Efficient organic solar cells with low-temperature *in situ* prepared Ga₂O₃ or In₂O₃ electron collection layers

Yiming Bai¹, Rongkang Shi¹, Yinglong Bai¹, Fuzhi Wang¹, Jun Wang³, Tasawar Hayat⁴, Ahmed Alsaedi⁴ and Zhan'ao Tan^{1,2*}

ABSTRACT Facile synthesis of an interfacial layer in organic solar cells (OSCs) is important for broadening material designs and upscaling photovoltaic conversion efficiency (PCE). Herein, a mild solution process of spin-coating In(acac)₃ and Ga(acac)₃ isopropanol precursors followed by low-temperature thermal treatment was developed to fabricate In₂O₃ and Ga₂O₃ cathode buffer layers (CBLs). The introduction of In₂O₃ or Ga₂O₃ CBLs endows PM6:Y6-based OSCs with outstanding performance and high PCEs of 16.17% and 16.01%, respectively. Comparison studies present that the In₂O₃ layer possesses a work function (WF) of 4.58 eV, which is more favorable for the formation of ohmic contact compared with the Ga₂O₃ layer with a WF of 5.06 eV and leads to a higher open circuit voltage for the former devices. Electrochemical impedance spectroscopy was performed to reveal how In₂O₃ and Ga₂O₃ affect the internal charge transfer and the origin of their performance difference. Although In₂O₃ possesses lower series resistance loss, Ga₂O₃ has a higher recombination resistance, which enhances the device fill factor and compensates for its series resistance loss to some extent. Comparative analysis of the photo-physics of In₂O₃ and Ga₂O₃ suggests that both are excellent CBLs for highly efficient OSCs.

Keywords: organic solar cells, cathode buffer layer, In₂O₃, Ga₂O₃, charge transfer

INTRODUCTION

Organic solar cells (OSCs) with merits of low-cost solution processability, high efficiency, and more than 10 years of predicted lifetime are currently considered promising technology for obtaining sustainable energy in the future [1–3]. Benefiting from the delicate electron-

donor/acceptor material design and diverse device engineering, the certified photovoltaic conversion efficiency (PCE) of the state-of-the-art single junction OSC devices has recently reached 17% [4], which motivates extensive interest in the academia and industry.

In general, OSCs are based on a bulk-heterojunction structure where the blended photoactive materials sandwich between a cathode buffer layer (CBL) and an anode buffer layer (ABL) to selectively facilitate charge extraction and minimize interfacial recombination loss, thereby boosting the device efficiency [5–7]. Consequently, synthesizing a novel appropriate interfacial layer is crucial for the development of efficient photovoltaic cells [8].

An ideal CBL in inverted OSCs (i-OSCs), which exhibit superior environmental stability to traditional OSCs, should possess facile solution-processible synthesis, suitable work function (WF), and favorable optical/electrical/morphological features to upscale device performance [9–11]. In the past decade, various n-type metal oxides, such as ZnO [12–14], TiO₂ [15–17], and In₂O₃ [18,19], have been explored as CBLs in OSCs targeting high charge extractions and desired active layer morphologies. Among these CBLs, In₂O₃ with high electron mobility has attracted wide attention in perovskite solar cells. Yoon *et al.* [20] used the sol-gel method to prepare In₂O₃ CBL and obtained PCE of 14.83%. However, the sol-gel method demands a high annealing temperature of 200°C to remove carbon impurities. In 2018, Huang *et al.* [21] synthesized an In₂O₃ CBL *via* combustion using indium nitrate hydrate as a precursor mixed with a small amount of additives and found that the resulting average PCE increases from 9.5% to 10.5%

¹ State Key Laboratory Of Alternate Electrical Power System With Renewable Energy Sources, North China Electric Power University, Beijing 102206, China

² Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

³ Institute of Information Photonics and Optical Communications, Beijing University of Posts and Telecommunications, Beijing 100876, China

⁴ NAAM Research Group, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

* Corresponding author (email: tanzhanao@buct.edu.cn)

in PBDTTTTEFT:PC₇₁BM OSCs and from 10.8% to 11.5% in PBDTTTTEFT:IEICO-4F OSCs. However, the fabrication of In₂O₃ CBL requires combustion reaction at 300°C and additional additives, inevitably increasing energy consumption and process complexity. Till date, few reports have focused on OSCs with In₂O₃ CBLs. Ga₂O₃ is a wide-bandgap semiconductor with ultrahigh transparency in the ultraviolet and visible wavelength (UV-vis) regions [22]. It is usually fabricated by atomic layer deposition [23], hydrothermal method [24], or chemical vapor deposition [25], and the fabrication or annealing temperature is usually higher than 400°C, which is unsuitable for OSCs. Furthermore, no literature regarded the application of Ga₂O₃ in OSCs. Hence, the present study aims to synthesize In₂O₃ and Ga₂O₃ at low temperature, tests the feasibility of Ga₂O₃ in OSCs, and provides an in-depth comparative analysis between In₂O₃ and Ga₂O₃ CBLs.

This study introduced a facile solution approach of spin-coating In(acac)₃ and Ga(acac)₃ isopropanol precursors at room temperature followed by thermal annealing in air at 100°C for 10 min to fabricate high-quality In₂O₃ and Ga₂O₃ CBLs. A comprehensive study was conducted to compare their optical/electrical/structural/energy level/surface free energy (SFE)/morphological properties and explore their applications in OSCs as CBLs. The results confirm that the OSCs based on a PM6:Y6 photoactive layer with In₂O₃ and Ga₂O₃ CBLs exhibit average PCEs of 16.17% and 16.01%, respectively. Electrochemical impedance spectroscopy (EIS) was performed to reveal the effect of In₂O₃ and Ga₂O₃ on the internal charge transfer and provided a quantitative interpretation regarding comparisons of some crucial parameters between them.

EXPERIMENTAL SECTION

Materials

In(acac)₃ (purity ≥ 99.0%) and Ga(acac)₃ (purity ≥ 99.99%) were purchased from Alfa Aesar (Shanghai, China). Indium tin oxide (ITO) glasses (12 Ω per square) were purchased from CSG Holding Co. Ltd. (Shenzhen, China). The electron donor of PM6 and the electron acceptor of Y6 were purchased from Solarmer Materials Inc. (Beijing, China), and the former possesses an average molecular weight (*M_n*) of about 26.8k and a polydispersity index of 1.62 as determined by gel permeation chromatography [26]. The processing solvents of chlorobenzene, chloronaphthalene, and isopropane were purchased from Alfa Aesar (Shanghai, China). All these

commercially available materials were used as received without further purification.

Preparation and characterization of In₂O₃ and Ga₂O₃ films

In₂O₃ and Ga₂O₃ films were synthesized by spin-coating with post low-temperature thermal treatment. First, In(acac)₃ and Ga(acac)₃ powders were dissolved in isopropanol at different concentrations and stirred for about 2 h at room temperature until they were completely dissolved. Then, In(acac)₃ and Ga(acac)₃ solutions were spun onto pre-cleaned substrates and annealed at 100°C for 10 min. Annealing was performed in air to ensure the chemical formation from metal-acetylacetonate chelates to their corresponding oxide. The results suggest that In(acac)₃ and Ga(acac)₃ at concentrations of 10 and 6 mg mL⁻¹ contribute to the formation of superior CBLs.

The chemical composition and electronic state of In(acac)₃ and Ga(acac)₃ powder (without annealing) and films (after annealing) were characterized using X-ray photoelectron spectroscopy (XPS) on an ESCA Lab220i-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation operated at a base pressure of 3 × 10⁻⁹ mbar. A D8 Advance (Bruker) diffractometer with an X-ray tube for Cu Kα radiation (λ = 0.1542 nm) was applied to investigate the crystal structures of the films. Ultraviolet photoelectric emission spectrum (UPS) was obtained by Kratos Axis Ultra DLD at a ultra-high vacuum of 3.0 × 10⁻⁸ Torr, and the ultraviolet photoelectron spectrometer was equipped with a monochrome ultraviolet light source (*hν* = 21.22 eV). The optical properties of the In₂O₃ and Ga₂O₃ films were evaluated on a Shimadzu 2450 UV-vis spectrophotometer. A VEECO DICP-II atomic force microscopy (AFM) system with a tapping mode was used to record the surface morphologies of the In₂O₃ and Ga₂O₃ films under ambient atmosphere at room temperature. Contact angle images were investigated via a JC2000D3 contact angle meter (Power-each), and thermogravimetric analysis was performed using a TG209F3 Nevio thermogravimetric analyzer under ambient conditions.

Device fabrication and characterization

The device structure was ITO/In₂O₃/Ga₂O₃/PM6:Y6/MoO₃/Ag. First, detergent, de-ionized water, acetone, and isopropanol in ultrasonic bath were successively used for cleaning the patterned ITO-coated substrates. Subsequently, the In₂O₃ or Ga₂O₃ layers with different thicknesses were spin-coated on the pre-cleaned ITO substrates in accordance with the abovementioned method. Then, PM6:Y6 (1:1.2 weight ratio, polymer

concentration of 16 mg mL^{-1}) chloroform:1-CN (99.5:0.5 volume ratio) solution was spin cast onto ITO/ In_2O_3 or ITO/ Ga_2O_3 in nitrogen environment at optimal 3000 rpm for 30 s and immediately baked at 110°C for 10 min. Finally, a vacuum evaporator was used to fabricate a MoO_3 (10 nm)/Ag (80 nm) anode layer at a pressure of $2 \times 10^{-4} \text{ Pa}$ [27]. The device area was about 4 mm^2 .

The current density–voltage (J – V) curves were measured using an AAA-grade solar simulator (SAN-EI ELECTRIC Co., Ltd., AM1.5G solar irradiation with a light intensity of 100 mW cm^{-2}) equipped with a Keithley 2400 source Measure Unit in a nitrogen-filled glove box. A standard single-crystal Si solar cell purchased from the National Renewable Energy Laboratory was adopted to calibrate the light intensity. The device parameters presented herein were averaged over 12 individual devices. The external quantum efficiency (EQE) was characterized using a QE-R system (Enli Tech., Kaohsiung, Taiwan) under an ambient atmosphere at room temperature. EIS under different illuminations (with the light source comprising a 625 nm light-emitting diode) was conducted using a ModuLab XM system (Ametek, Solartron Analytical, Beijing) to explore the charge transfer process.

RESULTS AND DISCUSSION

Fig. 1a–d show the XPS patterns of $\text{In}(\text{acac})_3$ powders and the annealed films prepared using $\text{In}(\text{acac})_3$ isopropanol precursor, which reveal the composition change from powders to films and verify that the composition of films is In_2O_3 . The full XPS spectrum survey given in Fig. 1a illustrates the presence of O and In. Two samples present a symmetric In 3d peak centered at 445 and 452 eV (Fig. 1b), corresponding to In $3d_{5/2}$ and In $3d_{3/2}$ peaks, respectively [28]. The slight differences in In $3d_{5/2}$ and In $3d_{3/2}$ are 7.5 and 7.6 eV for the powder (445.2 and 452.7 eV) and film (444.7 and 452.3 eV) samples, respectively, manifesting that the In^{3+} state exists in both samples [29]. The binding energies of 531.8 and 536.3 eV in the powders are attributed to the O 1s, representing oxygen vacancies and oxide lattice, respectively; while, the binding energies in the films are 531.7 and 529.8 eV, respectively. The former increased peak indicates more oxygen vacancies, and the latter suggests the disappeared peak of C=O (536.3 eV) and a new generated peak of In–O (529.8 eV) [30]. In Fig. 1d, the binding energy of 284.8 eV in powders represents the peak of C–C/C–H, and that of 286.8 eV represents the C=O peak [31]. Apparently, the disappeared C=O peak in the films demonstrates the disintegration of acetylacetone ligand. Similar analysis can be given for the $\text{Ga}(\text{acac})_3$ powders

and films, as shown in Fig. 1e–h. These results clearly indicate that the films prepared using $\text{In}(\text{acac})_3$ and $\text{Ga}(\text{acac})_3$ isopropanol precursors are In_2O_3 and Ga_2O_3 , respectively.

The X-ray diffraction (XRD) patterns were analyzed to verify the films prepared using $\text{In}(\text{acac})_3$ and $\text{Ga}(\text{acac})_3$ isopropanol precursors. Fig. 2a illustrates the XRD patterns of our samples and the standard patterns of In_2O_3 , Ga_2O_3 , and Si substrate [32]. The figure clearly shows the (222) and (400) diffraction peaks at $2\theta = 30.6^\circ$ and 35.5° for In_2O_3 thin films, respectively, and the (002), (020), and (221) diffraction peaks at $2\theta = 32.6^\circ$, 60.9° , and 64.3° for Ga_2O_3 thin films, respectively. The films show good crystallinity, which is conducive to carrier transportation. These results indicate that the low-temperature *in situ* processed films are In_2O_3 and Ga_2O_3 , respectively. These observations are consistent with the XPS results.

Fig. 2b shows the water contact angle (WCA) and the diiodomethane contact angle (DCA) of the In_2O_3 and Ga_2O_3 films. The WCA and DCA of In_2O_3 are 63.14° and 43.69° , respectively. The WCA and DCA of Ga_2O_3 are 55.51° and 39.17° , respectively. Correspondingly, the SFE calculated using the Owens–Wendt method for In_2O_3 and Ga_2O_3 is 45.44 and 50.73 mJ cm^{-2} , respectively [33]. Low SFEs favor the formation of a uniform photoactive layer, and the active layer on In_2O_3 is smoother than that on Ga_2O_3 .

The surface morphologies of ITO/ In_2O_3 , ITO/ Ga_2O_3 , ITO/ In_2O_3 /PM6:Y6, ITO/ Ga_2O_3 /PM6:Y6, and ITO/PM6:Y6 are illustrated in Fig. 2c to validate our speculation from the SFE. The root-mean-square (RMS) roughness values of the In_2O_3 and Ga_2O_3 films are only 1.45 and 2.25 nm, respectively. Both films evidently possess smooth surfaces, and the In_2O_3 film is smoother than the Ga_2O_3 film. The RMS values of ITO/PM6:Y6, ITO/ In_2O_3 /PM6:Y6, and ITO/ Ga_2O_3 /PM6:Y6 are 2.10, 1.77, and 2.05 nm, respectively. A smooth and uniform surface is a prerequisite for excellent carrier transportation [34]. Thus, an outstanding device performance can be achieved for solar cells with In_2O_3 CBLs.

The energy levels of the In_2O_3 and Ga_2O_3 layers were detected *via* UPS. As shown in Fig. 3a–c, the secondary electron cut-off edges are 16.64 and 16.16 eV, respectively. Given that the WF equals to the difference between the binding energy of He I low-energy photon source (21.22 eV) and the secondary electron cut-off edge [35], the WFs of the In_2O_3 and Ga_2O_3 layers are 4.58 and 5.05 eV, respectively, which contribute to the formation of a good ohmic contact between their interfaces and the photoactive layers. Thus, devices with the In_2O_3 interface

Figure 1 XPS of (a) survey, (b) In 3d, (c) O 1s, and (d) C 1s peaks for In(acac)₃ powders and films coated on silicon substrates; XPS of (e) survey, (f) Ga 2p, (g) O 1s, and (h) C 1s peaks for Ga(acac)₃ powders and films coated on silicon substrates.

can afford a high open circuit voltage (V_{oc}). The valance bands (VBs) for In₂O₃ and Ga₂O₃ are 7.50 and 7.59 eV, based on the sum of the onset and WF [36]. A deep VB value can selectively block the hole recombination at the

interface. As illustrated in Fig. 3d, the absorption of In₂O₃ and Ga₂O₃ is less than 5% and their transmittance is beyond 95% within the wavelength of 300–900 nm, which guarantees efficient light absorption in the active layer.

Figure 2 (a) XRD patterns of In₂O₃ and Ga₂O₃ films on crystalline silicon substrate. In each figure, the patterns from the top to the bottom are our sample, the standard pattern, and the Si substrate, respectively. (b) WCA and DCA images of In₂O₃ and Ga₂O₃. (c) AFM images of ITO/In₂O₃, ITO/Ga₂O₃, ITO/PM6:Y6, ITO/In₂O₃/PM6:Y6, and ITO/Ga₂O₃/PM6:Y6 with 5 $\mu\text{m} \times 5 \mu\text{m}$ scan size.

Fig. 4 presents the schematic diagram, energy level, and molecular structures of the materials involved in i-OSCs [37].

The J - V curves and EQE spectra of i-OSCs with In₂O₃ or Ga₂O₃ CBLs were obtained (Fig. 5) to understand the interplay between CBL and device performance. The corresponding photovoltaic parameters for devices under the illumination of AM 1.5G, 100 mW cm^{-2} , are listed in Table 1. Notably, champion devices with In₂O₃ show a PCE of 16.17% with a V_{oc} of 0.834 V, a short-circuit current (J_{sc}) of 26.40 mA cm^{-2} , and a fill factor (FF) of 73.44%. The devices with Ga₂O₃ layers afford a PCE of 16.01% with a V_{oc} of 0.825 V, a J_{sc} of 26.03 mA cm^{-2} , and an FF of 74.55%, as shown in Fig. 5a and Table 1. Obviously, In₂O₃ and Ga₂O₃ are excellent cathode layers, but devices with In₂O₃ afford higher V_{oc} and J_{sc} than those with Ga₂O₃. This result can be ascribed to the more suitable WF of 4.58 eV and smoother interface of In₂O₃ compared with that of Ga₂O₃, which fortify the charge separation and transportation [38]. The integrating currents calculated from the EQE spectra in Fig. 5b are in good accordance with the J - V results.

Fig. 5c, d plot the J - V curves and EQE spectra of i-OSCs with In₂O₃ layers fabricated from different con-

centrations (4–12 mg mL^{-1}) of In(acac)₃ solution. Table 1 shows that the PCE and FF of the devices initially increase as the concentration of the precursor solution increases from 4 to 10 mg mL^{-1} and then starts to reduce when it increases to 12 mg mL^{-1} , and the maximum efficiency appears at 12 mg mL^{-1} , benefiting from the pinhole-free In₂O₃ layers with a suitable thickness. Fig. 5e, f present the J - V curves and EQE spectra of the i-OSCs with Ga₂O₃ layers fabricated from different concentrations (2–10 mg mL^{-1}) of Ga(acac)₃ solution. The PCE and FF reach the highest values at 6 mg mL^{-1} . Comparative analysis indicates that the V_{oc} and J_{sc} of the devices with In₂O₃ layers are higher than those of the OSCs with Ga₂O₃ layers, further stating that In₂O₃ layers are more suitable for forming ohmic contact and reducing the interfacial recombination than Ga₂O₃ layers.

The roles of In₂O₃ and Ga₂O₃ films in OSCs were compared. EIS was performed at different light intensities (the light source is a 625 nm light-emitting diode, light intensity ranges from 10 to 60 mW cm^{-2} , and the measuring frequency changes from 1 MHz to 1 Hz) to explore the internal charge transfer of In₂O₃ and Ga₂O₃ thin films in this process. Fig. 6a, d are the Nyquist diagrams for the devices with the In₂O₃ and Ga₂O₃ films, respectively. Both

Figure 3 UPS spectra of (a) survey scan; (b) and (c) secondary electron cut-off and onset edge for the In_2O_3 and Ga_2O_3 films, respectively. (d) Absorption and transmittance spectra of the In_2O_3 and Ga_2O_3 layers on ITO substrates.

Figure 4 (a) Schematic diagram and (b) energy level diagram of i-OSCs with In_2O_3 and Ga_2O_3 CBLs, and (c) molecular structures of materials involved in the i-OSCs.

spectra manifest a semicircle dominating the response over most frequencies; obviously, the higher the light intensity, the smaller the radius and the lower the transport resistance (R_t) [39]. The equivalent circuit is shown in the inset of Fig. 6b to clarify the carrier trans-

portation and recombination and provide quantitative data about the different processes within the devices. R_s , R_t , and R_{rec} are the series, transport, and recombination resistances, respectively; C_u is the chemical capacitance; and C_g is the dielectric and geometrical capacitance [40].

Figure 5 (a) J - V curves and (b) EQE spectra of champion devices with In_2O_3 or Ga_2O_3 CBLs. (c) J - V curves and (d) EQE spectra of i-OSCs with In_2O_3 layers fabricated with different concentrations (4–12 mg mL^{-1}) of $\text{In}(\text{acac})_3$ solution. (e) J - V curves and (f) EQE spectra of i-OSCs with Ga_2O_3 layers fabricated from different concentrations (2–10 mg mL^{-1}) of $\text{In}(\text{acac})_3$ solution.

Table 1 Photovoltaic parameters for the i-OSCs with different CBLs under the illumination of AM 1.5G with a light intensity of 100 mW cm^{-2}

CBL	Concentration of precursor (mg mL^{-1})	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE_{avg} (%)	Integrated J_{sc} (mA cm^{-2})
In_2O_3	4	0.830	26.05	68.89	14.89 ± 0.18	25.96
	6	0.827	26.38	70.66	15.35 ± 0.16	26.09
	8	0.832	26.25	72.51	15.83 ± 0.17	26.07
	10	0.834	26.40	73.44	16.17 ± 0.12	26.19
	12	0.830	25.97	71.03	15.31 ± 0.15	25.79
Ga_2O_3	2	0.826	25.67	71.39	15.06 ± 0.16	25.18
	4	0.824	25.88	73.01	15.56 ± 0.17	25.60
	6	0.825	26.03	74.55	16.01 ± 0.15	26.06
	8	0.827	25.92	72.76	15.48 ± 0.18	25.74
	10	0.825	25.84	70.48	15.02 ± 0.13	25.36

R_s includes the resistance of the electrode, interface, active layer, and conductor, and it should be as small as possible. Similarly, low R_t corresponds to high exciton separation and carrier transportation, leading to significant enhancement of the current. Meanwhile, high R_{rec} implies a low recombination rate. Fig. 6b, c, e, and f are the Bode diagrams of OSCs under different light intensities. Table 2 shows the R_s , R_t , and R_{rec} of the OSCs with the In_2O_3 and Ga_2O_3 layers. The R_s values of the devices with

the In_2O_3 and Ga_2O_3 layers are close to 50 and 100 Ω , respectively, indicating that devices with In_2O_3 possess lower series resistance loss than those with Ga_2O_3 . The R_{rec} for OSCs with In_2O_3 is lower than that for OSCs with Ga_2O_3 under the same illumination. Although In_2O_3 possesses lower series resistance loss, Ga_2O_3 has a higher R_{rec} , which enhances the device FF and compensates for its series resistance loss to some extent. In addition, the R_t values of the devices with In_2O_3 layers are smaller than

Figure 6 (a) and (d) are Nyquist diagrams; (b), (c), (e), and (f) are impedance Bode diagrams for devices with In_2O_3 and Ga_2O_3 films under different light intensities. The inset in (b) presents the equivalent circuit model of OSC impedance data.

Table 2 Fitting data of the impedance for OSCs with In_2O_3 and Ga_2O_3 layers

CBL	Percentage of Light Intensity	R_s (Ω)	R_t (Ω)	R_{rec} (Ω)	C_u (F)
In_2O_3	10%	42.36	158.80	2765	9.40×10^{-9}
	20%	48.64	89.78	2142	4.25×10^{-8}
	30%	45.48	78.13	1759	3.32×10^{-9}
	40%	47.52	67.28	1492	3.78×10^{-9}
	50%	46.11	63.49	1321	3.95×10^{-9}
	60%	41.01	55.25	1124	3.71×10^{-9}
Ga_2O_3	10%	93.65	605.00	3011	4.01×10^{-9}
	20%	97.46	512.00	2478	1.42×10^{-9}
	30%	98.70	417.90	1964	4.09×10^{-9}
	40%	94.52	327.00	1619	1.88×10^{-9}
	50%	96.03	269.00	1411	3.26×10^{-9}
	60%	92.14	223.60	1336	3.24×10^{-9}

those of the devices with Ga₂O₃ layers under the same illumination, suggesting a higher J_{sc} , because the smaller the R_b , the faster the electrode charge collection [41]. These results are in line with the J - V results.

CONCLUSION

In₂O₃ and Ga₂O₃ layers were first synthesized by a facile spin-coating with low temperature annealing method from In(acac)₃ and Ga(acac)₃ isopropanol precursors and applied as CBLs in i-OSCs. Comparative studies show that the In₂O₃ and Ga₂O₃ layers have highly similar optoelectronic and morphological properties. However, In₂O₃ with a WF of 4.58 eV is more favorable for forming ohmic contact than Ga₂O₃ with a WF of 5.06 eV. Furthermore, although In₂O₃ possesses lower series resistance loss, Ga₂O₃ has a higher recombination resistance, which enhances the device FF and compensates for its series resistance loss to some extent. As a result, PM6:Y6-based OSCs with In₂O₃ exhibit higher V_{oc} than those with Ga₂O₃, but the latter devices manifest higher FF than the former devices. Hence, devices with In₂O₃ or Ga₂O₃ layers possess outstanding PCEs of over 16%. This study suggests that both In₂O₃ and Ga₂O₃ are desirable interfacial layers for highly efficient OSCs despite some differences in their photo-physics.

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- Gasparini N, Jiao X, Heumueller T, *et al.* Designing ternary blend bulk heterojunction solar cells with reduced carrier recombination and a fill factor of 77%. *Nat Energy*, 2016, 1: 16118
- Yan T, Song W, Huang J, *et al.* 16.67% rigid and 14.06% flexible organic solar cells enabled by ternary heterojunction strategy. *Adv Mater*, 2019, 31: 1902210
- Zhang Z, Miao J, Ding Z, *et al.* Efficient and thermally stable organic solar cells based on small molecule donor and polymer acceptor. *Nat Commun*, 2019, 10: 3271
- Wang T, Sun R, Shi M, *et al.* Solution-processed polymer solar cells with over 17% efficiency enabled by an iridium complexation approach. *Adv Energy Mater*, 2020, 10: 2000590
- Li J, Bai Y, Yang B, *et al.* Multifunctional bipyramid-Au@ZnO core-shell nanoparticles as a cathode buffer layer for efficient non-fullerene inverted polymer solar cells with improved near-infrared photoresponse. *J Mater Chem A*, 2019, 7: 2667–2676
- Wang F, Wang Y, Liu H, *et al.* Fine tuning the light distribution within the photoactive layer by both solution-processed anode and cathode interlayers for high performance polymer solar cells. *Sol RRL*, 2018, 2: 1800141
- Lin Y, Adilbekova B, Firdaus Y, *et al.* 17% efficient organic solar cells based on liquid exfoliated WS₂ as a replacement for PEDOT:PSS. *Adv Mater*, 2019, 31: 1902965
- Wang F, Tan Z, Li Y. Solution-processable metal oxides/chelates as electrode buffer layers for efficient and stable polymer solar cells. *Energy Environ Sci*, 2015, 8: 1059–1091
- Yang B, Zhang S, Li S, *et al.* A self-organized poly(vinylpyrrolidone)-based cathode interlayer in inverted fullerene-free organic solar cells. *Adv Mater*, 2019, 31: 1804657
- Bai Y, Yang B, Zhao C, *et al.* Synergy of a titanium chelate electron collection layer and a vertical phase separated photoactive layer for efficient inverted polymer solar cells. *J Mater Chem A*, 2018, 6: 7257–7264
- Kim CS, Lee SS, Gomez ED, *et al.* Transient photovoltaic behavior of air-stable, inverted organic solar cells with solution-processed electron transport layer. *Appl Phys Lett*, 2009, 94: 113302
- Yang B, Bai Y, Zeng R, *et al.* Low-temperature *in-situ* preparation of ZnO electron extraction layer for efficient inverted polymer solar cells. *Org Electron*, 2019, 74: 82–88
- Wang C, Luo D, Gao Y, *et al.* Delicate energy-level adjustment and interfacial defect passivation of ZnO electron transport layers in organic solar cells by constructing ZnO/In nanojunctions. *J Phys Chem C*, 2019, 123: 16546–16555
- Liang Z, Zhang Q, Jiang L, *et al.* ZnO cathode buffer layers for inverted polymer solar cells. *Energy Environ Sci*, 2015, 8: 3442–3476
- Kim J, Kim SH, Lee HH, *et al.* New architecture for high-efficiency polymer photovoltaic cells using solution-based titanium oxide as an optical spacer. *Adv Mater*, 2006, 18: 572–576
- Park MH, Li JH, Kumar A, *et al.* Doping of the metal oxide nanostructure and its influence in organic electronics. *Adv Funct Mater*, 2009, 19: 1241–1246
- Salim T, Yin Z, Sun S, *et al.* Solution-processed nanocrystalline TiO₂ buffer layer used for improving the performance of organic photovoltaics. *ACS Appl Mater Interfaces*, 2011, 3: 1063–1067
- Eisner F, Seitkhan A, Han Y, *et al.* Solution-processed In₂O₃/ZnO heterojunction electron transport layers for efficient organic bulk heterojunction and inorganic colloidal quantum-dot solar cells. *Sol RRL*, 2018, 2: 1800076
- Sun Y, Wang M, Liu C, *et al.* Realizing efficiency improvement of polymer solar cells by using multi-functional cascade electron transport layers. *Org Electron*, 2020, 76: 105482
- Yoon S, Kim SJ, Kim HS, *et al.* Solution-processed indium oxide electron transporting layers for high-performance and photo-stable perovskite and organic solar cells. *Nanoscale*, 2017, 9: 16305–16312
- Huang W, Zhu B, Chang SY, *et al.* High mobility indium oxide electron transport layer for an efficient charge extraction and optimized nanomorphology in organic photovoltaics. *Nano Lett*, 2018, 18: 5805–5811
- Pan YX, Sun ZQ, Cong HP, *et al.* Photocatalytic CO₂ reduction highly enhanced by oxygen vacancies on Pt-nanoparticle-dispersed gallium oxide. *Nano Res*, 2016, 9: 1689–1700
- Moloney J, Tesh O, Singh M, *et al.* Atomic layer deposited α -Ga₂O₃ solar-blind photodetectors. *J Phys D-Appl Phys*, 2019, 52: 475101
- Li X, Liu D, Mo X, *et al.* Nanorod β -Ga₂O₃ semiconductor modified activated carbon as catalyst for improving power generation of microbial fuel cell. *J Solid State Electrochem*, 2019, 23: 2843–2852
- Kumar SS, Rubio EJ, Noor-A-Alam M, *et al.* Structure, morphology, and optical properties of amorphous and nanocrystalline gallium oxide thin films. *J Phys Chem C*, 2013, 117: 4194–4200
- Zhang S, Qin Y, Zhu J, *et al.* Over 14% efficiency in polymer solar cells enabled by a chlorinated polymer donor. *Adv Mater*, 2018, 30: 1800868
- Du X, Zhao J, Zhang H, *et al.* Modulating the molecular packing and distribution enables fullerene-free ternary organic solar cells

with high efficiency and long shelf-life. *J Mater Chem A*, 2019, 7: 20139–20150

- 28 Qin M, Ma J, Ke W, *et al.* Perovskite solar cells based on low-temperature processed indium oxide electron selective layers. *ACS Appl Mater Interfaces*, 2016, 8: 8460–8466
- 29 Pan Y, Wang L, Gao DW, *et al.* Comparative analysis of Ga₂O₃/In₂O₃ incorporation in (Co-ZnS/Se) chalcogenide composite materials. *Mater Res Express*, 2019, 6: 106441
- 30 Rim YS, Chen H, Song TB, *et al.* Hexaaqua metal complexes for low-temperature formation of fully metal oxide thin-film transistors. *Chem Mater*, 2015, 27: 5808–5812
- 31 Tan Z, Zhang W, Zhang Z, *et al.* High-performance inverted polymer solar cells with solution-processed titanium chelate as electron-collecting layer on ITO electrode. *Adv Mater*, 2012, 24: 1476–1481
- 32 Kim DJ, Kim HK. Optimization of titanium-doped indium oxide anodes for heterojunction organic solar cells. *Phys Status Solidi A*, 2017, 214: 1600463
- 33 Shi Z, Liu H, Wang Y, *et al.* Incorporating an electrode modification layer with a vertical phase separated photoactive layer for efficient and stable inverted nonfullerene polymer solar cells. *ACS Appl Mater Interfaces*, 2017, 9: 43871–43879
- 34 Pan MA, Lau TK, Tang Y, *et al.* 16.7%-efficiency ternary blended organic photovoltaic cells with PCBM as the acceptor additive to increase the open-circuit voltage and phase purity. *J Mater Chem A*, 2019, 7: 20713–20722
- 35 Wang Z, Luo Z, Zhao C, *et al.* Efficient and stable pure green all-inorganic perovskite CsPbBr₃ light-emitting diodes with a solution-processed NiO_x interlayer. *J Phys Chem C*, 2017, 121: 28132–28138
- 36 Lee JH, Shin JH, Song JY, *et al.* Interface formation between ZnO nanorod arrays and polymers (PCBM and P3HT) for organic solar cells. *J Phys Chem C*, 2012, 116: 26342–26348
- 37 Yuan J, Zhang Y, Zhou L, *et al.* Single-junction organic solar cell with over 15% efficiency using fused-ring acceptor with electron-deficient core. *Joule*, 2019, 3: 1140–1151
- 38 Guan Z, Yu J, Zang Y, *et al.* Inverted organic solar cells with improved performance using varied cathode buffer layers. *Chin J Chem Phys*, 2012, 25: 625–630
- 39 Li Z, Guo W, Liu C, *et al.* Impedance investigation of the highly efficient polymer solar cells with composite CuBr₂/MoO₃ hole transport layer. *Phys Chem Chem Phys*, 2017, 19: 20839–20846
- 40 Kuwabara T, Iwata C, Yamaguchi T, *et al.* Mechanistic insights into UV-induced electron transfer from PCBM to titanium oxide in inverted-type organic thin film solar cells using AC impedance spectroscopy. *ACS Appl Mater Interfaces*, 2010, 2: 2254–2260
- 41 Bai Y, Zhao C, Guo Q, *et al.* Enhancing the electron blocking ability of n-type MoO₃ by doping with p-type NiO for efficient nonfullerene polymer solar cells. *Org Electron*, 2019, 68: 168–175

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Yiming Bai is an associate professor at the State Key Laboratory of Alternate Electrical Power System with Renewable Energy Sources, North China Electric Power University (NCEPU). She obtained PhD from the Institute of Semiconductor, Chinese Academy of Sciences (CAS) in 2007, and then worked in the Key Laboratory of Semiconductors, CAS. In Nov. 2009, she joined the Renewable Energy School, NCEPU. Her research interests concentrate on photovoltaic materials and devices.

Zhan'ao Tan has been a professor in Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology since 2018, and he worked as a professor in NCEPU from 2009 to 2019. Currently, he leads the Group of Organic Optoelectronic Materials and Devices. His present research interests include organic solar cells, colloidal nanocrystal and carbon dots-based optoelectronics, perovskite solar cells and light-emitting diodes.

基于低温原位法制备Ga₂O₃或In₂O₃电子收集层的高效有机太阳电池

白一鸣¹, 时融康¹, 白英龙¹, 王福芝¹, 王俊³, Tasawar Hayat⁴, Ahmed Alsaedi⁴, 谭占鳌^{1,2*}

摘要 有机太阳电池(OSCs)中, 温和的界面材料制备工艺对于拓宽材料适用范围和提高器件能量转换效率(PCE)具有重要作用. 本文提出了简便易行的In₂O₃和Ga₂O₃电子收集层的制备方法, 即旋涂In(acac)₃和Ga(acac)₃异丙醇前驱体溶液并结合低温热退火. 在基于PM6:Y6的OSCs中引入In₂O₃和Ga₂O₃电子收集层, 得到了性能优异的器件, PCE分别达到16.17和16.01. 对比研究发现, In₂O₃的功函数WF为4.58 eV, 这比WF为5.06 eV的Ga₂O₃更有利于与ITO电极形成欧姆接触, 因此基于前者的器件开路电压更高. 此外, 电化学阻抗谱EIS的研究进一步揭示了In₂O₃和Ga₂O₃对器件内部电荷转移过程的影响及其性能差异的由来: In₂O₃的串联电阻损耗虽然较低, 但Ga₂O₃的复合电阻较高, 所以一定程度上提高了基于Ga₂O₃的器件的填充因子, 进而补偿了其串联电阻的损失. 本论文的对比研究发现, In₂O₃和Ga₂O₃都是OSCs优异的电子收集层.