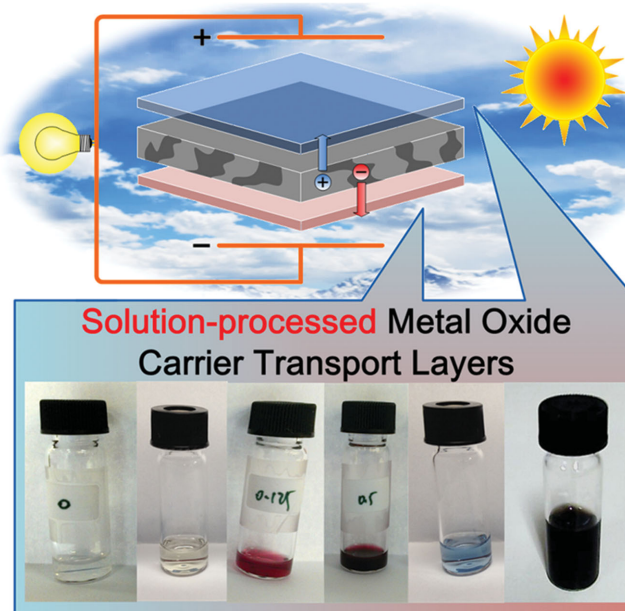


Solution-Processed Metal Oxides as Efficient Carrier Transport Layers for Organic Photovoltaics

Wallace C. H. Choy* and Di Zhang



From the Contents

1. Introduction 417
2. Solution-Processed Hole Transport Layers..... 417
3. Solution-Processed Electron Transport Layers..... 424
4. Conclusion 428

Carrier (electron and hole) transport layers (CTLs) are essential components for boosting the performance of various organic optoelectronic devices such as organic solar cells and organic light-emitting diodes. Considering the drawbacks of conventional CTLs (easily oxidized/unstable, demanding/costly fabrication, etc.), transition metal oxides with good carrier transport/extraction and superior stability have drawn extensive research interest as CTLs for next-generation devices. In recent years, many research efforts have been made toward the development of solution-based metal oxide CTLs with the focus on low- or even room-temperature processes, which can potentially be compatible with the deposition processes of organic materials and can significantly contribute to the low-cost and scale-up of organic devices. Here, the recent progress of different types of solution-processed metal oxide CTLs are systematically reviewed in the context of organic photovoltaics, from synthesis approaches to device performance. Different approaches for further enhancing the performance of solution-based metal oxide CTLs are also discussed, which may push the future development of this exciting field.

1. Introduction

Carrier (electron and hole) transport layers (CTLs) which are very thin layers (typically up to a few tens of nanometers) are important components in organic optoelectronics such as organic solar cells (OSCs) and organic light-emitting diodes (OLEDs). The existence of such layers can favor the efficient transport of carriers between the organic active layer and the electrode without inducing much optical absorption loss. For good conduction of carriers, the mobility of the electron and hole and the work function (WF) alignment of CTLs to the adjacent organic active layer and electrode are important. In addition, the blocking of counter carriers is essential for electron (ETL) and hole (HTL) transport layers to realize high-performance organic optoelectronic devices. Transition metal oxides are promising materials for CTLs because of their better environmental stability, high optical transparency, and easier synthesis.^[1] These transition metal oxides can possess a wide range of WFs (see **Figure 1**), spanning from an extremely low WF of 3.5 eV for defective ZrO_2 to an extremely high value of 7.0 eV for stoichiometric V_2O_5 .^[1b,2] As initially demonstrated for OLEDs by Tokito et al., metal oxides have the ability to decrease the binding energy of an organic molecule's highest occupied molecular orbital (HOMO) and the hole-injection barrier at the anode/organic interfaces.^[3] Subsequently, it was realized that some other metal oxides have the ability to increase the molecule's electron-orbital binding energy and decrease the barrier at cathode/organic interfaces.^[4] Consequently, metal oxides are now widely used in all types of organic electronic devices as both anode and cathode interface layers.

At present, many approaches are available for synthesizing different types of metal oxides. Conventionally, metal oxide films can be formed by sputtering and thermal evaporation. These fabrication methods are usually rather costly due to the rigorous vacuum or thermal conditions and a high energy consumption. For the low-cost, large-scale, and high-throughput production of optoelectronic devices, achieving

low-temperature solution processing of all functional layers is highly desired. Besides reducing the production costs, low-temperature solution processing of CTL metal oxides is also critical for realizing flexible organic devices, since flexible substrates are usually temperature sensitive, and cannot sustain high-temperature processes.^[6] Here, we review some of the widely used metal oxides as ETLs and HTLs in organic photovoltaic devices.

2. Solution-Processed Hole Transport Layers

In the last five years, solution-processed HTLs have been widely investigated. For solution-processed metal oxides, pre- or post-treatments such as annealing, air exposure, vacuum, UV-ozone, or O_2 -plasma have been used to modify the chemical and physical properties of the film for it to function as an efficient HTL. Depending on the synthesis approach, the HTL solutions can generally remain stable, with one report noting an ambient stability of several weeks for an oxide nanoparticle dispersion.^[7] Some of the promising solution-processed metal oxide HTLs, including molybdenum oxide (MoO_x), vanadium oxide (V_2O_x), tungsten oxide (WO_x), and nickel oxide (NiO_x), will be further described below. It should be noted that the stoichiometry of the metal oxides depends heavily on the synthesis approach. Therefore, in the following discussion, we will use the subscript "x" for the oxygen composition to refer to both the stoichiometric and nonstoichiometric metal oxides.

2.1. Solution-Processed Molybdenum Oxide (MoO_x)

Molybdenum oxide (MoO_x) is an n-type semiconductor metal oxide with a high work function of over 5.0 eV. Different from other types of p-type oxides, the strongly n-type electronic structure of MoO_x suggests that the hole injection process is generally fulfilled via electron extraction through its low-lying conduction band.^[8] Therefore, it should be noted that the term 'hole extraction layer' describes the function of MoO_x more accurately than 'hole transport layer'. For consistency in this review, we will use these terms interchangeably when discussing MoO_x . After MoO_x was introduced by an evaporation method to function as a hole transport layer in organic optoelectronic devices,^[9] the development of a solution processable MoO_x was demanded to simplify the device fabrication process. Both normal and inverted device architectures with solution-processed MoO_x as an HTL have been realized, yielding high efficiency.

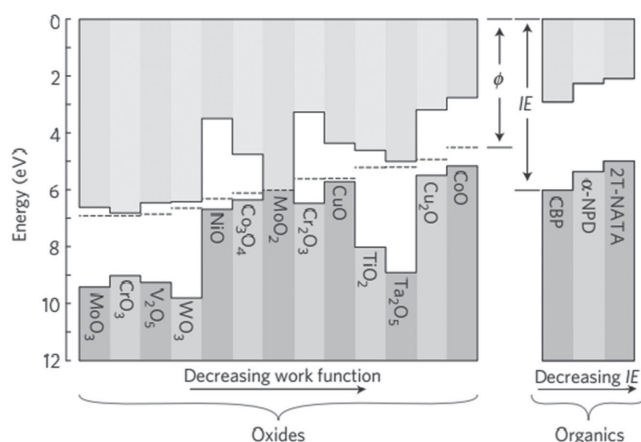


Figure 1. Energy levels of transition-metal oxides and organic semiconductors. Reproduced with permission.^[5] Copyright 2012, Macmillan Publishers Limited.

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Many preparation methods reported for solution-processed MoO_x were based on the sol-gel process.^[10] In these methods, the MoO_x precursor solution was prepared from molybdenum or molybdenum oxide powder in hydrogen peroxide (H_2O_2), which was then cast onto a glass substrate and converted to MoO_x film by hydrolysis during thermal treatment. A high power conversion efficiency (PCE) of 5.86% was achieved in OSCs with solution-processed MoO_x , which was comparable with the PCE obtained from OSCs using the conventional poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) HTL (5.89%).^[10c] Furthermore, OSCs made with solution-processed MoO_3 (s MoO_3) demonstrated superior stability compared to devices based on PEDOT:PSS HTL, which was similar to devices made from evaporated MoO_3 (e MoO_3), as shown in **Figure 2**.^[10b] These approaches require, however, a relatively high temperature (250–275 °C) for crystallizing the MoO_x film, limiting their use on flexible substrates.^[10b,10c]

Furthermore, different precursors have been explored for synthesizing solution-processed MoO_x , including $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ and $\text{Mo}(\text{CO})_3(\text{EtCN})_3$.^[11] Notably, bis(2,4-pentanedionate)molybdenum dioxide ($\text{MoO}_2(\text{acac})_2$) was another promising precursor investigated recently.^[12] It has been demonstrated that a solution-processed MoO_x can be prepared by either an anhydrous or an ambient synthetic route, with both routes achieving optimal films at a low annealing temperature of 70 °C (as shown in **Figure 3**).^[12a] However, the methanol precursor solution must be aged in ambient conditions for several days before use. A more simple and time-saving approach was reported by Li and co-workers using $\text{MoO}_2(\text{acac})_2$ precursor in isopropanol solution, with a baking time of only 10 min in air at 150 °C.^[12b]

Differently to this, solution-processed MoO_x films can be formed directly by spin coating a MoO_3 nanoparticle (NP) suspension with a block copolymer dispersing agent.^[13] O_2 -plasma treatment was adopted for the removal of the copolymer. Studies showed that the spin-coated MoO_3 films offered an identical hole-injection efficiency to evaporated MoO_3 , demonstrating the feasibility of their method.

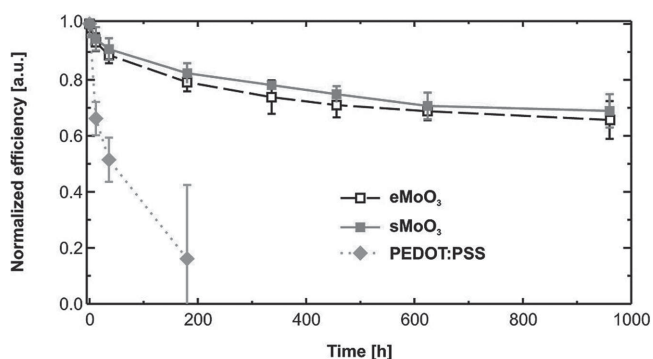


Figure 2. Normalized efficiency extracted from regular measurements of P3HT:PCBM-based devices stored in 'shelf' conditions. Reproduced with permission.^[10b] Copyright 2011, American Chemical Society.



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Recently, Choy and co-workers proposed a new scheme for the one-step synthesis of low-temperature solution-processed MoO_x from hydrogen molybdenum oxide bronze (H_xMoO_3).^[14] Through controlling the oxidation reaction rate between the metal powder and the H_2O_2 by ethanol (which acts as a reducing agent), metal oxide films with small amount of oxygen vacancies could be obtained at annealing temperature lower than 100 °C. While excessive oxygen vacancies are highly undesirable for organic devices, the authors found that an appropriate level of oxygen vacancies in the metal oxide HTLs introduced an n-type band configuration (as shown in **Figure 4**), which facilitated hole transport by electron extraction through the low-lying conduction band. By using a MoO_x film formed from H_xMoO_3 as the HTL, OSCs could reach a high PCE of over 7.7% compared to the PCE of 7.2% with the commonly used PEDOT:PSS HTL (as shown in **Figure 5**).^[14] Later, Vasilopoulou and co-workers showed that the stoichiometry of the obtained MoO_x film from the hydrogen molybdenum bronze is strongly related to the annealing process, which can be exploited for forming highly efficient HTLs with good hole transport.^[15]

In a subsequent work, based on the H_xMoO_3 method, a room-temperature and water-free solution-processed MoO_x HTL was demonstrated in inverted OSCs.^[16] The WF of the MoO_x film can be aligned favorably to the HOMO level of the absorber polymer by vacuum treatment (as shown in **Figure 6**). The authors also showed that the PCE of the OSCs could be further enhanced to $\approx 8\%$ by incorporating small silver nanoparticles (Ag NPs) into the metal oxide solution, thus forming a MoO_x -Ag NP composite HTL (as shown in **Figure 7**).

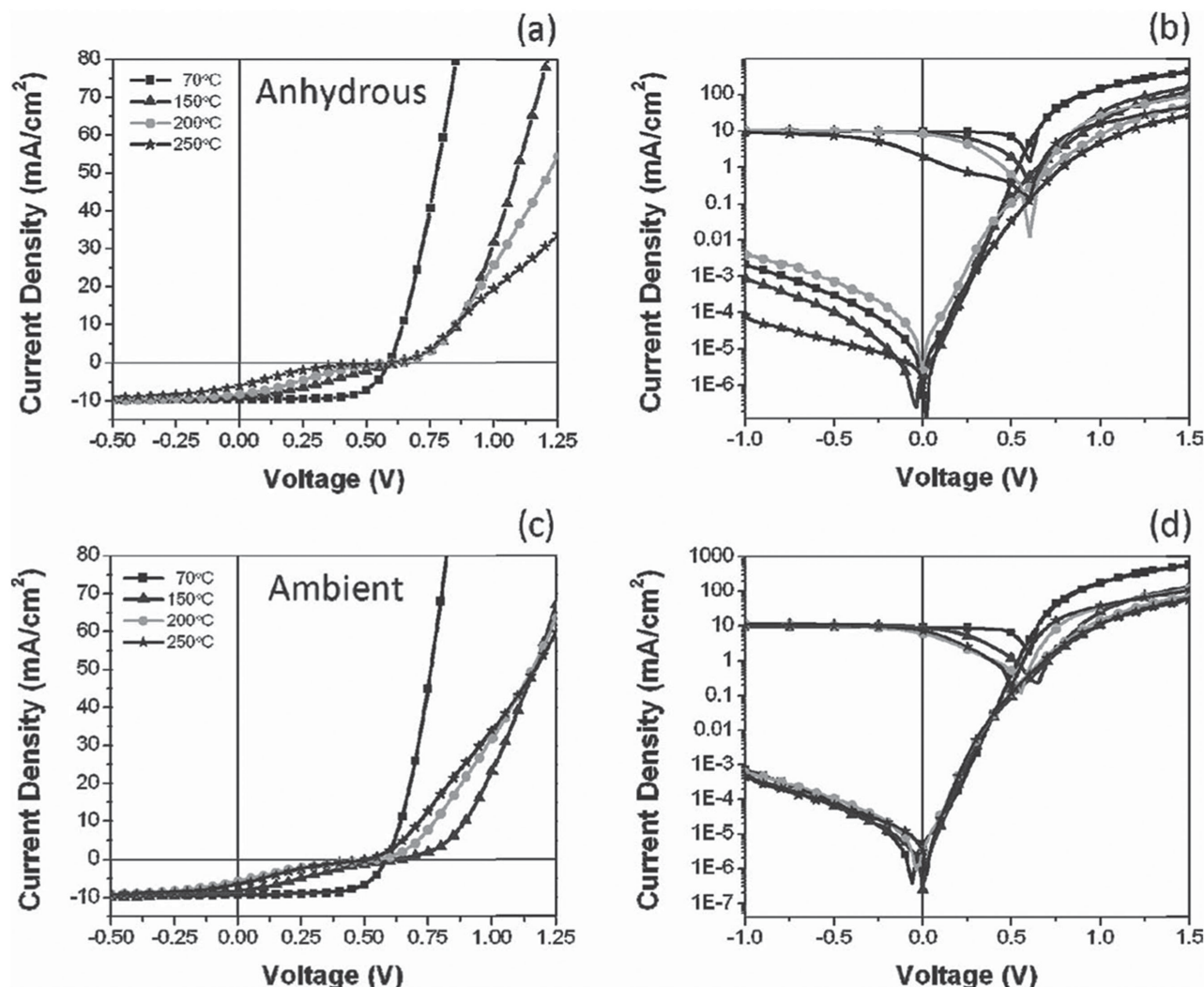


Figure 3. J - V characteristics of P3HT:PC₆₁BM solar cells fabricated with an anhydrous- (a,b) or ambient-based (c,d), 10 nm-thick, sMoO_x anode modifying layer annealed at different temperatures. Reproduced with permission.^[12a] Copyright 2012, John Wiley & Sons, Inc.

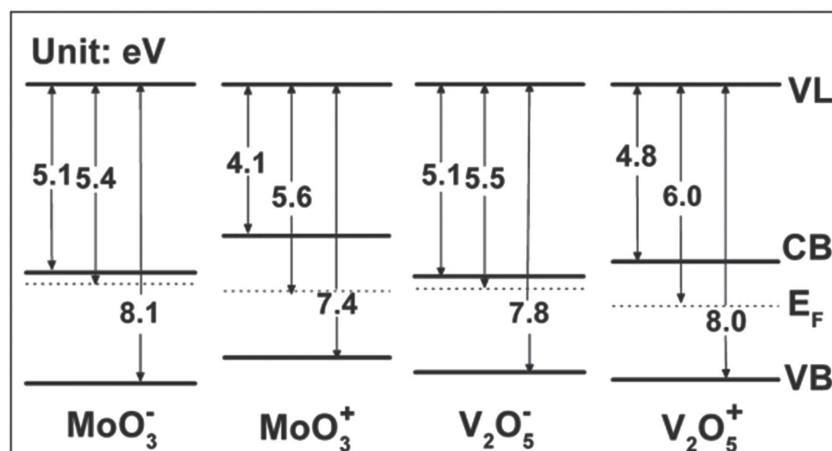


Figure 4. Band diagrams for molybdenum oxide with oxygen vacancies (MoO₃⁻), molybdenum oxide with excess oxygen (MoO₃⁺), vanadium oxide with oxygen vacancies (V₂O₅⁻), and vanadium oxide with excess oxygen (V₂O₅⁺), where VL is vacuum level, EF is the Fermi level, CB is the conduction band, VB is the valence band. Reproduced with permission.^[14] Copyright 2013, John Wiley & Sons, Inc.

2.2. Solution-Processed Vanadium Oxide (V₂O_x)

Conventionally, vanadium oxide (V₂O_x) is commonly prepared by thermal evaporation. The wide usage of V₂O_x owing to its high WF has promoted research into solution-processed V₂O_x in recent years. Solution-processed V₂O₅ HTLs have been demonstrated through directly dispersing V₂O₅ powder in an organic solvent using ultrasonic agitation or wet-milling.^[17] Besides electrically enhancing the hole extraction in OSCs, the V₂O₅ HTL also served as an optical spacer for improving light absorption, as shown in Figure 8.^[17a]

Through a sol-gel-based approach, Riedl and co-workers reported a solution-processed V₂O_x HTL spin-coated from an isopropanol solution of vanadium(v)

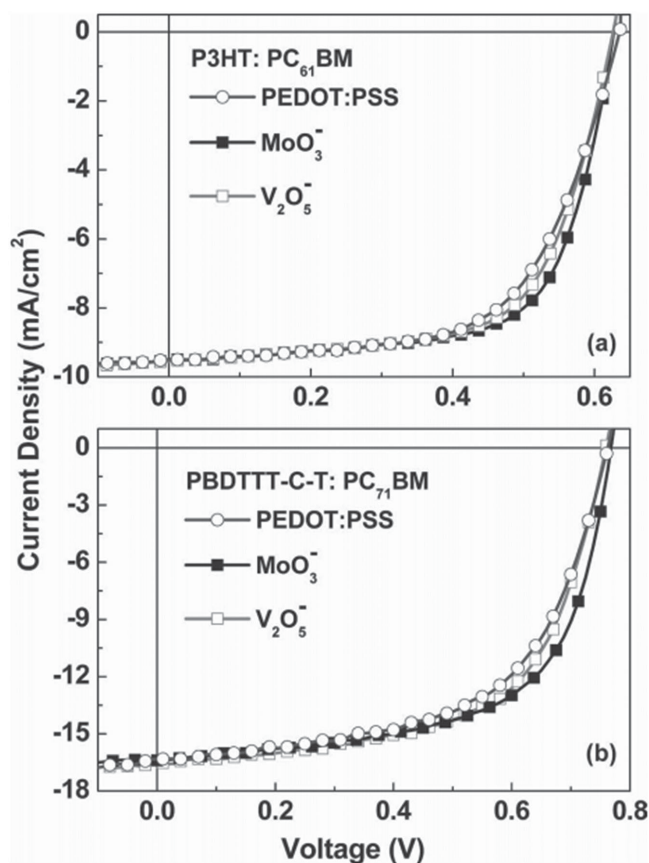


Figure 5. Current density–voltage (J – V) characteristics under AM1.5G solar spectrum with a light intensity of 100 mW cm^{-2} for organic solar cells. The device structures are: a) ITO/ MoO_3^- , V_2O_5^- , or PEDOT:PSS/P3HT:PC₆₁BM/Ca/Al; b) ITO/ MoO_3^- , V_2O_5^- , or PEDOT:PSS/PBDTTT-C-T:PC₇₁BM/Ca/Al. Reproduced with permission.^[14] Copyright 2013, John Wiley & Sons, Inc.

oxitriisopropoxide precursor, which was applied in both the normal and inverted-structure OSCs.^[18,19] Notably, the ambiently deposited V_2O_x HTL showed a very high WF of 5.6 eV without any post-deposition thermal or plasma treatment,

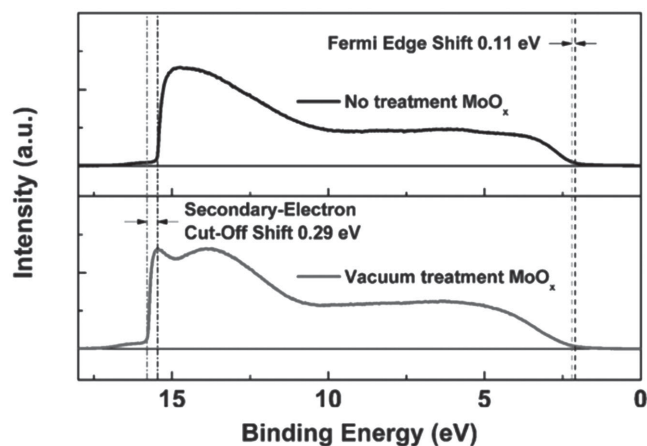


Figure 6. Ultraviolet photoelectron spectroscopy (UPS) spectra of no vacuum treatment MoO_x film and vacuum treatment MoO_x film. The shifts of the Fermi edge and the secondary-electron cut-off are 0.11 eV and 0.29 eV, respectively. Reproduced with permission.^[16] Copyright 2013, Royal Society of Chemistry.

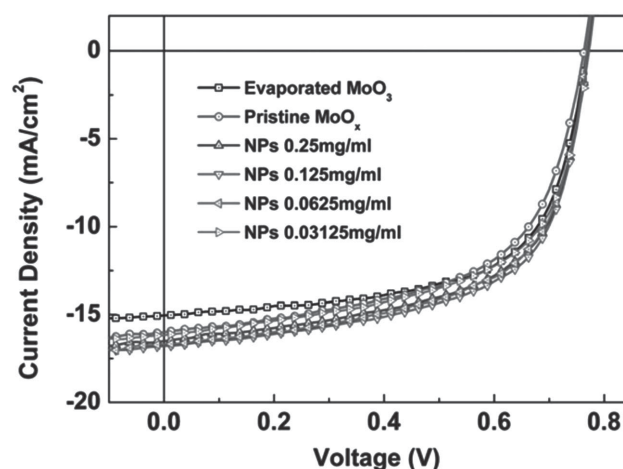


Figure 7. J – V characteristics of PBDTTT-C-T:PC₇₁BM OSCs with various weight ratios of Ag NPs in the MoO_x –Ag NP composite HTLs. Reproduced with permission.^[16] Copyright 2013, Royal Society of Chemistry.

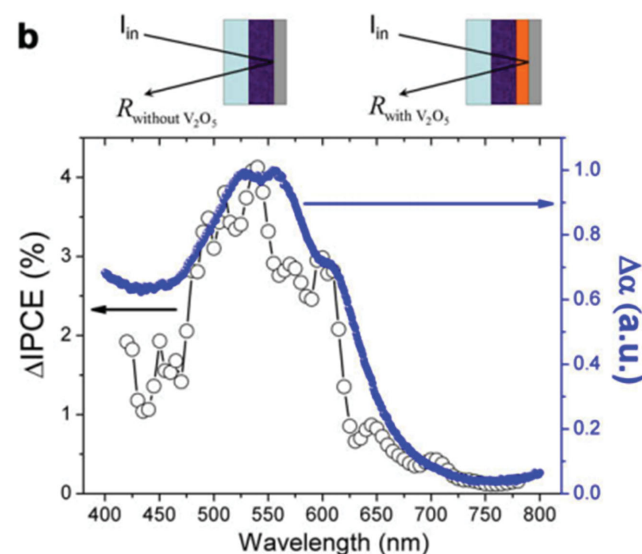
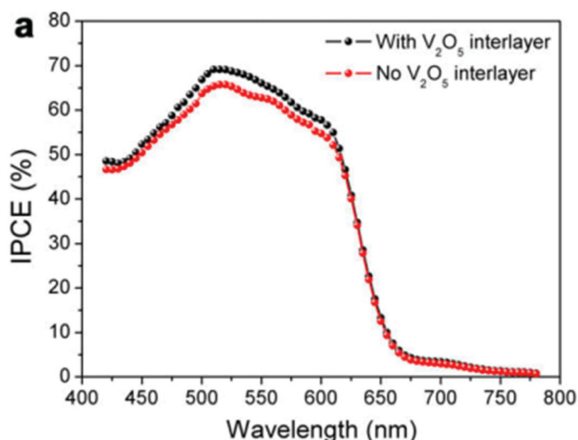


Figure 8. a) Incident photon to converted electron (IPCE) spectra for the devices with and without the optimum V_2O_5 interlayer. b) The change in absorption spectrum [$\Delta\alpha(\lambda)$] and the difference in IPCE spectrum [$\Delta\text{IPCE}(\lambda)$] resulting from the insertion of the optimum V_2O_5 interlayer. The inset is a schematic of the optical beam path in the both samples. Reproduced with permission.^[17a] Copyright 2009, Elsevier B.V.

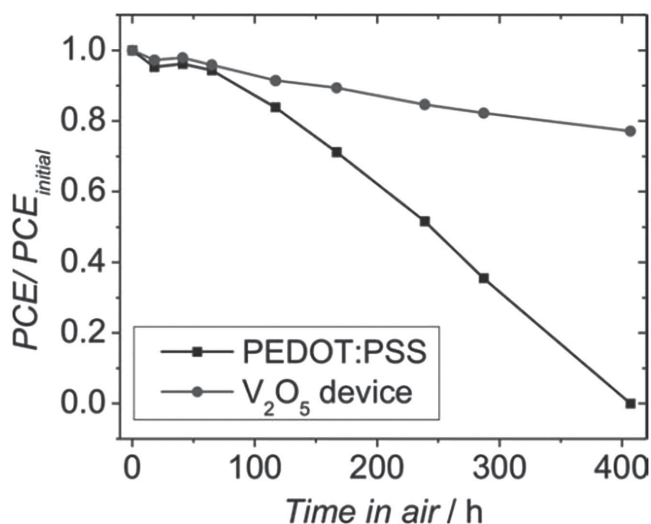


Figure 9. Stability study of the PCE of OSCs with a PEDOT:PSS and a sol-gel V_2O_5 hole extraction layer. The samples were kept in ambient conditions in air. Reproduced with permission.^[18] Copyright 2011, John Wiley & Sons, Inc.

which was comparable to evaporated V_2O_5 prepared in high vacuum. Moreover, OSCs made from solution-processed V_2O_5 were able to maintain 80% efficiency after 400 h, whereas devices using PEDOT:PSS completely failed, as shown in **Figure 9**.^[18] A different sol-gel-based approach was reported by Li and co-workers using a different precursor of vanadyl acetylacetonate ($VO(acac)_2$) in isopropyl alcohol solution, with a thermal annealing temperature of 150 °C.^[20]

Low-temperature (<100 °C), water-free, solution-processed V_2O_x HTLs based on hydrogen vanadium oxide bronze ($H_xV_2O_5$) have been demonstrated by Choy and co-workers in efficient OSCs, with a process similar to the preparation of MoO_x from H_xMoO_3 .^[14] Again, the n-doping offered by the controlled oxygen vacancies in the V_2O_x HTL contributed to energetically favorable alignment between the HTL and the absorber polymer for hole transport. Consequently, OSCs using the low-temperature, solution-processed V_2O_x HTL exhibited a high average PCE of 7.6%, which was better than a control device using the conventional PEDOT:PSS HTL (7.2%).^[14]

Based on the preparation technique, a versatile approach for modifying solution-processed V_2O_x and MoO_x into HTLs or ETLs using a water-free solvent at room temperature was demonstrated by the same group.^[21,22] Notably, the approach featured a large and continuous WF tuning range of over 1.1 eV by cesium (Cs) intercalation in the metal oxide solution, as shown in **Figure 10**.^[21] By tuning WF to the desired level, metal oxides can fulfill the role of either HTL or ETL in both normal and inverted-structure OSCs and OLEDs, achieving good performance.

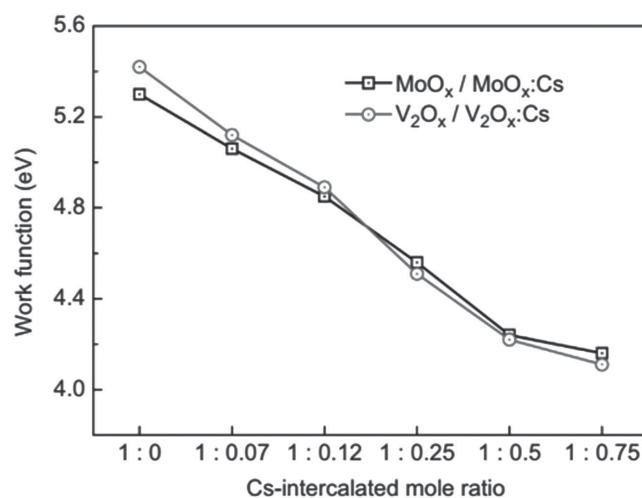


Figure 10. The continuous work function variation of metal oxides using the Cs intercalation method with different intercalated mole ratios. Reproduced with permission.^[21] Copyright 2015, Changchun Institute of Optics, Fine Mechanics and Physics.

2.3. Solution-Processed Tungsten Oxide (WO_x)

A solution-processed, mixed HTL of WO_3 and V_2O_5 was demonstrated by Huang et al. in an inverted device through the spin-coating of the colloidal mixed oxide particles dissolved in isopropanol solution, as schematically shown in **Figure 11**.^[23] Later, a solution-processed WO_3 HTL was reported by Brabec and co-workers, obtained from a WO_3 nanoparticle (NP) suspension in an alcohol-based solvent.^[24] The authors concluded that a low annealing temperature of 80 °C was sufficient for forming fully functional HTLs without any oxygen-plasma treatment. The solution-processed WO_3 HTL was able to be applied in both normal and inverted OSCs, showing a better fill factor (FF) and open circuit voltage (V_{OC}) than devices using PEDOT:PSS HTL.

Solution-processed WO_x films based on a sol-gel method have also been well studied, using precursors including $WOCIO_4$ in ethanol,^[26] tungsten ethoxide ($W(OC_2H_5)_6$),^[25] and tungsten(VI) isopropoxide in isopropanol.^[27] The

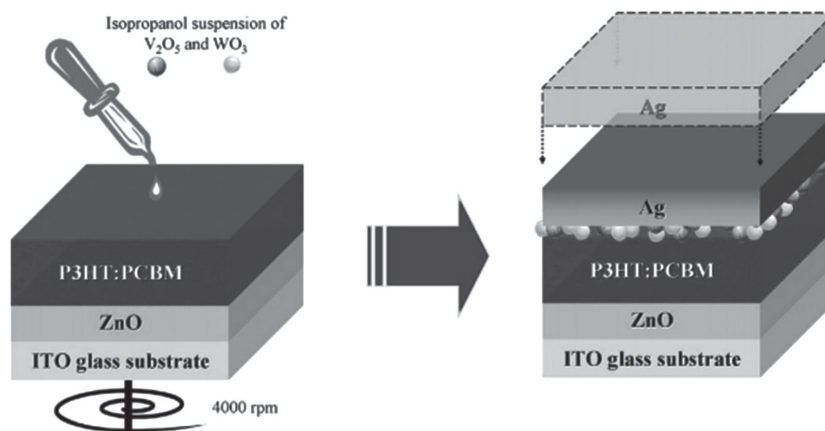


Figure 11. Schematic of the deposition of metal oxides. Reproduced with permission.^[23] Copyright 2010, IEEE.

average PCE of OSCs using solution-processed WO_3 (s WO_3) with a structure of ITO/s WO_3 /P3HT:IC₆₀BA/Ca/Al reached 6.14%, higher than that of the device using PEDOT:PSS HTL (6.06%).^[27] It should also be noted that the cell stability of OSCs using s WO_3 was better than for PEDOT:PSS devices under harsh (exposed to light in air) and mild (stored in a glove box in the dark) conditions, as shown in **Figure 12**.^[25] Recently, a low-temperature, solution-processed approach for preparing WO_x HTLs using peroxide and tungsten with an alcohol-based solvent was reported.^[28]

2.4. Solution-Processed Nickel Oxide (NiO_x)

Nickel oxide (NiO_x) has also been widely adopted in organic optoelectronics due to the fact that its valence band is well

aligned with the HOMO levels of many typical p-type polymers.^[30] Conventionally, NiO_x has been reported to be fabricated as an HTL in OSCs by methods including pulsed-laser deposition (PLD),^[31] thermal evaporation,^[32] and sputtering.^[33] The low-cost, large-area, and roll-to-roll production creates considerable incentive for developing solution-processed NiO_x films, which have been reported in recent years with high PCEs in OSCs.^[29,34] Many of the reported approaches focused on using sol-gel methods for converting precursors to NiO_x by thermal and/or oxygen-plasma post-treatment. For instance, Olson and co-workers^[29] and So and co-workers^[34] both reported solution-processed NiO_x HTLs made from thermally converted precursor films (both at 275 °C), with PCEs of NiO_x -incorporated OSCs achieving 6.7% and 7.8%, respectively. Both reported PCEs are noticeably higher than those of OSCs using conventional

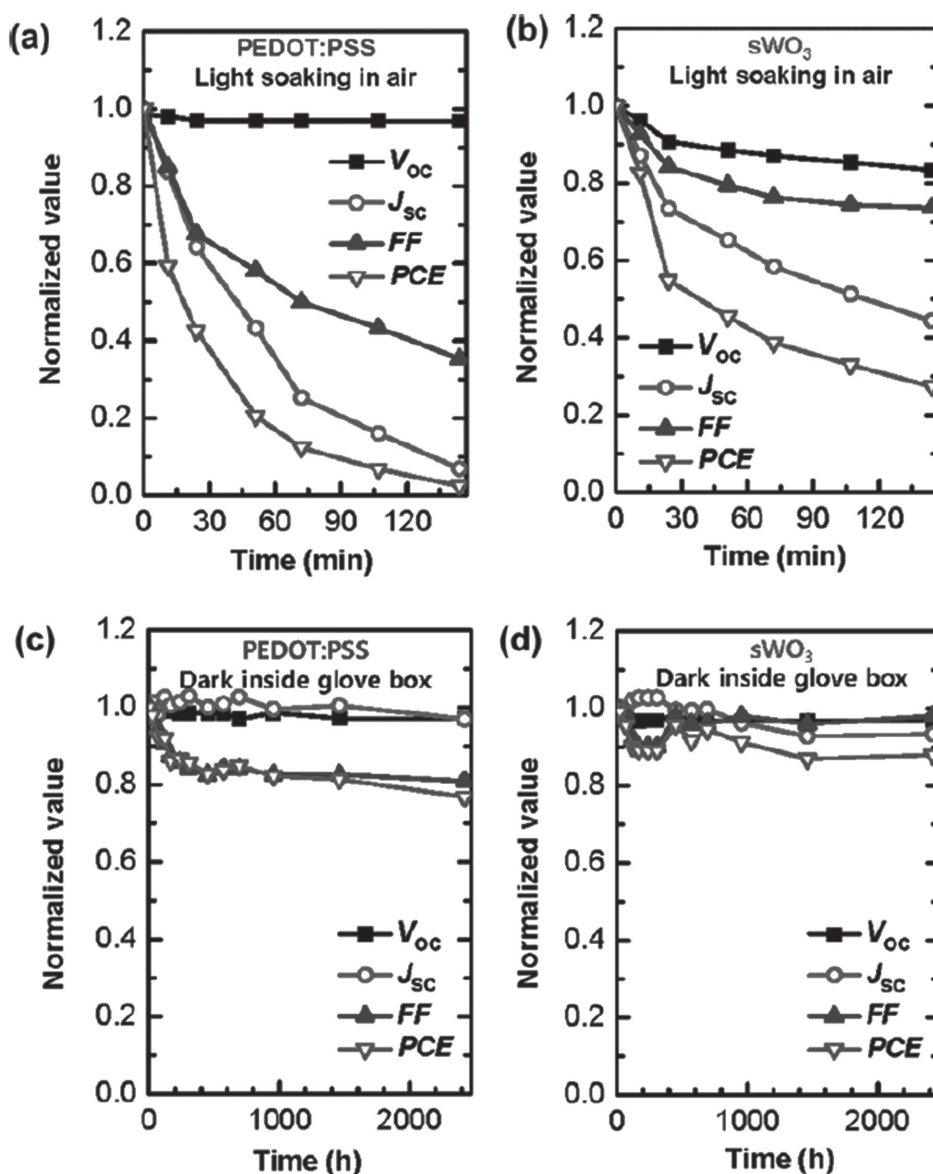


Figure 12. a,b) Cell stability of ITO/HTL/P3HT:PCBM/Al devices using PEDOT:PSS and s WO_3 layers, respectively, stored in air under continuous light soaking conditions. c,d) Cell stability of ITO/HTL/P3HT:PCBM/Al devices using PEDOT:PSS and s WO_3 layers, respectively, stored inside a glove box in the dark. Devices were not encapsulated. Reproduced with permission.^[25] Copyright 2012, Elsevier B.V.

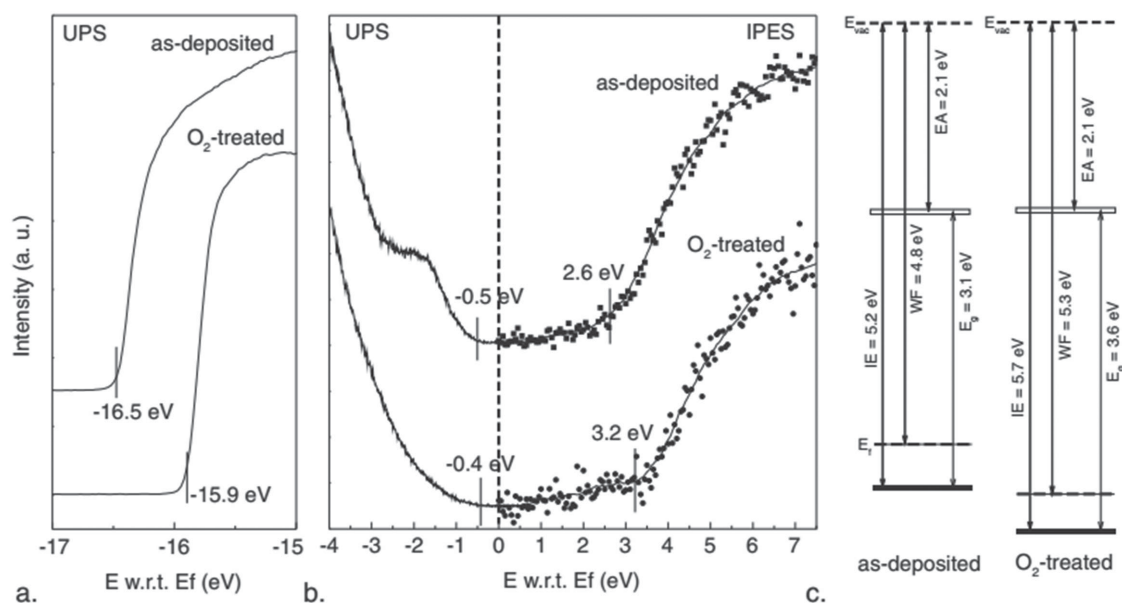


Figure 13. UPS and inverse photoemission spectroscopy (IPES) measurements of the density of states near the valence band edge and conduction band and the resulting band energies. a) UPS spectra (He I) of the photoemission cut-off showing an increase in ϕ after O_2 -plasma treatment of the NiO_x ; b) Combined UPS and IPES spectra of the NiO_x near the valence and conduction band edges; c) Energy level diagrams of NiO_x before and after O_2 -plasma treatment. Reproduced with permission.^[29] Copyright 2011, John Wiley & Sons, Inc.

PEDOT:PSS. As shown in **Figure 13**, in the former work, the increment of NiO_x work function (from 4.8 eV to 5.3 eV) by oxygen-plasma treatment for improving the contact properties of the anode is noted by the authors.^[29] In a later publication, using simultaneous thermal and UV ozone post-treatments, Ma and co-workers reported effective solution-processed NiO_x with a significantly reduced treatment temperature (150 °C).^[34c] OSCs based on polymers with different HOMO energy levels using the treated NiO_x HTL were demonstrated, which could achieve similar or enhanced performance as well as improved stability compared to PEDOT:PSS device (as shown in **Figure 14**).^[34c]

Recently, Choy and co-workers have demonstrated a post-treatment-free approach for making solution-processed, nonstoichiometric NiO_x films for OSCs and OLEDs.^[7] Different from the precursor method, these colloidal nonstoichiometric NiO_x nanoparticles (NPs) were prepared from a chemical precipitation method using $Ni(NO_3)_2 \cdot 6H_2O$ and NaOH and a calcination process, and the particles were subsequently dispersed in water. Once deposited from spin-coating, the NiO_x solution can readily form efficient NiO_x HTL films without using any post-treatment, while the film itself offers wide temperature applicability from room temperature to 150 °C (as shown in

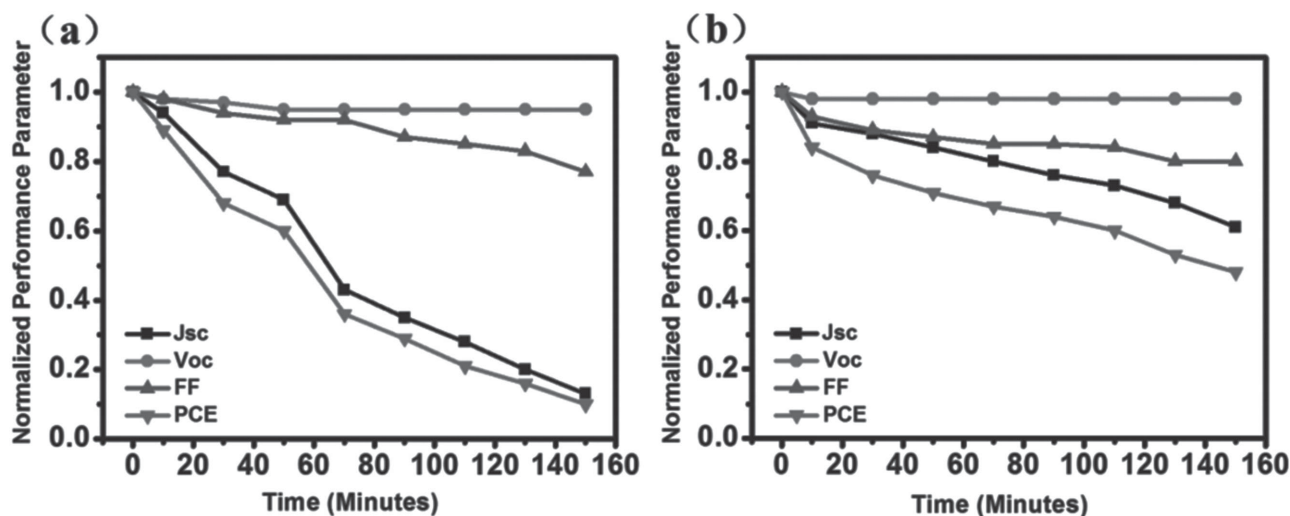


Figure 14. Normalized device characteristics as a function of air exposure time for a) PEDOT:PSS- and b) NiO_x -buffered devices. Reproduced with permission.^[34c] Copyright 2013, John Wiley & Sons, Inc.

Table 1. Device performance of different annealing temperatures of NiO_x-based OSCs with a conventional structure of ITO/NiO_x/P3HT:PC₆₁BM/Ca/Al. Reproduced with permission.^[7] Copyright 2015, John Wiley & Sons, Inc.

NiO _x Annealing Temperature	V _{OC} [V]	J _{SC} [mA cm ⁻²]	FF [%]	R _s [Ω cm ²]	PCE [%]
w/o	0.588 ± 0.001	9.72 ± 0.24	67.31 ± 0.76	2.10 ± 0.07	3.83 ± 0.10
50 °C	0.587 ± 0.003	9.68 ± 0.31	66.16 ± 0.80	2.24 ± 0.10	3.77 ± 0.15
100 °C	0.588 ± 0.002	9.67 ± 0.16	67.20 ± 0.62	2.13 ± 0.04	3.81 ± 0.07
150 °C	0.581 ± 0.004	9.82 ± 0.22	66.50 ± 0.65	2.16 ± 0.07	3.80 ± 0.09
200 °C	0.560 ± 0.004	9.01 ± 0.37	57.90 ± 1.35	4.17 ± 0.11	2.92 ± 0.24
300 °C	0.481 ± 0.008	8.96 ± 0.35	42.99 ± 2.58	7.36 ± 0.09	1.85 ± 0.32

Table 1).^[7] For annealing temperatures above 200 °C, the WF of NiO_x decreased significantly, preventing the NiO_x HTL from efficiently extracting holes to the electrode due to the large energy mismatch. An enhanced average PCE of 9.16% was achieved in OSCs using the NiO_x HTL compared to the conventional PEDOT:PSS, and a similar trend was also observed in OLED devices (as shown in **Figure 15** and **Figure 16**, respectively).^[7]

3. Solution-Processed Electron Transport Layers

Equally as important as the HTL, the ETL serves as an essential component in the multilayered organic optoelectronic device for efficiently extracting electrons from the cathode. Among n-type metal oxides, titanium oxide (TiO_x), zinc oxide (ZnO), and cesium carbonate (Cs₂CO₃) are popular choices

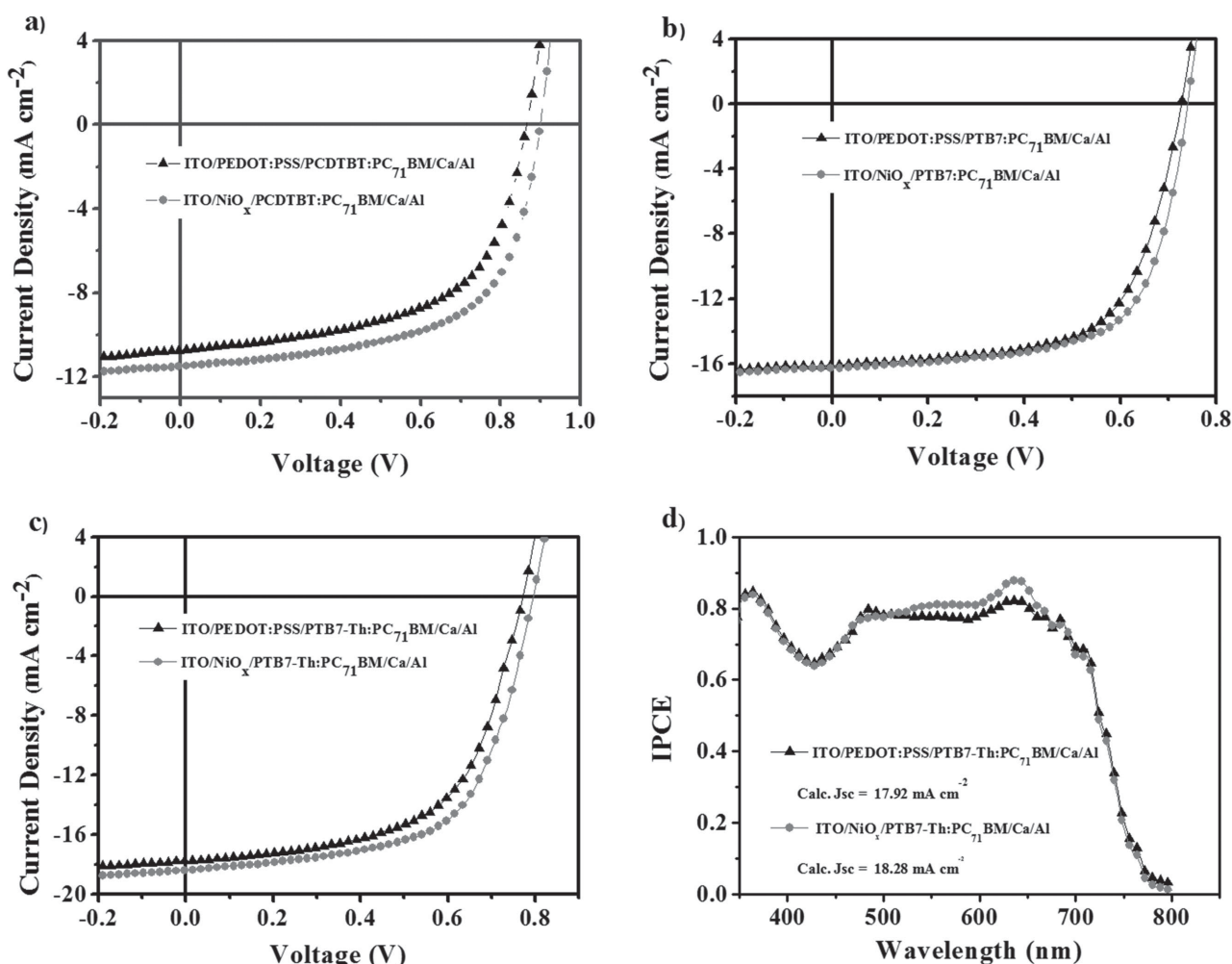


Figure 15. Representative *J*-*V* characteristics under AM1.5G solar spectrum for OSCs. The device structures are a) ITO/NiO_x or PEDOT:PSS / PCDTBT:PC₇₁BM / Ca / Al; b) ITO/NiO_x or PEDOT:PSS / PTB7:PC₇₁BM / Ca / Al; c) ITO/NiO_x or PEDOT:PSS / PTB7-Th:PC₇₁BM / Ca / Al; d) IPCE measurements for ITO/NiO_x or PEDOT:PSS / PTB7-Th:PC₇₁BM / Ca / Al. Reproduced with permission.^[7] Copyright 2015, John Wiley & Sons, Inc.

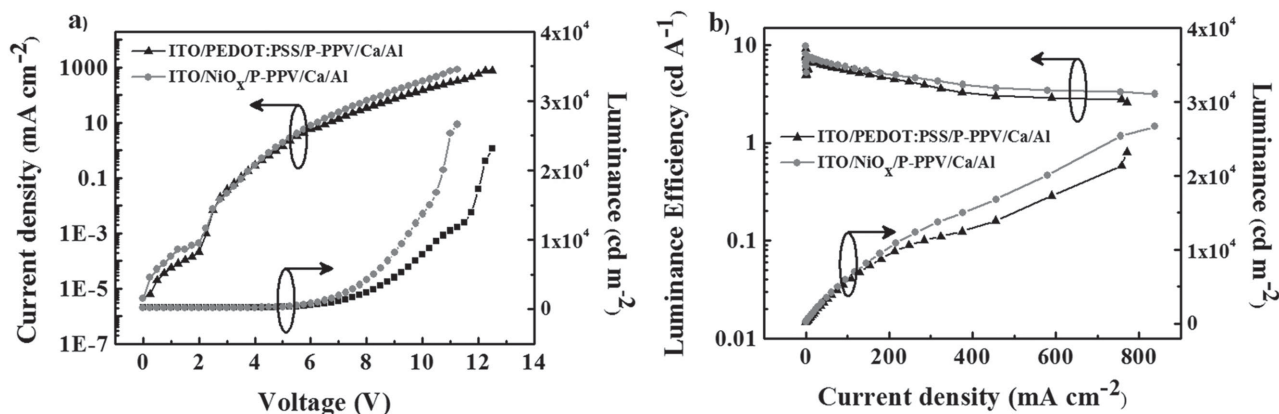


Figure 16. Representative a) J - V - L and b) LE - J - L characteristics of OLEDs (triangular markers for PEDOT:PSS device, circular markers for NiO_x device). Reproduced with permission.^[7] Copyright 2015, John Wiley & Sons, Inc.

for solution-processed ETLs for high-performance organic devices. Recent efforts for further improving the feasibility and performance of the metal oxide ETLs include developing low-cost, low-temperature, and large-area solution-processed approaches which are easily scalable to large-area applications, and enhancing the optical and electrical properties of the solution-processed ETLs (including some interesting optically induced electrical effects) by doping with nanomaterials, oxides with different WFs, small molecules, etc., which will be discussed below.

3.1. Solution-Processed Titanium Oxide (TiO_x)

Owing to its low WF, wide bandgap, good electron conduction, and optical properties, TiO_x has been widely adopted

in organic optoelectronics for electron-selective transport and extraction. Found in many inverted-structure OSCs, titanium oxide (TiO_x) ETLs are mainly categorized into amorphous TiO_x and anatase/rutile TiO_2 , with different material properties.

A sol-gel process with a TiO_x precursor solution is one of the commonly used approaches for preparing solution-based TiO_x ETLs in OSCs. The reaction based on titanium(IV) isopropoxide mainly consists of hydrolysis, condensation, and stabilization to obtain the precursor solution.^[35,36] It has been reported that such sol-gel-based approaches can achieve low-temperature^[36b] or even room-temperature processing without requiring any initial (UV-ozone or oxygen-plasma) or additional (thermal annealing or air exposure) treatments before or after the coating of the TiO_x ETL.^[35] As shown in **Figure 17**, inverted

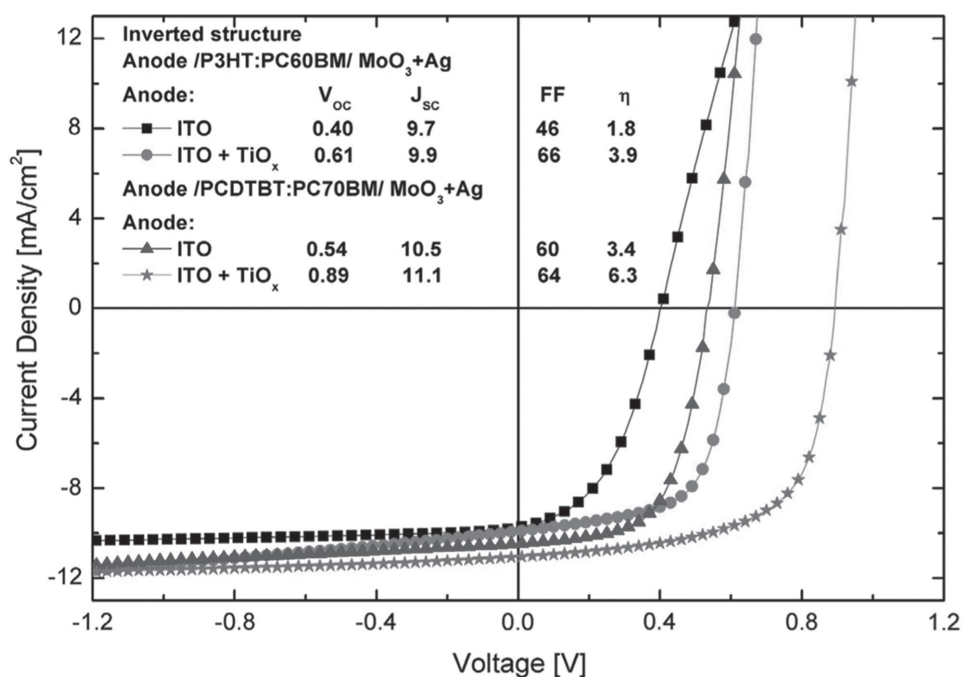


Figure 17. J - V measurements of inverted solar cells based on P3HT:PC60BM and PCDTBT:PC70BM active layers. The active layer was directly spin-cast onto the glass/ITO/ TiO_x or glass/ITO surfaces at room temperature. Reproduced with permission.^[35] Copyright 2013, Elsevier B.V.

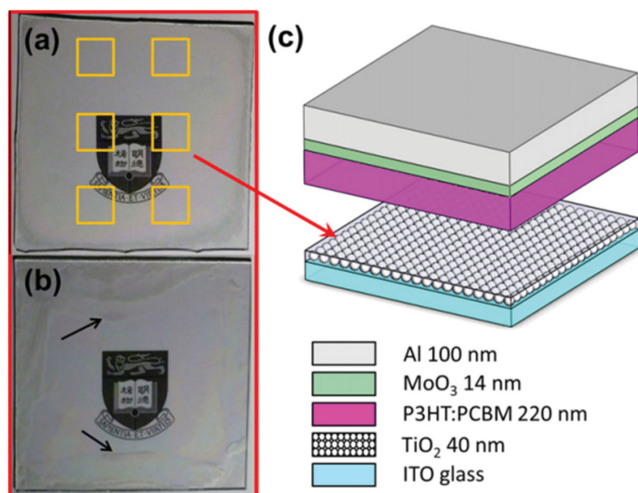


Figure 18. a) Large-area 4" × 4" self-assembled TiO₂ film. The marked regions are extracted and utilized in TiO₂ OSC devices. b) TiO₂ film of the same size fabricated without controlling the solvent evaporation: defects can be found on the film, as indicated by the black arrows. c) Schematic of inverted OSCs with TiO₂ as electron transport layer. Reproduced with permission.^[37] Copyright 2012, Elsevier B.V.

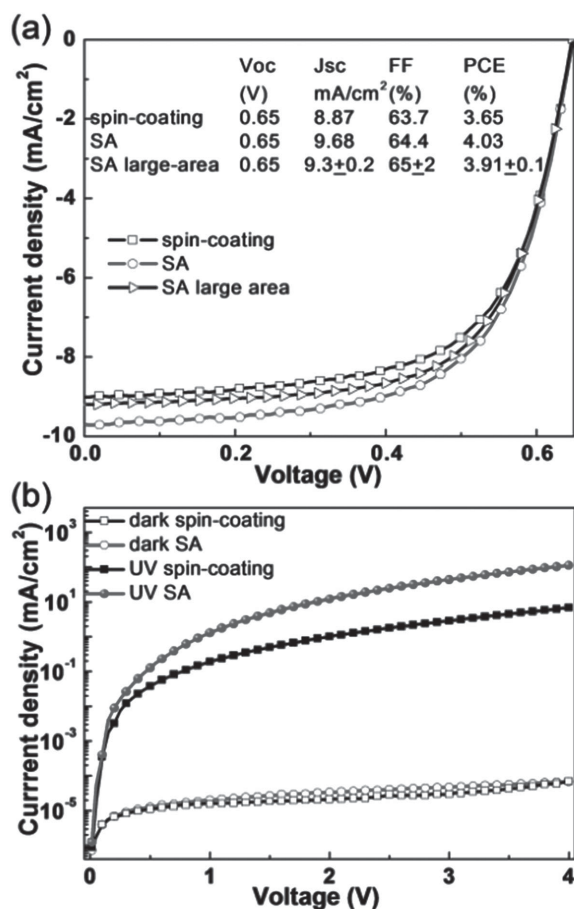


Figure 19. a) *J*–*V* characteristics of inverted OSCs with TiO₂ films as electron transport layers by spin-coating and self-assembly (SA) methods, under AM1.5G 100 mW cm^{−2} illumination. The device performances are summarized in the inset table (including average device performance of large-area SA TiO₂ films). (b) *J*–*V* characteristics of electron-only devices with spin-coated and self-assembled TiO₂ films. Reproduced with permission.^[37] Copyright 2012, Elsevier B.V.

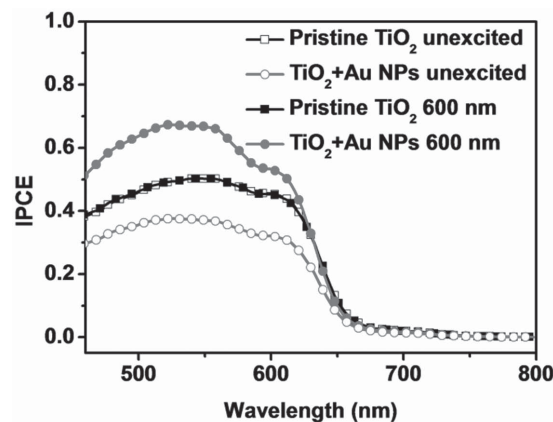


Figure 20. Incident photon-to-current conversion efficiency (IPCE) spectra of pristine TiO₂ and Au NP–TiO₂ composite (TiO₂+Au NPs) P3HT:PC₆₁BM OSCs before and after plasmonic illumination with 600 nm light and an applied voltage bias. All OSCs are measured from the as-fabricated state and the wavelength range of the IPCE measurement is from 450 nm to 800 nm, to avoid the UV region. Reproduced with permission.^[39] Copyright 2013, John Wiley & Sons, Inc.

OSCs employing the room-temperature solution-processed TiO_x ETL demonstrated a high PCE of 6.3% in a PCDTBT:PC₇₀BM blend system.^[35]

Alternatively, TiO_x ETL films may be formed directly from anatase TiO_x NPs dispersed in an alcohol-based solution obtained from TiCl₄ via a nonaqueous method.^[38] Based on this preparation method, Choy and co-workers demonstrated a facile solution-deposition approach for forming uniform TiO_x ETL film which can be easily scalable to large area applications.^[37] After a small amount of TiO_x NP solution was cast onto the substrate, a petri dish cover was used to slow the rate at which the solvent (ethanol) evaporated, allowing the ETL NPs to align and assemble instead of aggregating. Thus, large-area, smooth, and uniform films could be formed (self-assembled films as large as 4" × 4" were demonstrated), which showed a different morphology to films formed by drop-casting (**Figure 18**).^[37] Consequently, OSCs made from different locations of the large-area film (cut into smaller pieces) showed enhanced PCE compared to spin-coated ETL with small variation, as shown in **Figure 19**.^[37]

To further improve the optical/electrical properties of solution-processed ETLs for high-performance optoelectronic devices, doping of the ETL solutions with different types of materials has been studied, with considerable enhancement observed. Yang and co-workers reported the doping of cesium carbonate (CsCO₃) into a TiO_x precursor.^[41] Besides stabilizing the morphology of the ETL, the doped cesium TiO_x also led to a more desirable WF for charge extraction in OSCs. As a result, a very high PCE of 4.2% was reached in P3HT:PC₇₀BM-based OSCs using the Cs-doped TiO_x ETL.^[41] Furthermore, doping of n-type ETLs with metal nanomaterials in OSCs is another attractive way to further enhance the device performance. Light soaking is a common occurrence for wide-bandgap n-type oxides such as TiO_x and ZnO, which typically require high-energy UV exposure before the oxides can

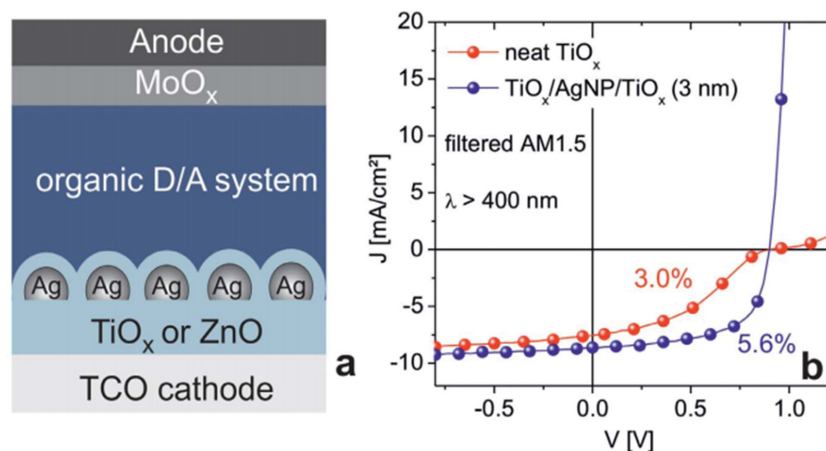


Figure 21. a) Layer sequence of inverted OSCs with a plasmonically sensitized cathode interlayer, and b) *J*/*V* characteristics of a corresponding PCDTBT/PC₇₀BM-based OSC under AM1.5 illumination with a UV blocking filter (λ > 400 nm). The characteristics of an OSC with a neat TiO_x interlayer (w/o Ag NP) are shown as a reference. Reproduced with permission.^[40] Copyright 2015, Macmillan Publishers Limited.

be activated and efficiently conduct electrons.^[42] Due to the concern that the organic active layer in OSCs may degrade from long UV exposure,^[43] it is therefore desirable to develop metal oxide ETLs which do not need UV activation. Recently, a novel solution-processed composite TiO_x ETL incorporating Au or Ag NPs was proposed for high-performance OSCs, reaching a PCE of 8.74%.^[39,44] Remarkably, by employing plasmonic excitation (at longer wavelengths of 560–600 nm), charge extraction in the TiO_x ETL could be activated and enhanced by a charge-transfer process from the NPs to the TiO_x, lowering the effective extraction barrier (as demonstrated by the incident photon-to-current conversion efficiency (IPCE) spectra of OSCs using the composite ETL after 600 nm illumination shown in **Figure 20**).^[39] The optically induced electrical

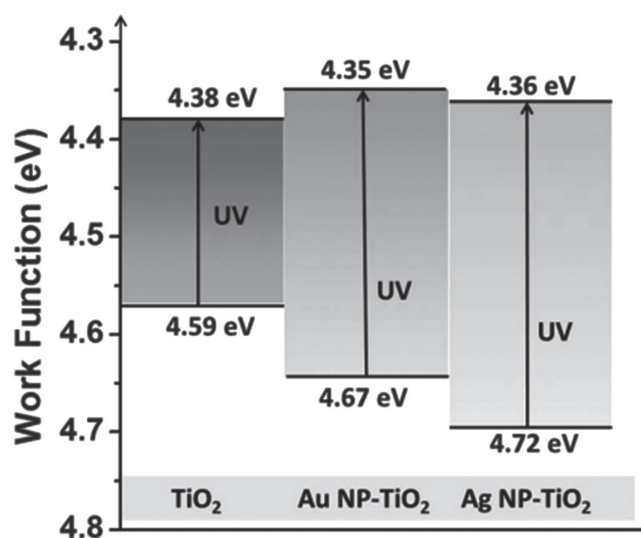


Figure 22. Diagram of WF changes of the TiO₂ film, Au NP-TiO₂ film, and Ag NP-TiO₂ film from dark conditions to UV illumination (for 15 min), as measured by a Kelvin probe. Reproduced with permission.^[44] Copyright 2013, Royal Society of Chemistry.

effect (termed the plasmonic-electrical effect) was later confirmed and further studied by Riedl and co-workers (as shown in **Figure 21**),^[40] although hot holes were considered to be transferred during plasmonic illumination. Besides these plasmonic-electrical effects, electrical enhancement under just UV light (e.g., under solar illumination) by the charge accumulation effect of the metal NPs embedded in the TiO_x ETL was also reported, which gave rise to lowered WFs for assisting charge extraction (**Figure 22**).^[44] The charge accumulation was evidenced by a blue-shift of the resonance frequency of the localized plasmonic resonance, which confirmed the transfer and accumulation of electrons from TiO_x into metal NPs to be the dominant process.^[44]

3.2. Solution-Processed Zinc Oxide (ZnO)

Zinc oxide (ZnO) is another widely used n-type ETL with a wide bandgap of 3.40 eV^[45] and a low WF of −4.1 eV.^[46] Similar to TiO_x, solution-processed ZnO ETLs can be prepared from sol-gel precursors^[46,47] or ZnO NP solutions.^[48]

Using zinc acetate dehydrate as precursor in 2-methoxyethanol and thermal annealing, Heeger and co-workers reported inverted OSCs with low-temperature solution processed ZnO ETL, yielding a high average efficiency of 6.08% at an annealing temperature of 200 °C (**Figure 23**).^[47c] Interestingly, the inverted OSCs with ZnO ETLs were air-stable, retaining ≈80% PCE after a month (**Figure 23**).^[47c] Similarly, the ZnO ETLs prepared from ZnO NP solutions reported by Jen and co-workers demonstrated excellent stability in inverted, flexible OSC devices in air as well, with superior lifetimes of >40 days for unencapsulated cells compared to normal-structure devices (**Figure 24**).^[48a] Besides increasing device stability, ZnO has also been shown to offer optical enhancement by fulfilling the role of an optical spacer for improving photocarrier generation.^[47d]

Through the combinational plasmonic effects of a metal grating and metal NPs (doped into ZnO ETLs), broadband absorption enhancements in the range of 350–800 nm due to multiple plasmonic effects in a single OSC device was observed.^[50] Recently, a novel design doping the light absorber perylene bisimide (PBI-H) into a sol-gel ZnO ETL to enhance its photoconductivity was reported.^[49] Simultaneous enhancements in short-circuit current density (*J*_{sc}), *V*_{oc}, and FF were observed in OSCs using doped ZnO ETLs compared to devices using neat ZnO, as shown in **Figure 25**.^[49] As a result, a very high PCE of 10.5% was achieved in PTB7-Th-based OSCs, which is one of the highest PCEs for single-junction cells. Interestingly, owing to the high conductivity of the doped ETL, the performance of OSCs remained stable over a wide range of ZnO thicknesses (from 30 to 60 nm), as shown in **Figure 26**.^[49]

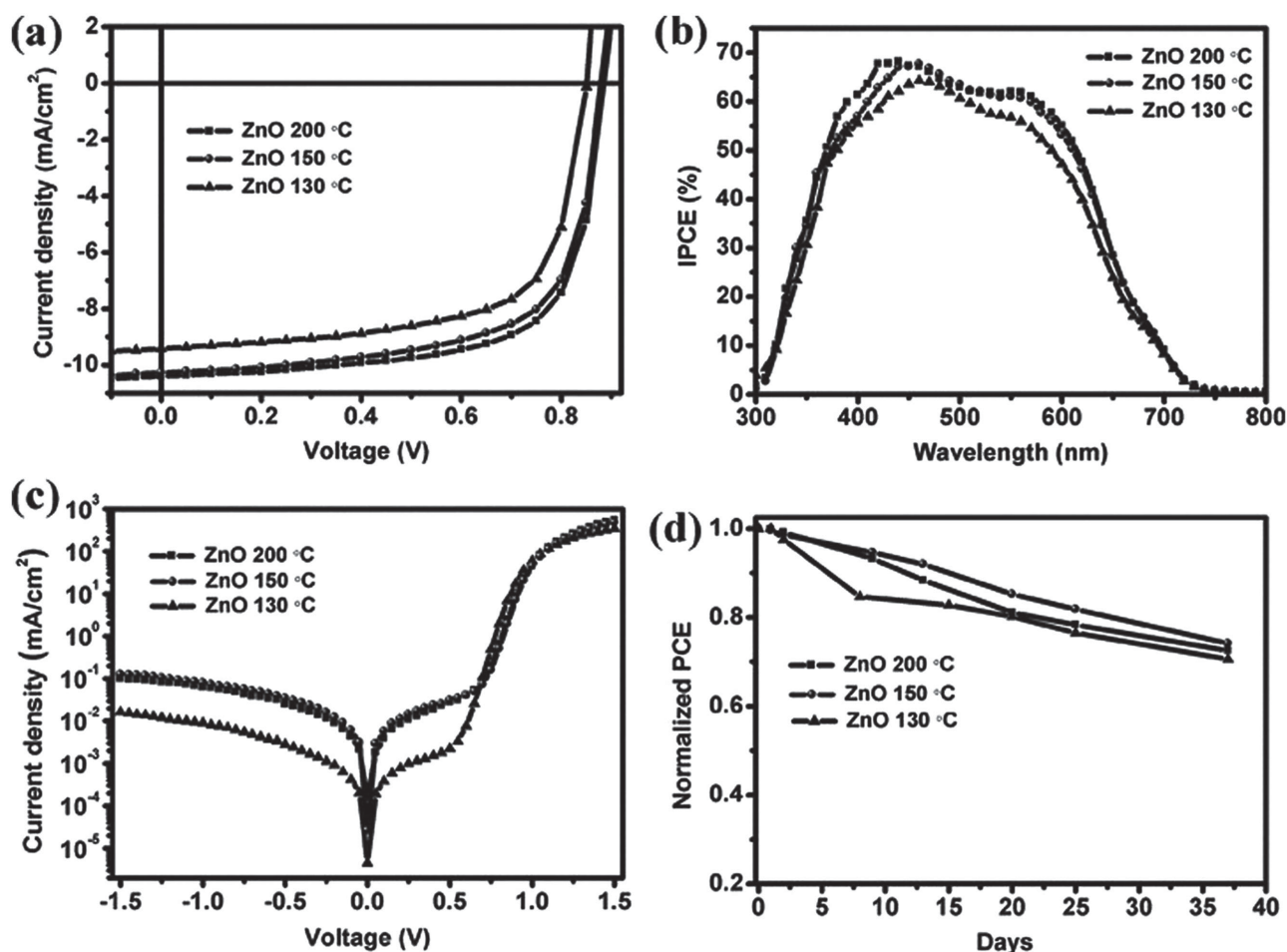


Figure 23. a) *J*-*V* characteristics of inverted PCDTBT:PC₇₀BM solar cells incorporating ZnO films with the indicated annealing temperatures. b) IPCE spectra of inverted PCDTBT:PC₇₀BM solar cells. c) Dark current of inverted PCDTBT:PC₇₀BM solar cells. d) Normalized PCEs for inverted PCDTBT:PC₇₀BM solar cells as a function of storage time in air under ambient conditions. Reproduced with permission.^[47c] Copyright 2011, John Wiley & Sons, Inc.

3.3. Solution-Processed Cesium Carbonate (Cs₂CO₃)

Cesium carbonate (Cs₂CO₃) is another promising candidate for solution-processed ETLs which has been extensively employed in OLEDs and OSCs, due to its good electron-injecting capability.^[51] Solution-processed Cs₂CO₃ ETLs can be prepared directly by spin-coating Cs₂CO₃ in aqueous,^[52] 2-methoxyethanol,^[51a] or 2-ethoxyethanol solutions.^[53]

Yang and co-workers reported highly efficient inverted OSCs using solution-processed Cs₂CO₃ dissolved in 2-ethoxyethanol.^[53c] Upon thermal annealing, Cs₂CO₃ decomposed into the doped oxide of Cs₂O with a low WF, which was responsible for the improvement in device performance. An inverted OSCs using a Cs₂CO₃ ETL with 150 °C annealing reached a high PCE of 4.2%, as shown in Figure 27.^[53c]

Recently, Liao and co-workers demonstrated an adjustable WF of an aqueous, solution-processed Cs₂CO₃ ETL by doping MoO₃ or Na₂WO₄.^[52] Continuous WF tuning with a large variation range was achieved, as shown in Figure 28. The lowering of the effective WF led to the improvement of *V*_{OC} in P3HT:ICBA OSCs, yielding a high PCE of 5.25% by Na₂WO₄-doped Cs₂CO₃. Accordingly, the authors concluded

that the decreased WF of the doped ETL was from the generated Mo–O–Cs and/or W–O–Cs composites.^[52]

4. Conclusion

With the promise of being low-cost, light-weight, mechanically flexible, and highly efficient, organic optoelectronic devices such as OSCs and OLEDs have spurred extensive interest aiming for practical applications within the near future. The development of organic optoelectronics has, however, reached a pivotal stage, with the PCE of single-junction OSCs surpassing the 10% threshold. Due to concerns over the stability (e.g., air or temperature sensitivity) and fabrication costs (e.g., high vacuum or thermal deposition) of conventional materials, solution-processed metal oxide CTLs (both ETLs and HTLs) are an important step towards achieving low-cost, stable, and flexible organic devices. Here, we have reviewed the recent progress in solution-processed metal oxide CTLs in organic optoelectronic devices. Significant advances in metal oxide CTLs have enabled low- or even room-temperature processing for many types of metal oxides, which is essential for improving the processability and scalability for mass and large-area production. Besides further improving

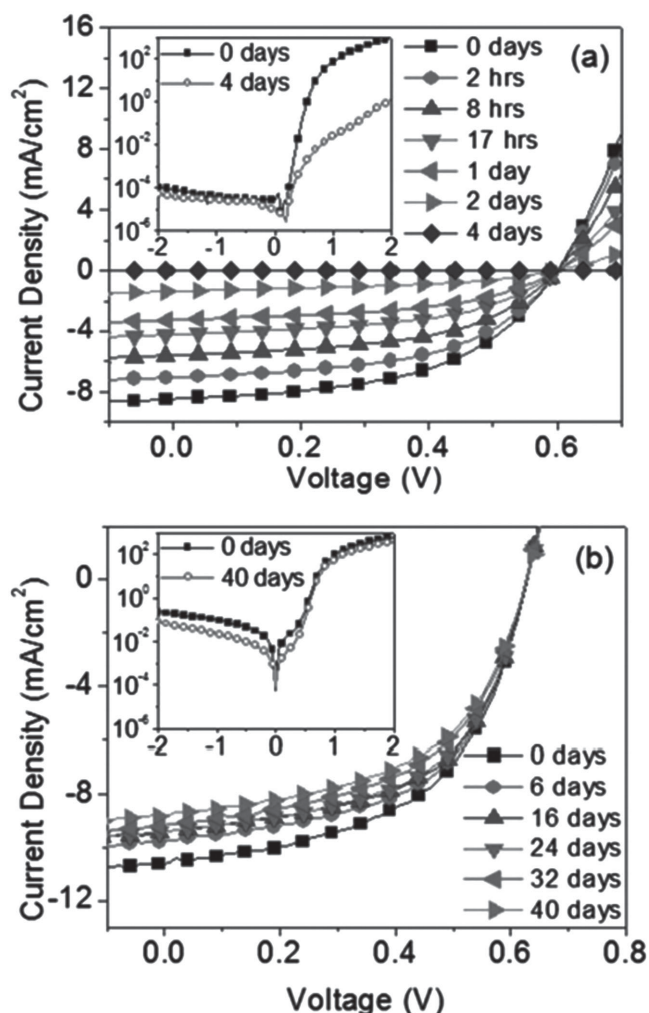


Figure 24. a) $J-V$ characteristics of unencapsulated, conventional P3HT:PCBM bulk-heterojunction solar cells over a period of four days in air under ambient conditions. b) $J-V$ characteristics of unencapsulated inverted P3HT:PCBM bulk-heterojunction solar cells (ZnO NPs on an ITO-coated plastic substrate) over a period of 40 days in air under ambient conditions. Inset: unencapsulated dark current device characteristics at 0 and 40 days in air under ambient conditions. Reproduced with permission.^[48a] Copyright 2008, AIP Publishing LLC.

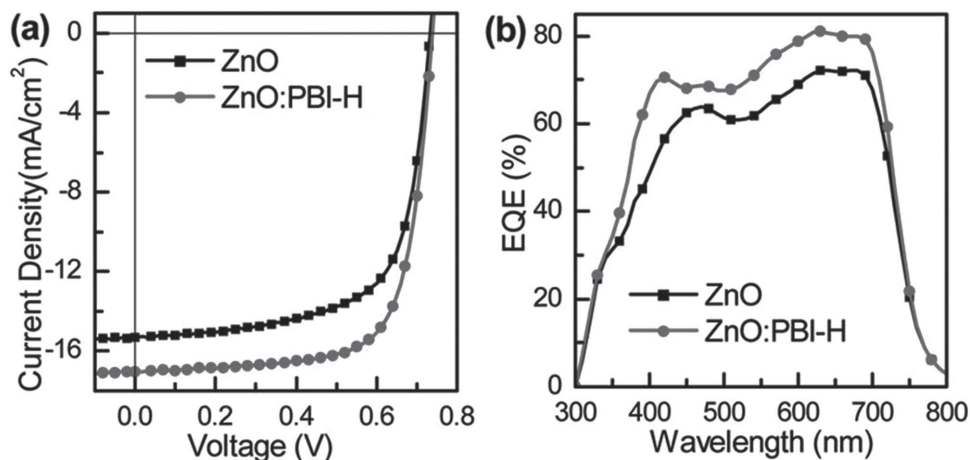


Figure 25. a) $J-V$ characteristics of the OSCs under 1000 W m^{-2} AM1.5G illumination. b) EQE curves. Device configurations are ITO/ZnO (30 nm) or ZnO:PBI-H (30 nm)/PTB7:PC₇₁BM (100 nm)/MoO₃ (10 nm)/Al (100 nm). Reproduced with permission.^[49] Copyright 2015, American Chemical Society.

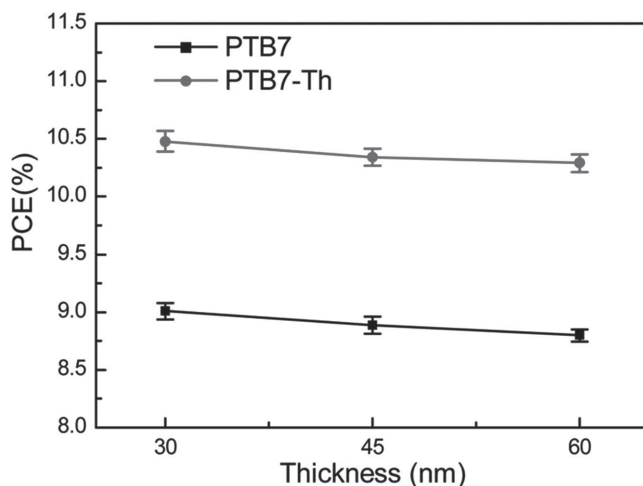


Figure 26. Effects of the thickness of the ZnO:PBI-H cathode interlayer on device performance. Device configuration: ITO/ZnO:PBI-H (30–60 nm)/PTB7 or PTB7-Th:PC₇₁BM (100 nm)/MoO₃ (10 nm)/Al (100 nm). Average values of seven cells with standard deviation. Reproduced with permission.^[49] Copyright 2015, American Chemical Society.

the feasibility and quality of the synthesized metal oxides, the doping of metal oxide CTLs has recently been demonstrated as an efficient tool for the enhancement of device performance. Furthermore, other low-cost OSC materials, such as non-fullerene material systems promising lowered costs from replacing the fullerene and higher output voltage,^[54] are attractive platforms for further incorporating solution-processed metal oxide CTLs for the future development of affordable and high-performance OSCs. Besides the popular choice of oxide materials reviewed here, other types of metal oxides may also be considered for solution processing for versatile energy alignment and diverse applications, such as chromium oxide,^[55] iridium oxide,^[56] and rhenium oxide; solution-processed rhenium oxide was recently reported.^[57] To overcome the current limitations to the optical, electrical, chemical, and mechanical properties of metal oxide CTLs, further research efforts are required in this field to improve the performance of the OSCs and OLEDs.

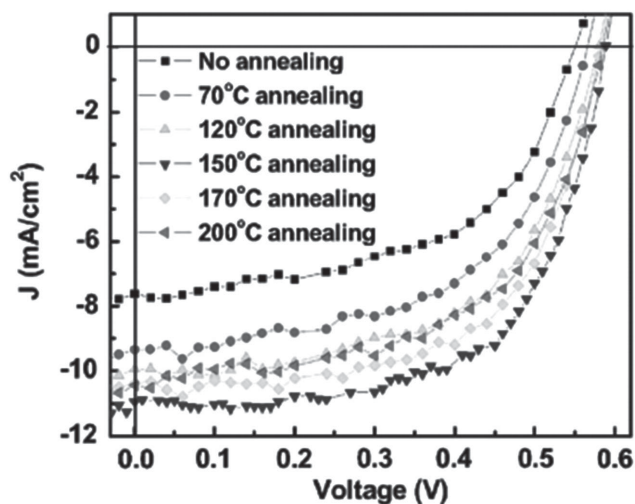


Figure 27. J - V characteristics of the inverted OSC devices under illumination with various annealing temperatures of the Cs_2CO_3 layer. Reproduced with permission.^[53d] Copyright 2008, AIP Publishing LLC.

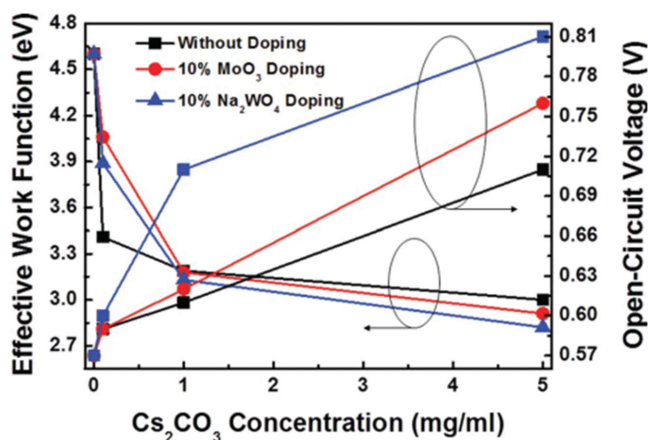


Figure 28. The effective WF and V_{OC} of different concentrations of Cs_2CO_3 with and without doping MoO_3 or Na_2WO_4 . Reproduced with permission.^[52] Copyright 2014, Royal Society of Chemistry.

Acknowledgements

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