H. Bao, L. Lei, P. Jin, *J. Mater. Chem. C* **2016**, 4, 10839; d) X. Wan, Y. Jiang, Z. Qiu, H. Zhang, X. Zhu, I. Sikandar, X. Liu, X. Chen, B. Cao, *ACS Appl. Energy Mater.* **2018**, 1, 3947; e) H. Xu, M. Zeng, J. Li, X. Tong, *RSC Adv.* **2015**, 5, 91493; f) K. Yao, F. Li, Q. He, X. Wang, Y. Jiang, H. Huang, A. K. Y. Jen, *Nano Energy* **2017**, 40, 155.
- [28] a) Z. Yin, Q. Zheng, S.-C. Chen, D. Cai, L. Zhou, J. Zhang, *Adv. Energy Mater.* **2014**, 4, 1301404; b) S. Wang, Y. Guo, D. Feng, L. Chen, Y. Fang, H. Shen, Z. Du, *J. Mater. Chem. C* **2017**, 5, 4724; c) A. Ohtomo, M. Kawasaki, T. Koida, K. Masubuchi, H. Koinuma, Y. Sakurai, Y. Yoshida, T. Yasuda, Y. Segawa, *Appl. Phys. Lett.* **1998**, 72, 2466; d) F. Wang, Z. Ye, D. Ma, L. Zhu, F. Zhuge, *J. Cryst. Growth* **2005**, 283, 373; e) L. Kukreja, S. Barik, P. Misra, *J. Cryst. Growth* **2004**, 268, 531.
- [29] A. Janotti, C. G. Van de Walle, *Phys. Rev. B* **2007**, 75, 121201(R).
- [30] X. Qiu, L. Li, J. Zheng, J. Liu, X. Sun, G. Li, *J. Phys. Chem. C* **2008**, 112, 12242.
- [31] A. M. Ganose, D. O. Scanlon, *J. Phys. Chem. C* **2016**, 4, 1467.
- [32] a) E. Burstein, *Phys. Rev.* **1954**, 93, 632; b) A. Walsh, J. L. F. Da Silva, S.-H. Wei, *Phys. Rev. B* **2008**, 78, 075211.
- [33] N. Mott, *Philos. Mag.* **1961**, 6, 287.
- [34] a) V.-A. Ha, D. Waroquiers, G.-M. Rignanese, G. Hautier, *Appl. Phys. Lett.* **2016**, 108, 201902; b) J. Robertson, S. J. Clark, *Phys. Rev. B* **2011**, 83, 075205.
- [35] K. H. Zhang, K. Xi, M. G. Blamire, R. G. Egdell, *J. Phys.: Condens. Matter* **2016**, 28, 383002.
- [36] E. Verwey, E. Heilmann, *J. Chem. Phys.* **1947**, 15, 174.
- [37] M. Pena, J. Fierro, *Chem. Rev.* **2001**, 101, 1981.
- [38] H. N. Abdelhamid, *Mater. Sci. Forum* **2015**, 832, 28.
- [39] A. Buljan, M. Llunell, E. Ruiz, P. Alemany, *Chem. Mater.* **2001**, 13, 338.
- [40] J. Tate, H. L. Ju, J. C. Moon, A. Zakutayev, A. P. Richard, J. Russell, D. H. McIntyre, *Phys. Rev. B* **2009**, 80, 165206.
- [41] J. Crépellière, P. L. Popa, N. Bahlawane, R. Leturcq, F. Werner, S. Siebentritt, D. Lenoble, *J. Mater. Chem. C* **2016**, 4, 4278.
- [42] a) D. O. Scanlon, G. W. Watson, *J. Mater. Chem.* **2011**, 21, 3655; b) J. Wang, Y.-J. Lee, J. W. P. Hsu, *J. Mater. Chem. C* **2016**, 4, 3607.
- [43] S. B. Singh, L. T. Yang, Y. F. Wang, Y. C. Shao, C. W. Chiang, J. W. Chiou, K. T. Lin, S. C. Chen, B. Y. Wang, C. H. Chuang, D. C. Ling, W. F. Pong, M. H. Tsai, H. M. Tsai, C. W. Pao, H. W. Shiu, C. H. Chen, H. J. Lin, J. F. Lee, H. Yamane, N. Kosugi, *Phys. Rev. B* **2012**, 86, 241103.
- [44] P. Lunca-Popa, J. Crépellière, P. Nukala, R. Leturcq, D. Lenoble, *Appl. Mater. Today* **2017**, 9, 184.
- [45] P. L. Qin, Q. He, C. Chen, X. L. Zheng, G. Yang, H. Tao, L. B. Xiong, L. Xiong, G. Li, G. J. Fang, *Sol. RRL* **2017**, 1, 1700058.
- [46] S. Jeong, S. Seo, H. Shin, *RSC Adv.* **2018**, 8, 27956.
- [47] N. Ray, V. Gupta, L. Sarma, P. Kush, J. Nag, S. Sapra, *ACS Omega* **2018**, 3, 509.
- [48] a) K. Yang, Y. Zhang, C. Meng, F. Cao, X. Chen, X. Fu, W. Dai, C. Yu, *Appl. Surf. Sci.* **2017**, 391, 635; b) Z. Shi, H. Lu, Q. Liu, K. Deng, L. Xu, R. Zou, J. Hu, Y. Bando, D. Golberg, L. Li, *Energy Technol.* **2014**, 2, 517; c) I. T. Papadas, A. Ioakeimidis, G. S. Armatas, S. A. Choulis, *Adv. Sci.* **2018**, 5, 1701029.
- [49] P. F. Ndione, A. Garcia, N. E. Wijdjarko, A. K. Sigdel, K. X. Steirer, D. C. Olson, P. A. Parilla, D. S. Ginley, N. R. Armstrong, R. E. Richards, E. L. Ratcliff, J. J. Berry, *Adv. Energy Mater.* **2013**, 3, 524.
- [50] J. Song, E. Zheng, X.-F. Wang, W. Tian, T. Miyasaka, *Sol. Energy Mater. Sol. Cells* **2016**, 144, 623.
- [51] H. Guo, H. Zhang, J. Yang, H. Chen, Y. Li, L. Wang, X. Niu, *ACS Appl. Energy Mater.* **2018**, 1, 6936.
- [52] Q. Jiang, L. Zhang, H. Wang, X. Yang, J. Meng, H. Liu, Z. Yin, J. Wu, X. Zhang, J. You, *Nat. Energy* **2017**, 2, 16177.
- [53] K. Wang, Y. Shi, B. Li, L. Zhao, W. Wang, X. Wang, X. Bai, S. Wang, C. Hao, T. Ma, *Adv. Mater.* **2016**, 28, 1891.
- [54] M.-H. Park, J.-H. Li, A. Kumar, G. Li, Y. Yang, *Adv. Funct. Mater.* **2009**, 19, 1241.
- [55] X. Li, F. Xie, S. Zhang, J. Hou, W. C. H. Choy, *Adv. Funct. Mater.* **2014**, 24, 7348.
- [56] M. G. Kim, M. G. Kanatzidis, A. Facchetti, T. J. Marks, *Nat. Mater.* **2011**, 10, 382.
- [57] T. Stubhan, I. Litzov, N. Li, M. Salinas, M. Steidl, G. Sauer, K. Forberich, G. J. Matt, M. Halik, C. J. Brabec, *J. Mater. Chem. A* **2013**, 1, 6004.
- [58] K. Wang, Y. Shi, L. Gao, R. Chi, K. Shi, B. Guo, L. Zhao, T. Ma, *Nano Energy* **2017**, 31, 424.
- [59] a) J. Ahmed, C. K. Blakely, J. Prakash, S. R. Bruno, M. Yu, Y. Wu, V. V. Poltavets, *J. Alloys Compd.* **2014**, 591, 275; b) A. P. Amrute, Z. Łodziana, C. Mondelli, F. Krumeich, J. Pérez-Ramírez, *Chem. Mater.* **2013**, 25, 4423; c) B. Das, A. Renaud, A. M. Volosin, L. Yu, N. Newman, D. K. Seo, *Inorg. Chem.* **2015**, 54, 1100.
- [60] B. J. Ingram, G. B. González, T. O. Mason, D. Y. Shahriari, A. Barnabe, D. Ko, K. R. Poeppelmeier, *Chem. Mater.* **2004**, 16, 5616.
- [61] a) D. Xiong, X. Zeng, W. Zhang, H. Wang, X. Zhao, W. Chen, Y. B. Cheng, *Inorg. Chem.* **2014**, 53, 4106; b) D. Xiong, Z. Xu, X. Zeng, W. Zhang, W. Chen, X. Xu, M. Wang, Y.-B. Cheng, *J. Mater. Chem.* **2012**, 22, 24760; c) D. Xiong, Y. Qi, X. Li, X. Liu, H. Tao, W. Chen, X. Zhao, *RSC Adv.* **2015**, 5, 49280; d) Z. Xu, D. Xiong, H. Wang, W. Zhang, X. Zeng, L. Ming, W. Chen, X. Xu, J. Cui, M. Wang, S. Powar, U. Bach, Y.-B. Cheng, *J. Mater. Chem. A* **2014**, 2, 2968.
- [62] C. Wang, Y. Tang, Y. Hu, L. Huang, J. Fu, J. Jin, W. Shi, L. Wang, W. Yang, *RSC Adv.* **2015**, 5, 52041.
- [63] a) B. Tan, E. Toman, Y. Li, Y. Wu, *J. Am. Chem. Soc.* **2007**, 129, 4162; b) A. Bera, A. D. Sheikh, M. A. Haque, R. Bose, E. Alarousu, O. F. Mohammed, T. Wu, *ACS Appl. Mater. Interfaces* **2015**, 7, 28404.
- [64] W. Chen, L. Xu, X. Feng, J. Jie, Z. He, *Adv. Mater.* **2017**, 29, 1603923.
- [65] D. Ouyang, J. Xiao, F. Ye, Z. Huang, H. Zhang, L. Zhu, J. Cheng, W. C. H. Choy, *Adv. Energy Mater.* **2018**, 8, 1702722.
- [66] S. S. Shin, W. S. Yang, J. H. Noh, J. H. Suk, N. J. Jeon, J. H. Park, J. S. Kim, W. M. Seong, S. I. Seok, *Nat. Commun.* **2015**, 6, 7410.
- [67] S. S. Shin, E. J. Yeom, W. S. Yang, S. Hur, M. G. Kim, J. Im, J. Seo, J. H. Noh, S. I. Seok, *Science* **2017**, 356, 167.
- [68] a) M. Hiramoto, H. Fujiwara, M. Yokoyama, *J. Appl. Phys.* **1992**, 72, 3781; b) J. Halls, C. Walsh, N. C. Greenham, E. Marseglia, R. H. Friend, S. Moratti, A. Holmes, *Nature* **1995**, 376, 498; c) G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science* **1995**, 270, 1789.
- [69] a) H. Frohne, S. E. Shaheen, C. J. Brabec, D. C. Müller, N. S. Sariciftci, K. Meerholz, *ChemPhysChem* **2002**, 3, 795; b) O. J. Sandberg, M. Nyman, R. Österbacka, *Phys. Rev. Appl.* **2014**, 1, 024003; c) M. D. Irwin, D. B. Buchholz, A. W. Hains, R. P. H. Chang, T. J. Marks, *Proc. Natl. Acad. Sci. USA* **2008**, 105, 2783.

- [70] a) M. Gaceur, S. B. Dkhil, D. Duché, F. Bencheikh, J.-J. Simon, L. Escoubas, M. Mansour, A. Guerrero, G. Garcia-Belmonte, X. Liu, M. Fahlman, W. Dachraoui, A. K. Diallo, C. Videlot-Ackermann, O. Margeat, J. Ackermann, *Adv. Funct. Mater.* **2016**, *26*, 243; b) L. Qiao, D. Wang, L. Zuo, Y. Ye, J. Qian, H. Chen, S. He, *Appl. Energy* **2011**, *88*, 848; c) H. Oh, J. Krantz, I. Litzov, T. Stubhan, L. Pinna, C. J. Brabec, *Sol. Energy Mater. Sol. Cells* **2011**, *95*, 2194.
- [71] L. K. Jagadamma, M. Al-Senani, A. El-Labban, I. Gereige, N. Ndjawa, O. Guy, J. C. Faria, T. Kim, K. Zhao, F. Cruciani, *Adv. Energy Mater.* **2015**, *5*, 1500204.
- [72] K.-S. Shin, K.-H. Lee, H. H. Lee, D. Choi, S.-W. Kim, *J. Phys. Chem. C* **2010**, *114*, 15782.
- [73] a) H. P. Kim, A. R. bin Mohd Yusoff, H. M. Kim, H. J. Lee, G. J. Seo, J. Jang, *Nanoscale Res. Lett.* **2014**, *9*, 150; b) J. You, C. C. Chen, L. Dou, S. Murase, H. S. Duan, S. A. Hawks, T. Xu, H. J. Son, L. Yu, G. Li, Y. Yang, *Adv. Mater.* **2012**, *24*, 5267; c) F. Zuo, S. T. Williams, P. W. Liang, C. C. Chueh, C. Y. Liao, A. K. Jen, *Adv. Mater.* **2014**, *26*, 6454.
- [74] C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez, J. C. Hummelen, *Adv. Funct. Mater.* **2001**, *11*, 374.
- [75] H.-H. Liao, L.-M. Chen, Z. Xu, G. Li, Y. Yang, *Appl. Phys. Lett.* **2008**, *92*, 156.
- [76] a) M. Gratzel, *Nat. Mater.* **2014**, *13*, 838; b) W. J. Yin, T. Shi, Y. Yan, *Adv. Mater.* **2014**, *26*, 4653; c) Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao, J. Huang, *Science* **2015**, *347*, 967.
- [77] a) M. Deepa, M. Salado, L. Calio, S. Kazim, S. M. Shivaprasad, S. Ahmad, *Phys. Chem. Chem. Phys.* **2017**, *19*, 4069; b) C.-H. Chiang, M. K. Nazeeruddin, M. Grätzel, C.-G. Wu, *Energy Environ. Sci.* **2017**, *10*, 808; c) H. Chen, F. Ye, W. Tang, J. He, M. Yin, Y. Wang, F. Xie, E. Bi, X. Yang, M. Gratzel, L. Han, *Nature* **2017**, *550*, 92; d) I. Levchuk, Y. Hou, M. Gruber, M. Brandl, P. Herre, X. Tang, F. Hoegl, M. Batentschuk, A. Osvet, R. Hock, W. Peukert, R. R. Tykwinski, C. J. Brabec, *Adv. Mater. Interfaces* **2016**, *3*, 1600593; e) W. Zhu, T. Yu, F. Li, C. Bao, H. Gao, Y. Yi, J. Yang, G. Fu, X. Zhou, Z. Zou, *Nanoscale* **2015**, *7*, 5427; f) Z. Xiao, Q. Dong, C. Bi, Y. Shao, Y. Yuan, J. Huang, *Adv. Mater.* **2014**, *26*, 6503; g) S. Heo, G. Seo, Y. H. Lee, D. Lee, M. Seol, J. Lee, J.-B. Park, K. Kim, D.-J. Yun, Y. Kim, J. Shin, T. K. Ahn, M. K. Nazeeruddin, *Energy Environ. Sci.* **2017**, *10*, 1128; h) W. Chen, Y. Wu, Y. Yue, J. Liu, W. Zhang, X. Yang, H. Chen, E. Bi, I. Ashraful, M. Grätzel, *Science* **2015**, *350*, 944.
- [78] D. Yang, R. Yang, K. Wang, C. Wu, X. Zhu, J. Feng, X. Ren, G. Fang, S. Priya, S. F. Liu, *Nat. Commun.* **2018**, *9*, 3239.
- [79] a) J. Ciro, D. Ramirez, M. A. Mejia Escobar, J. F. Montoya, S. Mesa, R. Betancur, F. Jaramillo, *ACS Appl. Mater. Interfaces* **2017**, *9*, 12348; b) X. Yin, P. Chen, M. Que, Y. Xing, W. Que, C. Niu, J. Shao, *ACS Nano* **2016**, *10*, 3630; c) H. Rao, S. Ye, W. Sun, W. Yan, Y. Li, H. Peng, Z. Liu, Z. Bian, Y. Li, C. Huang, *Nano Energy* **2016**, *27*, 51; d) Y. Bai, H. Chen, S. Xiao, Q. Xue, T. Zhang, Z. Zhu, Q. Li, C. Hu, Y. Yang, Z. Hu, F. Huang, K. S. Wong, H.-L. Yip, S. Yang, *Adv. Funct. Mater.* **2016**, *26*, 2950.
- [80] K. O. Brinkmann, J. Zhao, N. Pourdavoud, T. Becker, T. Hu, S. Olthof, K. Meerholz, L. Hoffmann, T. Gahlmann, R. Heiderhoff, M. F. Oszajca, N. A. Luechinger, D. Rogalla, Y. Chen, B. Cheng, T. Riedl, *Nat. Commun.* **2017**, *8*, 13938.
- [81] Z. Zhu, Y. Bai, X. Liu, C. C. Chueh, S. Yang, A. K. Jen, *Adv. Mater.* **2016**, *28*, 6478.
- [82] a) J. Feng, Z. Yang, D. Yang, X. Ren, X. Zhu, Z. Jin, W. Zi, Q. Wei, S. Liu, *Nano Energy* **2017**, *36*, 1; b) D. Yang, R. Yang, X. Ren, X. Zhu, Z. Yang, C. Li, S. F. Liu, *Adv. Mater.* **2016**, *28*, 5206; c) D. Yang, R. Yang, J. Zhang, Z. Yang, S. Liu, C. Li, *Energy Environ. Sci.* **2015**, *8*, 3208.
- [83] a) Y. Cheng, Q. D. Yang, J. Xiao, Q. Xue, H. W. Li, Z. Guan, H. L. Yip, S. W. Tsang, *ACS Appl. Mater. Interfaces* **2015**, *7*, 19986; b) H. Si, Q. Liao, Z. Zhang, Y. Li, X. Yang, G. Zhang, Z. Kang, Y. Zhang, *Nano Energy* **2016**, *22*, 223.
- [84] X. Yin, Z. Xu, Y. Guo, P. Xu, M. He, *ACS Appl. Mater. Interfaces* **2016**, *8*, 29580.
- [85] a) H. Zhang, H. Wang, W. Chen, A. K. Jen, *Adv. Mater.* **2017**, *29*, 1604984; b) S. Akin, Y. Liu, M. I. Dar, S. M. Zakeeruddin, M. Grätzel, S. Turan, S. Sonmezoglu, *J. Mater. Chem. A* **2018**, *6*, 20327.
- [86] H. Zhang, H. Wang, H. Zhu, C.-C. Chueh, W. Chen, S. Yang, A. K. Y. Jen, *Adv. Energy Mater.* **2018**, *8*, 1702762.
- [87] a) J.-H. Kim, C.-Y. Han, K.-H. Lee, K.-S. An, W. Song, J. Kim, M. S. Oh, Y. R. Do, H. Yang, *Chem. Mater.* **2015**, *27*, 197; b) H.-M. Kim, J.-H. Youn, G.-J. Seo, J. Jang, *J. Mater. Chem. C* **2013**, *1*, 1567; c) S. Cao, J. Zheng, J. Zhao, Z. Yang, C. Li, X. Guan, W. Yang, M. Shang, T. Wu, *ACS Appl. Mater. Interfaces* **2017**, *9*, 15605; d) F. Cao, H. Wang, P. Shen, X. Li, Y. Zheng, Y. Shang, J. Zhang, Z. Ning, X. Yang, *Adv. Funct. Mater.* **2017**, *27*, 1704278; e) H. C. Wang, H. Zhang, H. Y. Chen, H. C. Yeh, M. R. Tseng, R. J. Chung, S. Chen, R. S. Liu, *Small* **2017**, *13*, 1603962.
- [88] a) C.-H. Gao, X.-Z. Zhu, L. Zhang, D.-Y. Zhou, Z.-K. Wang, L.-S. Liao, *Appl. Phys. Lett.* **2013**, *102*, 153301; b) M. Helander, Z. Wang, J. Qiu, M. Greiner, D. Puzzo, Z. Liu, Z. Lu, *Science* **2011**, *332*, 944.
- [89] X. Liang, Y. Ren, S. Bai, N. Zhang, X. Dai, X. Wang, H. He, C. Jin, Z. Ye, Q. Chen, L. Chen, J. Wang, Y. Jin, *Chem. Mater.* **2014**, *26*, 5169.
- [90] Y.-H. Li, X. Lu, R. Wang, Y.-Y. Ma, S. Duhm, M.-K. Fung, *J. Mater. Chem. C* **2017**, *5*, 11751.
- [91] H. Wu, Y. Zhang, X. Zhang, M. Lu, C. Sun, T. Zhang, W. W. Yu, *Adv. Opt. Mater.* **2017**, *5*, 1700377.
- [92] a) J. Son, P. Moetakef, B. Jalan, O. Bierwagen, N. J. Wright, R. Engel-Herbert, S. Stemmer, *Nat. Mater.* **2010**, *9*, 482; b) S. Kobayashi, Y. Mizumukai, T. Ohnishi, N. Shibata, Y. Ikuhara, T. Yamamoto, *ACS Nano* **2015**, *9*, 10769.
- [93] F. Cao, W. Tian, M. Wang, L. Li, *ACS Photonics* **2018**, *5*, 3731.