

Self-Assembled Quasi-3D Nanocomposite: A Novel p-Type Hole Transport Layer for High Performance Inverted Organic Solar Cells

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Hole transport layer (HTL) plays a critical role for achieving high performance solution-processed optoelectronics including organic electronics. For organic solar cells (OSCs), the inverted structure has been widely adopted to achieve prolonged stability. However, there are limited studies of p-type effective HTL on top of the organic active layer (hereafter named as top HTL) for inverted OSCs. Currently, p-type top HTLs are mainly 2D materials, which have an intrinsic vertical conduction limitation and are too thin to function as practical HTL for large area optoelectronic applications. In the present study, a novel self-assembled quasi-3D nanocomposite is demonstrated as a p-type top HTL. Remarkably, the novel HTL achieves ≈ 15 times enhanced conductivity and ≈ 16 times extended thickness compared to the 2D counterpart. By applying this novel HTL in inverted OSCs covering fullerene and non-fullerene systems, device performance is significantly improved. The champion power conversion efficiency reaches 12.13%, which is the highest reported performance of solution processed HTL based inverted OSCs. Furthermore, the stability of OSCs is dramatically enhanced compared with conventional devices. The work contributes to not only evolving the highly stable and large scale OSCs for practical applications but also diversifying the strategies to improve device performance.

1. Introduction

Replacing the hygroscopic and acidic poly(3,4-ethylenedioxythiophene): poly(styrenesulfonic acid) (PEDOT:PSS) by other hole transport layer (HTL) alternatives contribute to the realization of much more stable organic electronic devices.^[1] In the field of organic solar cells (OSCs), an inverted structure, which

discards both PEDOT:PSS and easily oxidized low work function (WF) cathodes, has been widely adopted to achieve prolonged stability.^[2] The most commonly used HTL in inverted OSCs, on top of organic active layer (hereafter named as p-type top HTL), is thermally evaporated molybdenum oxide (MoO_3).^[3,4] MoO_3 , once mistakenly identified as p-type semiconductor, is actually n-type semiconductor. Alternatively, like vanadium oxide (V_2O_5),^[5] tungsten oxide (WO_3),^[6] and copper iodide (CuI),^[7] have also been evaporated onto organic active layer to function as top HTL. However, the thermal evaporation process under high vacuum condition is energy consuming and not compatible with the facile solution-processed fabrication. Thus it is highly desirable to develop solution-processed top HTL for inverted OSCs and other organic electronic devices.

Researchers have developed a series of solution processed methods to prepare the n-type transition metal oxide HTLs, i.e., MoO_3 ,^[8] V_2O_5 ,^[9] and WO_3 .^[10] However, the

intrinsically poor electrical conductivity and electron blocking ability of these n-type HTLs are long-existing concern when acting as HTL.^[11] Other alternatives, like isopropyl alcohol processed phosphomolybdic acid (PMA)^[12] and methanol processed phenothiazin-10-yl-anisole (APS),^[13] have also been developed as top HTLs. The carrier transporting mechanisms of PMA and APS have not been clearly depicted and the optimized thicknesses, i.e., 15 and 6–10 nm, indicate the same concern of poor conductivity. As a result, developing p-type solution-processed top HTL with good conductivity and electron blocking ability becomes favorable.

The literature reported solution-processed p-type top HTLs are mainly 2D materials, including molybdenum disulfide (MoS_2),^[14,15] niobium diselenide (NbSe_2),^[16] and graphene oxide (GO).^[17] These 2D materials have different unique properties and optoelectronic property tunability, which have attracted intensive attention in the field of catalysis,^[18] water splitting,^[19] sensors,^[20] and supercapacitor.^[21] MoS_2 and NbSe_2 , representatives of metal dichalcogenide 2D materials, show poor vertical conductivity due to its weak van der Waals interaction between adjacent sheets though they exhibit excellent in-plane conductivity.^[14,16] As another kind of 2D material, GO has also been used in inverted

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OSCs.^[17,22,23] Simply synthesized by oxidation of graphite, GO exhibits easily synthesized, mass producibility, low-cost, and solution processability. However, functionalization of hydroxyl, carboxyl, and epoxy groups on the basal plane and at the edges of GO seriously degrades the conductivity.^[24] Therefore, all these 2D HTL materials show thickness limitation and the reported optimized thickness is typically very thin. For example, the optimized thickness of GO functioning as HTL in inverted OSCs is only 1–2 nm.^[22,25] To date, there is a shortage of solution-processed p-type semiconductor functioning as top HTL which can address the vertical conduction limitation and is critical to practical application in scalable manufacturing of organic electronics and other emerging solution-processed optoelectronics.

Solution-processed nickel oxide (NiO_x) has been proven to be a p-type semiconductor with the advantages of good conductivity and electron blocking ability.^[26] However, most reported NiO_x HTLs involve post-treatments including oxygen-plasma treatment, UVO treatment or high-temperature annealing.^[27] These harsh post-treatments would seriously damage the organic active layer due to a destroying of the π -conjugation system of organic semiconductors.^[28] Thus, these existing NiO_x HTL preparation methods are not compatible with top HTL application in inverted OSCs. Recently, a post-treatment-free solution-processed NiO_x nanoparticles (NPs) has been reported for HTL application.^[29] However, this NiO_x NPs can only be well dispersed into water, which hinders its application in inverted OSCs due to the poor wetting property of water on hydrophobic active layer surface. Furthermore, a 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) doped NiO_x nanocomposite has also been developed as HTL for conventional structure based OSCs.^[30] However, there is no report for applying NiO_x as top HTL to achieve high performance and stable organic optoelectronic devices.

In this work, we demonstrated a novel self-assembled quasi-3D nanocomposite for high performance inverted OSCs. We

realize an efficient p-type top HTL by preparing a novel self-assembled quasi-3D material to form high quality film with good morphology (dense and well-cover) and electrical properties. We demonstrate that through (i) introducing controllable hydrogen bonds between GO nanosheets (NSs) and NiO_x nanoparticles (NPs), newly developed self-assembled quasi-3D GO: NiO_x nanocomposite is realized; (ii) using oxidation degree of GO to critically control its dispersion to achieve uniform and pinhole-free HTL film. Our results show that the optimized GO: NiO_x film shows ≈ 15 times better conductivity compared with GO films. The long-time concern of too thin optimized thickness of only about 2 nm can also be addressed by an extension of thickness by ≈ 16 times to as thick as 32 nm. With the enhanced conductivity and electron blocking ability of quasi-3D nanocomposite film, the short-current density (J_{SC}), fill factor (FF), and power conversion efficiency (PCE) are all improved in the optimized quasi-3D GO: NiO_x top HTL based inverted OSCs. Overall, a 15% improvement of PCE is realized as compared with GO based OSCs. The PCE reaching 12.13% is also the highest reported performance of inverted OSCs based on solution-processed top HTL. Furthermore, this quasi-3D nanocomposite HTL is successfully applied to improve the performance of both fullerene and non-fullerene OSCs, which contributes to the robust and practical applications in not only organic optoelectronic devices but also other emerging solution-processed optoelectronics.

2. Results and Discussion

2.1. Preparation and Characterization of Quasi-3D Nanocomposite Films

The schematic illustration of preparing the self-assembled quasi-3D GO: NiO_x nanocomposite is shown in **Figure 1**. The ethanol dispersible NiO_x NPs are synthesized by a solvothermal

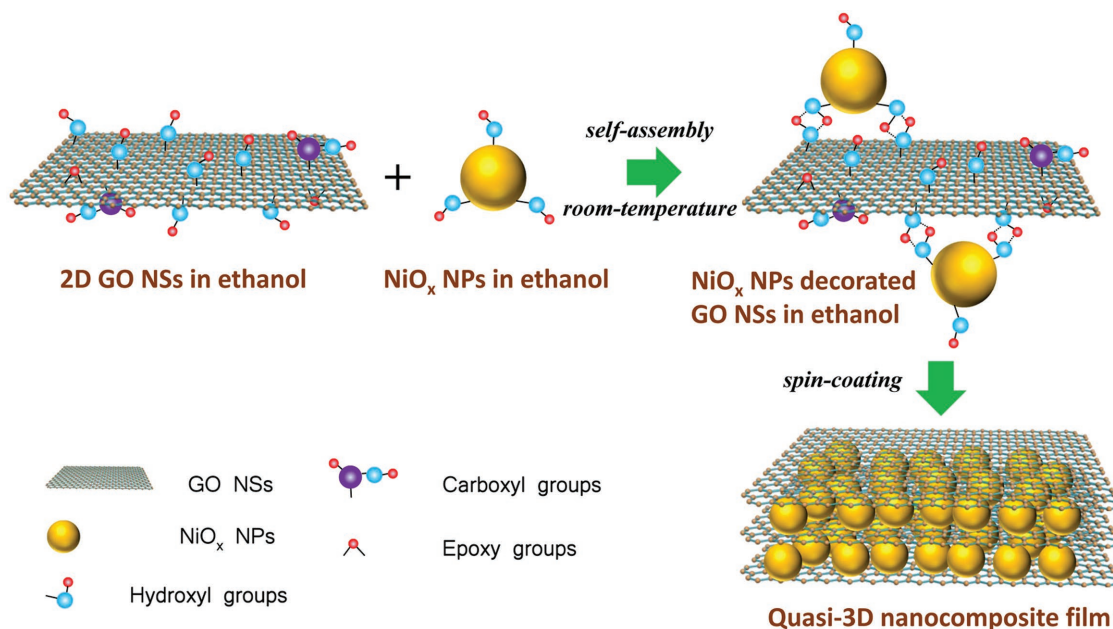


Figure 1. Schematic illustration of preparing room-temperature ethanol processed self-assembled quasi-3D GO: NiO_x nanocomposite.

method^[30,31] and GO NSs are synthesized by a modified Hummers' method with details shown in Experimental Section.^[32,33] The NiO_x NPs solution is shown in Figure S1a–I in the Supporting Information. Through strategically controlling the hydrogen bond interaction between hydroxyl groups of GO NSs and hydroxyl groups attached to the coordination unsaturated metal atoms of NiO_x ,^[34] the NiO_x NPs are assembled onto the GO NSs surface to form the self-assembled quasi-3D GO:NiO_x nanocomposite at room temperature. The hydrogen bond interaction between GO NSs and NiO_x NPs is also schematically illustrated in Figure 1. Importantly, we found that the oxidation degree of GO is a critical factor to achieve good dispersion of quasi-3D GO:NiO_x solution for high-quality film formation. The GO NSs with low and high oxidation are denoted L-GO and H-GO hereafter. The synthesized GO dispersed in ethanol with different oxidation degrees, as shown in Figure S1a–II,III in the Supporting Information, show slightly different appearance. The L-GO solution shows a yellow-like color while the H-GO solution shows slight red-like color.

GO can be regarded as graphene functionalized with carboxyl groups, hydroxyl groups and epoxy groups. The oxidation degree of GO depends on the density of the functional groups formed on the basal panel. The oxidation degree variance between L-GO and H-GO has been verified by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) characterization as shown in Figure 2a,b. XPS spectra of both L-GO and H-GO show C–C (284.8 eV), C–O (286.8 eV), and C=O (288.6 eV) species functionalized on the GO basal panel. The peak amplitudes show significant differences in two kinds of GO. In the spectrum of L-GO, the C–C peak is obviously higher than C–O peak while the situation is reverse in the case of H-GO. The ratio between C–C, C–O, and C=O is 1:0.54:0.15 for L-GO while the ratio is 1:1.32:0.11 for

H-GO. The higher ratio of C–O over C–C indicates a higher oxidation degree of H-GO and this higher oxidation degree is indeed mainly attributed to higher concentration of C–O species. FTIR has also been used to identify various oxygen functional groups on the carbon basal plane of GO. The spectrum is normalized at 1625 cm^{-1} , which arises from asymmetric vibrational stretching of sp^2 -hybridized C=C. The spectrum identifies the presence of carboxyl groups (C=O stretching at 1731 cm^{-1} , O–H of COOH bending at 1400 cm^{-1}), tertiary hydroxyl groups (phenolic C–O at 1227 cm^{-1} , and C–O at 1075 cm^{-1}) and epoxy groups (C–O at 1260 cm^{-1}). The stronger peak at 1227 and 1075 cm^{-1} indicates a higher density of hydroxyl groups of H-GO. Both XPS and FTIR spectra indicates that the successful synthesis and significant variation of L-GO and H-GO.

The morphology of GO and the self-assembled quasi-3D GO:NiO_x nanocomposite have been investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) as shown in Figure 2c–h. Both L-GO and H-GO exhibit NSs morphology with a similar horizontal size around 1–2 μm (see Figure 2c,d). The influence of oxidation degree of GO on the morphology of self-assembled quasi-3D GO:NiO_x nanocomposite is schematically shown in Figure S2 in the Supporting Information. Because of the higher density of hydroxyl groups on the H-GO NSs, the drastic hydrogen bonds induce the shrinking of H-GO NSs, and thus self-assembled H-GO: NiO_x aggregates with a size of several hundred nanometers (see Figure 2f). These aggregates cannot stably disperse in ethanol and precipitate at the bottom of a vial as shown in Figure S1a–V in the Supporting Information. By spin coating this suspension, the large H-GO: NiO_x aggregates scatter on the underlying substrate which cannot effectively prevent the direct contact between metal electrode and bulk heterojunction

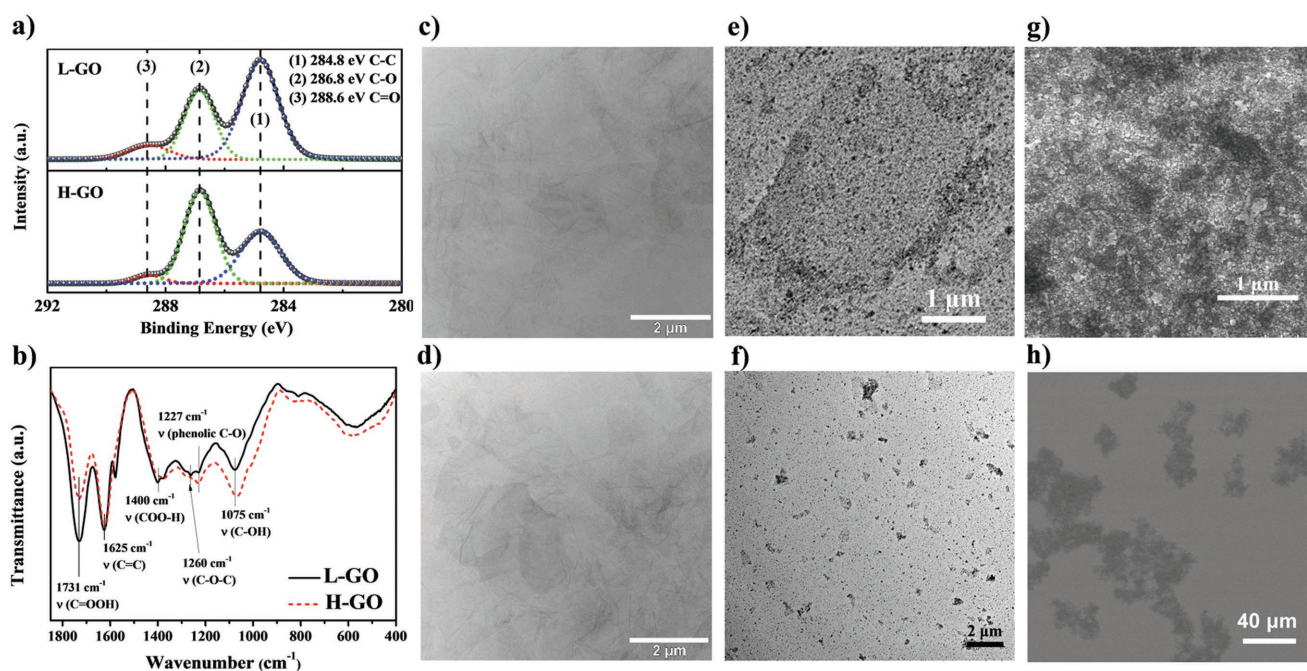


Figure 2. a) C 1s XPS spectrum of GO. b) FTIR spectrum of GO (normalized at 1625 cm^{-1}). TEM images of c) L-GO NSs, d) H-GO NSs, e) self-assembled NiO_x :L-GO nanocomposite and f) H-GO: NiO_x aggregates. SEM images of g) L-GO: NiO_x film and h) H-GO: NiO_x film.

active layer as shown in Figure 2h. Interestingly, through self-assembly process, stable disperse quasi-3D NiO_x :L-GO nanocomposite with many black dots (NiO_x NPs) assembled onto the surface of L-GO NSs are achieved (Figure 2e) through introducing proper amount of hydrogen bonds between GO NSs and NiO_x NPs. As a result, we successfully realize high-quality (dense and well-cover) L-GO: NiO_x nanocomposite film as demonstrated from SEM image shown in Figure 2g, and decent HTL film application potential as described later.

Conventionally, due to the destruction of π -conjugation system resulted from functional groups, GO exhibits poor conductivity in vertical direction as shown in Figure 3a.^[35] We demonstrate the self-assembled quasi-3D L-GO: NiO_x nanocomposite can fundamentally address the vertical conductivity limitation of GO (as a representative of 2D HTL materials) as schematically show in Figure 3b. We have investigated and compared the conductivity of bare L-GO and quasi-3D L-GO: NiO_x nanocomposite films by conductive atomic force microscopy (c-AFM) measurements as described in Figure 3c. The film thickness is fixed at ≈ 20 nm and the corresponding current-voltage (I - V) curves are as shown in Figure 3d. The vertical current of quasi-3D GO: NiO_x nanocomposite films at the bias voltage of 2 V is 3.06 nA, which is significantly higher than that of pristine GO (0.06 nA). The enhanced vertical current demonstrates significant enhancement (≈ 15 times) of electrical conductivity in quasi-3D nanocomposite ($2.30 \times 10^{-5} \text{ S cm}^{-1}$) compared to bare GO ($1.59 \times 10^{-6} \text{ S cm}^{-1}$). This result clearly shows that the self-assembled 3D nanocomposite breaks the trade-off between vertical conductivity and film thickness of 2D materials. WF of L-GO, NiO_x , and L-GO: NiO_x films have been

determined as 4.98, 4.76, and 4.97 eV by Kelvin Probe measurement as shown in Figure S3 in the Supporting Information.

2.2. Performance Enhancement in Inverted OSCs and Breaking the Vertical Conduction Limitation

To directly investigate the potential HTL application of the self-assembled quasi-3D L-GO: NiO_x nanocomposite in inverted OSCs, fullerene based inverted OSCs have been fabricated. Indium tin oxide (ITO) works as the cathode, zinc oxide (ZnO) works as the electron transport layer (ETL) and the blend of poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene)-2-carboxylate-2,6-diyl] (PTB7-Th) and [6,6]-Phenyl- C_{71} -butyric acid methyl ester (PC_{71}BM) works as the bulk heterojunction active layer. The structure is described as ITO/ZnO/PTB7-Th: PC_{71}BM /HTL/Ag. Due to the good wetting property of ethanol on the hydrophobic surface of active layer, L-GO, L-GO: NiO_x , and NiO_x films can be formed on the active layer simply by spin coating without further treatment. Figure 4a shows representative J - V curves and the photovoltaic parameters are summarized in Table 1. The optimized ratio between GO: NiO_x is 0.5:5 mg mL^{-1} . As discussed above, the L-GO based devices shows an optimized average PCE of 8.80% with an average J_{SC} of 18.39 mA cm^{-2} , an average open-circuit voltage (V_{OC}) of 0.78 V and an average FF of 0.61. The NiO_x based devices show poor V_{OC} due to mismatched WF values^[36] and the SEM image of bare NiO_x film is as shown in Figure S4 in the Supporting Information. After the decoration of NiO_x

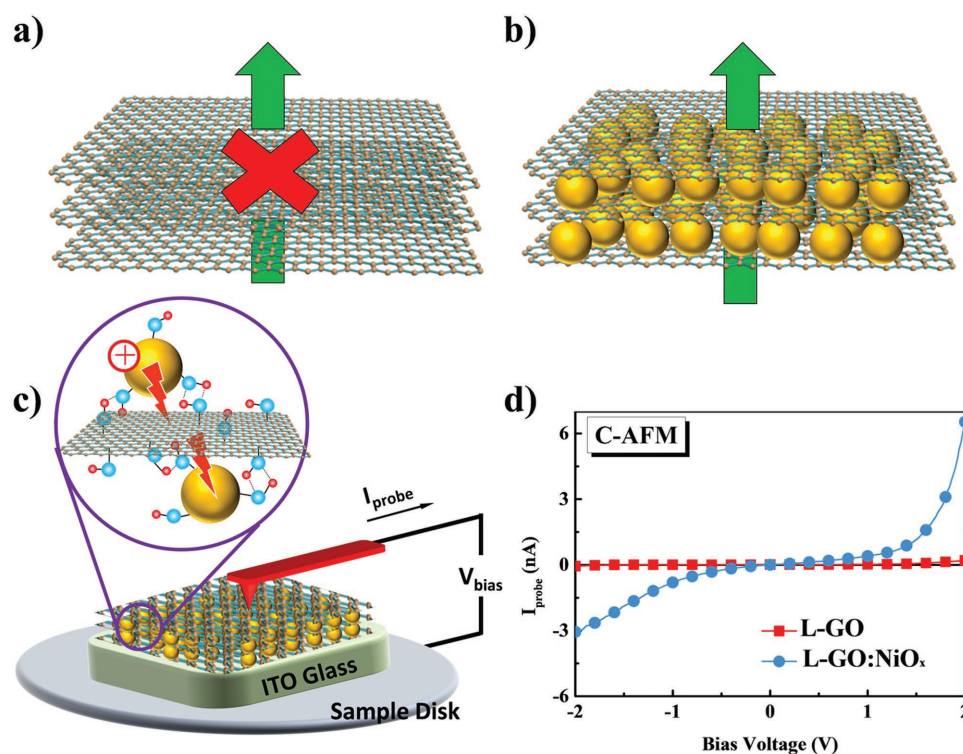


Figure 3. a) Schematic illustration of vertical conduction limitation of GO film. b) Schematic illustration of breaking the vertical conduction limitation in quasi-3D nanocomposite film. c) Schematic illustration of c-AFM measurement. d) I - V curves of GO and GO: NiO_x measured by c-AFM.

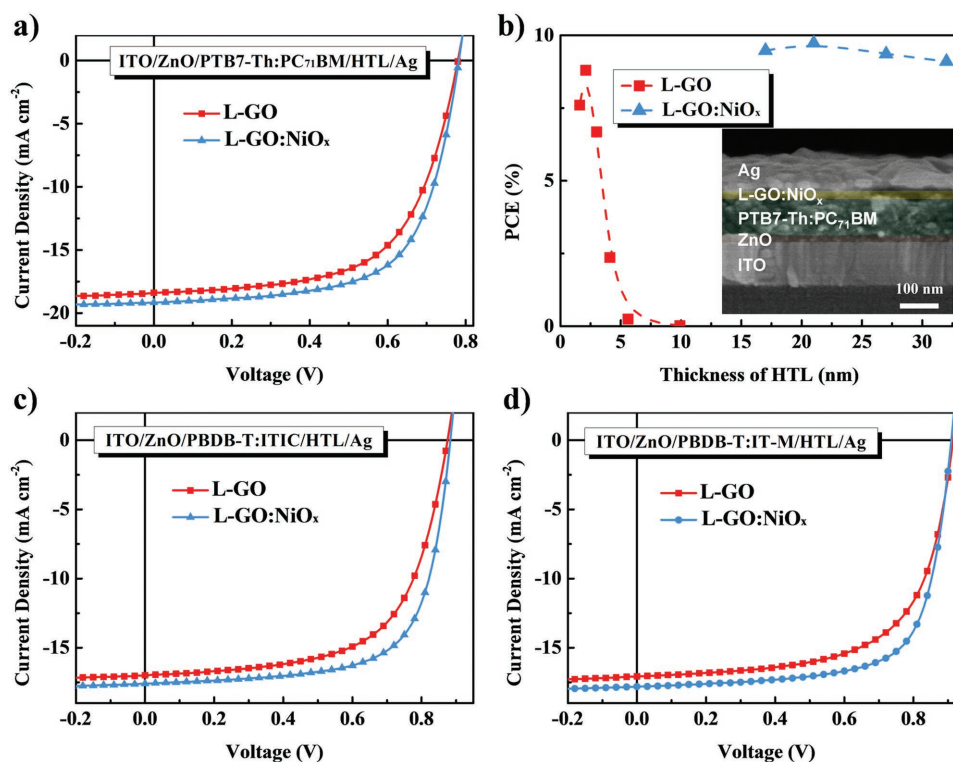


Figure 4. a) Representative J - V characteristics of inverted OSCs with GO (2.1 nm) and L-GO: NiO_x (21 nm) as HTL. b) PCE of inverted OSCs based on GO and L-GO: NiO_x with different thicknesses (inset shows the cross-section SEM of the device with a structure of ITO/ZnO/PTB7-Th:PC₇₁BM/L-GO: NiO_x /Ag). The dashed lines added as a guide to the eye. c) Representative J - V characteristics of OSCs (ITO/ZnO/PBDB-T:ITIC/HTL/Ag). d) Representative J - V characteristics of OSCs (ITO/ZnO/PBDB-T:IT-M/HTL/Ag).

on L-GO, the average PCE significantly increases to 9.73% (with best PCE of 9.93%) with an increased average J_{SC} of 19.16 mA cm^{-2} and an increased FF of 0.65. The increase of J_{SC} is ascribed to the enhanced conductivity of the self-assembled quasi-3D L-GO: NiO_x compared with the bare GO.

More importantly, the thickness of GO can be significantly increased by using the self-assembled quasi-3D L-GO: NiO_x nanocomposite. The thickness dependence performance of L-GO and L-GO: NiO_x based OSCs is as shown in Figure 4b and the detailed J - V characteristics of GO based devices is as shown in Table S1 in the Supporting Information. When GO is used as the HTL, the thickness requirement is strict and any small alteration of thickness would degrade the performance obviously (see Table S1 and Figure S5 in the Supporting Information). Here, the thickness tuning of the HTL is realized by

varying the concentration while maintaining a constant spin speed. Taking the case of L-GO as an example, The optimized L-GO thickness is very thin with a value of 2.1 nm (agree well with other reports^[22]) and the optimized PCE is 8.80%. The device performances are very sensitive to the GO thickness. For instance, when the thickness increases from 2.1 to 4.1 nm by only a 2 nm increment, the average PCE degrades to 2.36%, which is only a quarter of the optimized average PCE (8.80%). When the thickness further increases to 5.6 nm, the average PCE decreases to almost zero. Meanwhile, when the thickness decreases to 1.6 nm, PCE quickly degrades due to a decrease of V_{OC} . Remarkably, our developed novel self-assembled quasi-3D L-GO: NiO_x nanocomposite can effective break the vertical conduction limitation faced by GO, and other 2D HTL materials. By using this nanocomposite as the HTL, the device performance

will become less sensitive to the change of HTL thickness. When the L-GO: NiO_x thickness is 21 nm, the devices show an optimized average PCE of 9.73%. When the thickness increases to 32 nm (over 15 times of the bare L-GO thickness), the average PCE only slightly drops to 9.10% which is still better than the pristine L-GO case. It is noteworthy that all the devices are measured as prepared without additional shadow mask unless otherwise specified. To investigate on the edge effects, we have fabricated another batch of devices (15 pcs in total) with the structure

Table 1. Performance summary of OSCs with the structure of ITO/ZnO/PTB7-Th:PC₇₁BM/HTL/Ag.

HTL	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	PCE _{ave} [PCE _{max}] [%]
L-GO [2.1 nm]	18.39 ± 0.26	0.78 ± 0.01	0.61 ± 0.01	8.80 ± 0.15 [9.01]
L-GO: NiO_x [17 nm]	19.04 ± 0.48	0.78 ± 0.01	0.63 ± 0.01	9.33 ± 0.25 [9.78]
L-GO: NiO_x [21 nm]	19.16 ± 0.33	0.78 ± 0.00	0.65 ± 0.01	9.73 ± 0.08 [9.93]
L-GO: NiO_x [27 nm]	18.34 ± 0.31	0.78 ± 0.01	0.65 ± 0.02	9.36 ± 0.37 [9.77]
L-GO: NiO_x [32 nm]	18.22 ± 0.24	0.78 ± 0.01	0.64 ± 0.02	9.10 ± 0.15 [9.27]
NiO_x [21 nm]	17.63 ± 0.17	0.57 ± 0.02	0.55 ± 0.02	5.52 ± 0.32 [5.71]

of ITO/ZnO/PTB7-Th:PC₇₁BM/L-GO:NiO_x/Ag and measured them both with and without shadow mask. The measured $J-V$ characteristics are summarized in Table S2 in the Supporting Information for a reference. The incident photoelectron conversion efficiency (IPCE) spectrum as shown in Figure S6 in the Supporting Information confirms the J_{SC} variation. The integrated J_{SC} values for L-GO (2.1 nm) and L-GO:NiO_x (21 nm) based devices are 18.01 and 18.73 mA cm⁻² respectively, which match well with the values determined by $J-V$ characteristics. To better understand the IPCE difference, the optical properties of L-GO, L-GO:NiO_x films have been investigated as shown in Figure S7 in the Supporting Information. The L-GO:NiO_x film shows a better transparency compared with L-GO film. The extracted absorption, $1 - \text{diffuse transmission } (T) - \text{diffuse reflection } (R)$, of L-GO:NiO_x based device is also increased compared with L-GO based device, especially in the blue region, which contributes to the IPCE difference.

Recently, non-fullerene electron acceptor based OSCs have attracted a broad interest,^[4,37] but available top HTL material for non-fullerene OSCs is still limited. We further study the potential application of our newly developed quasi-3D L-GO:NiO_x HTL in non-fullerene inverted OSCs. The optimized photovoltaic parameters and representative $J-V$ characteristics are summarized in Table 2 and Figure 4c,d, respectively. By using the combination of the polymer donor named poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene)-co-(1,3-di(5-thiophene-2-yl)-5,7-bis(2-ethylhexyl)-benzo[1,2-c:4,5-c']dithiophene-4,8-dione)] (PBDB-T) and the non-fullerene acceptor 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone)-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']-dithiophene (ITIC),^[38] the average PCE of L-GO:NiO_x based devices reach 10.68% (with best PCE of 11.12%), which shows a 15.0% improvement compared with 9.28% of bare GO based OSCs. This 15.0% improvement in PCE is mainly resulted from the increasing of both J_{SC} and FF. We have also investigated the application of quasi-3D L-GO:NiO_x HTL in the system of PBDB-T and methyl groups modulated ITIC (IT-M).^[39] Compared with PBDB-T:ITIC based devices, weaker energy loss in the charge transfer process of PBDB-T:IT-M results a higher V_{OC} (0.91 V).^[40] The averaged PCE of GO:NiO_x based devices reach 11.45%, which shows a 14.4% improvement compared with bare GO based devices (from 10.01% to 11.45%). The improvement of J_{SC} (from 17.07 to 17.81 mA cm⁻²) and FF (from 0.64 to 0.71) contributes to this PCE improvement. The IPCE spectra are as shown in Figure S8 in the Supporting Information and the integrated J_{SC} values are shown in Table S3 in the Supporting Information, matches well with those obtained from $J-V$ measurements. Importantly,

the champion device reaches at a PCE of 12.13%, with a J_{SC} of 18.07 mA cm⁻², V_{OC} of 0.92 V, FF of 0.73. The $J-V$ characteristics of the champion device is shown in Figure S9 in the Supporting Information and this is the highest reported PCE of inverted OSCs based on solution-processed top HTL as shown in Table S4 in the Supporting Information. Consequently, the advantages of the thickness independence, thick thickness of the self-assembled quasi-3D L-GO:NiO_x HTL and the improved device performance make it useful for practical application of both fullerene and non-fullerene OSCs.

2.3. Contributions of the Quasi-3D Nanocomposite HTL

This self-assembled quasi-3D nanocomposite contributes to performance enhancement from two aspects, i.e., better hole extraction property and hole blocking ability. Due to the self-assembled NiO_x NPs on GO NSs, the vertical conductivity limitation has been resolved and carrier extraction property can be enhanced. The surface recombination (i.e., surface recombination "i" in Figure 5a) at the active layer/HTL interface induced by inefficient hole extraction would be suppressed. The NiO_x typically has a smaller conduction band energy level (1.55 eV)^[30] compared with that of L-GO (2.51 eV), which is determined by the Tauc plot ($(\alpha h\nu)^{1/2} - h\nu$) and ultraviolet photoelectron spectroscopy (UPS) as shown in Figure S10 in the Supporting Information. Consequently, this novel nanocomposite has a better electron blocking ability than bare L-GO intrinsically as shown in Figure 5b.^[41] Also, electrons may easy tunnel through GO with the tiny thickness (≈ 2 nm) or diffuse through the defects of GO NSs.^[42] All these intrinsic and mechanical factors result in a better electron blocking ability of the self-assembled nanocomposite. Dark $J-V$ characteristics (Figure S11, Supporting Information) are consistent with the enhancement of electron blocking ability. The L-GO:NiO_x based device shows lower leakage current density (0.06 vs 0.96 mA cm⁻²) and higher rectification ratio (1.5×10^4 vs 1.1×10^3 at ± 2 V) compared with L-GO based device. As a result of the better electron blocking ability of self-assembled nanocomposite, the recombination of holes and electrons within HTL or at the HTL/anode contact (i.e., surface recombination "ii" in Figure 5a) is suppressed. The suppression of both surface recombinations "i" and "ii" would contribute to a carrier lifetime prolongation, which will be discussed below.

Carrier extraction properties have been investigated by transient photocurrent (TPC) decay analysis and impedance spectroscopy (IS) as shown in Figure 5c,d. The optimized L-GO (2.1 nm) based device shows a charge extraction time of 0.34 μ s.

The thicker L-GO based devices, due to more difficult hole extraction resulted from larger extraction resistance, show longer extraction time. For example, the L-GO (5.6 nm) and L-GO (3.4 nm) based devices show extraction time of 0.60 and 0.44 μ s respectively, as illustrated in Figure S12 in the Supporting Information. However, by using the self-assembled quasi-3D L-GO:NiO_x nanocomposite, the extraction time decreases from 0.34 to 0.23 μ s as depicted in Figure 5c. This reduction

Table 2. Performance summary of OSCs with the structure of ITO/ZnO/PBDB-T:ITIC/HTL/Ag or ITO/ZnO/PBDB-T:IT-M/HTL/Ag.

Active layer	HTL	J_{SC} [mA cm ⁻²]	V_{OC} [V]	FF	PCE _{ave} [PCE _{max}] [%]
PBDB-T:ITIC	GO	16.98 $\pm$ 0.31	0.88 $\pm$ 0.01	0.62 $\pm$ 0.01	9.28 $\pm$ 0.22 [9.68]
	L-GO: NiO _x	17.59 $\pm$ 0.22	0.88 $\pm$ 0.01	0.69 $\pm$ 0.02	10.68 $\pm$ 0.29 [11.12]
PBDB-T:IT-M	GO	17.07 $\pm$ 0.43	0.91 $\pm$ 0.01	0.64 $\pm$ 0.01	10.01 $\pm$ 0.21 [10.28]
	L-GO: NiO _x	17.81 $\pm$ 0.33	0.91 $\pm$ 0.01	0.71 $\pm$ 0.02	11.45 $\pm$ 0.44 [12.13]

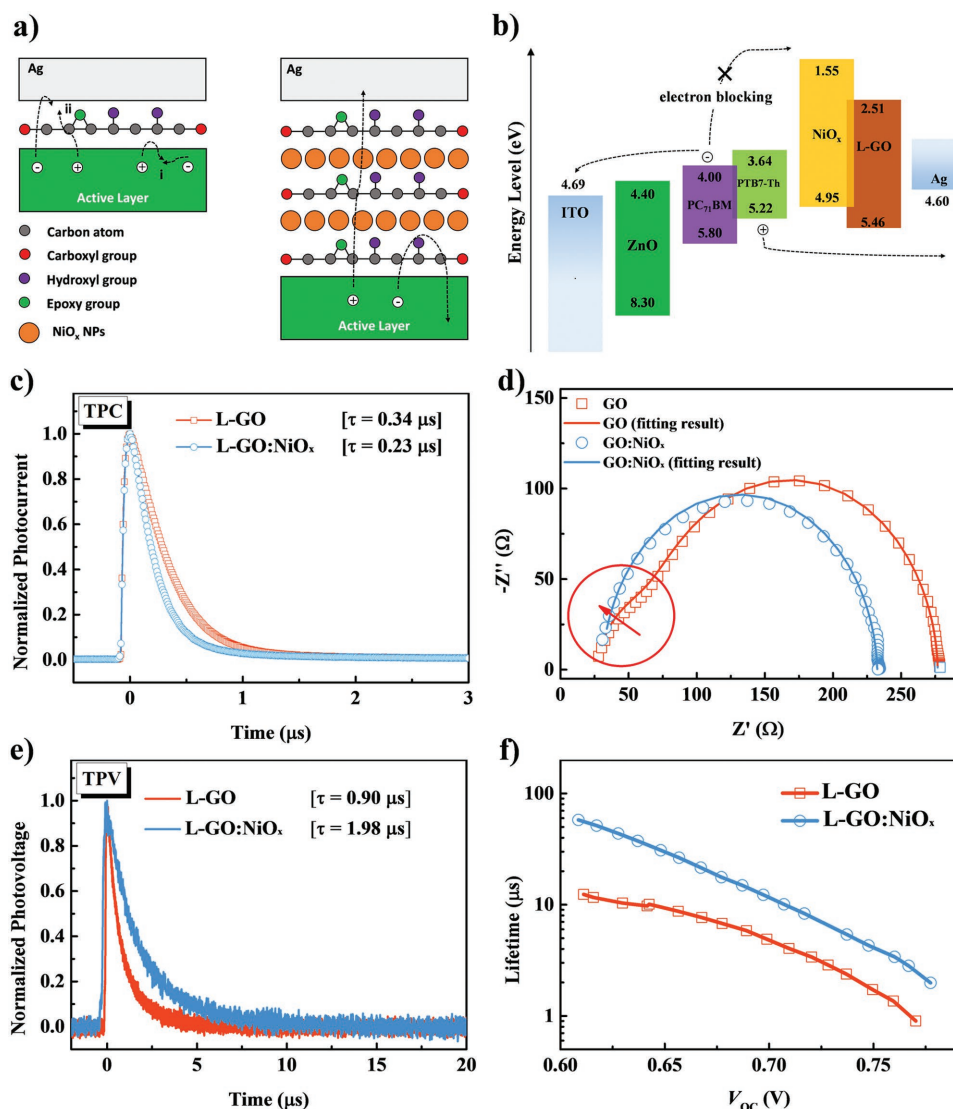


Figure 5. a) Carrier extraction properties and interface dynamics at the interface (the process “i” indicates surface recombination induced by poor conductivity and “ii” indicates surface recombination induced by poor electron blocking ability). b) Energy level diagram of materials used in OSCs. c) Change in photocurrent as a function of time. d) The impedance spectrum of OSCs (potential: 0.8 V) under 1 sun illumination (100 mW cm⁻²). e) Change in photovoltage as a function of time. f) Carrier lifetime of OSCs under different illumination light intensity conducted from TPV.

of extraction time signifies a better carrier extraction property of L-GO:NiO_x based HTL. This enhanced carrier extraction property has also been testified by IS measurements as shown in Figure 5d.^[43] A typical impedance spectrum of L-GO based device shows two obvious semicircles, indicating a carrier transport resistance (R_{tran}) and a bulk recombination channel (R_{bulk}).^[44] This IS spectrum is fitted by an equivalent circuit as shown in Figure S13 in the Supporting Information and an R_{tran} of 38.7 Ω is extracted. After the decoration of NiO_x, R_{tran} decreases to 7.1 Ω under the same equivalent circuit model, which results in a visual disappearance of the first semicircle. This reduction of R_{tran} is supposed to be highly correlated to the enhanced conductivity after the decoration of NiO_x NPs.

The suppression of surface recombination at the interface resulted from the synergic effects of better conductivity and electron blocking ability of self-assembled quasi-3D

nanocomposite, contributes to the prolonging of carrier's lifetime. The interface recombination dynamics has been examined by transient photovoltage (TPV) measurement as shown in Figure 5e,f. A small laser-pulse-induced ΔV is detected by oscilloscope under tunable background illumination. OSCs are kept under open circuit situation, thus the photovoltage decay curve in Figure 5e reflects the lifetime of photogenerated carriers. As shown in Figure 4f, lifetime is longer in the L-GO:NiO_x based devices compared with control devices at all the V_{oc} range. Under 1 sun illumination, the lifetime for L-GO based devices is only 0.90 μs. This value is considerably prolonged to 1.98 μs after decoration with NiO_x, which indicates the suppression of recombination dynamics in the L-GO:NiO_x based OSCs. The longer lifetime indicates a suppressed surface recombination in L-GO:NiO_x based OSCs, which could explain the enhancement of FF.

By using a differential capacitance technique, the steady-state carrier concentration under illumination of different background light intensities can be also determined. The differential capacitance (C) and carrier concentration (N) analysis, as shown in Figure S14 in the Supporting Information, further clarify the suppression of recombination. C is extracted through dividing generated charge (ΔQ) by the voltage increment (ΔV). As illustrated in Figure S14a in the Supporting Information, C increases exponentially with V_{OC} . After integrating C with respect to V_{OC} , N is determined and the relationship between N and V_{OC} is plotted in Figure S14b in the Supporting Information. L-GO:NiO_x based device shows a larger carrier concentration compared with L-GO based device at different V_{OC} values. Under AM 1.5G illumination, the carrier concentration is $1.64 \times 10^{17} \text{ cm}^{-3}$ for L-GO:NiO_x based device, which is higher than the carrier concentration of $1.28 \times 10^{17} \text{ cm}^{-3}$ for L-GO based device. The higher carrier concentration in the self-assembled quasi-3D L-GO:NiO_x nanocomposite based device indicates a suppressed recombination resulted from both better conductivity and electron blocking ability.

2.4. Enhanced Stability

The stability of OSCs is critical for practical applications. To assess the stability of our developed quasi-3D p-type top HTL, we have investigated the stability of unencapsulated L-GO and L-GO:NiO_x based inverted OSCs with a structure of ITO/ZnO/PTB7-Th:PC₇₁BM/HTL/Ag. We have also investigated the stability of unencapsulated conventional OSCs with a structure of ITO/PEDOT:PSS/PTB7-Th:PC₇₁BM/Ca/Al for comparison.

The unencapsulated devices are stored in the ambient environment and measured under 1 sun illumination. The variation of J_{SC} , V_{OC} , FF, and PCE are shown in Figure 6. The L-GO:NiO_x based device shows similar stability performance compared with L-GO based device. While compared with conventional device, the stability of L-GO:NiO_x based device is significantly improved. After 164 h storage in ambient environment, the conventional device's PCE quickly degrades to zero while the L-GO or L-GO:NiO_x based device still remain half of its initial PCE. The quick degradation of conventional device is mainly ascribed to the decreasing in J_{SC} and FF after 90 h. This is caused by the quick oxidation of Ca in the air and the acidic and hygroscopic properties of PEDOT:PSS. Consequently, our quasi-3D p-type top HTL based OSCs could significantly enhance the stability of OSCs compared with conventional devices, which will greatly benefit their commercialization.

3. Conclusion

In summary, a solution-processed self-assembled quasi-3D p-type top HTL, which breaks the vertical conductivity limitation of traditional 2D HTL materials, has been developed for application in high efficiency and stable inverted OSCs for the first time. The oxidation degree is proven to be a key parameter in determining the interaction between NiO_x and GO. A high oxidized GO would result in excessive decoration of NiO_x NPs and shrinking of self-assembled nanocomposite. By strategically choosing a suitable oxidation degree of GO, the well dispersed self-assembled quasi-3D nanocomposite can realize uniform film with full coverage. Thanks to the strategic

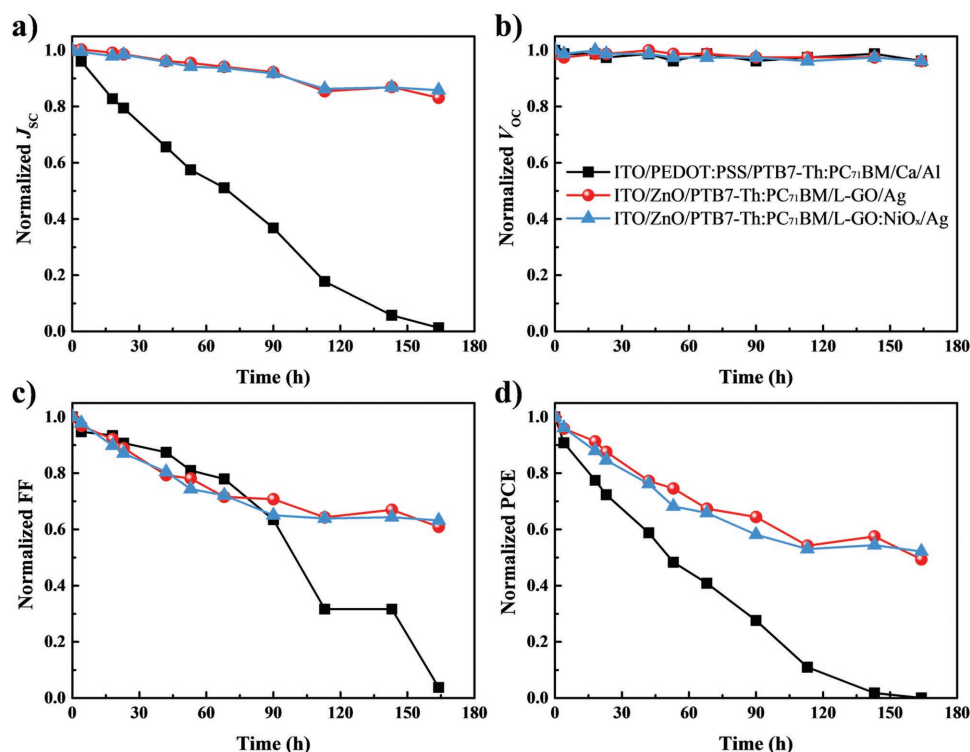


Figure 6. Normalized device characteristics, a) J_{SC} , b) V_{OC} , c) FF, and d) PCE, as a function of air exposure time.

introduction of hydrogen bond between GO NSs and NiO_x NSs, the newly developed self-assembled quasi-3D nanocomposite HTL addresses the vertical conductivity limitation faced by traditional 2D HTL materials. The conductivity is enhanced by ≈ 15 times compared with GO and the thickness of HTL can increase significantly by ≈ 16 times compared to pristine GO HTL. Due to enhanced conductivity and electron blocking ability of self-assembled quasi-3D nanocomposite, J_{SC} and FF are both enhanced and thus high PCE with significant improvement can be achieved in both fullerene and non-fullerene OSCs. The highest PCE of 12.13% is realized, which is the highest reported performance of solution-processed HTL based inverted OSCs. Furthermore, the stability of OSCs is dramatically enhanced by using our quasi-3D nanocomposite HTL.

4. Experimental Section

Materials: Graphite flakes were purchased from Sigma-Aldrich. Nickel acetylacetonate (Ni(acac)₃, 99% purity), *tert*-butanol (98% purity), potassium permanganate (KMnO₄, GR), and hydrogen peroxide (H₂O₂, 30% GR ACS) were purchased from International Laboratory USA. Sodium nitrate (NaNO₃, 99.99% metals basis) was purchased from Aladdin. Zinc acetate dihydrate (Zn(OAc)₂, ACS reagent, 98%), ethanolamine (ACS reagent, 99.9%), and chlorobenzene (CB, anhydrous, 99.8%) were purchased from Sigma-Aldrich. PTB7-Th, PC₇₁BM, PBDB-T, and ITIC were purchased from Solarmer Co., Ltd. IT-M was synthesized at ICCAS following the reported work.^[39] 1,8-Diiodooctane (DIO, >95.0%) was purchased from Tokyo Chemical Industry Co., Ltd. (TCI). All chemicals were used as received.

GO/NiO_x Film Preparation and Characterization: GO was synthesized by a modified Hummers' method.^[32] 1 g graphite and 0.5 g NaNO₃ were stirred with concentrated H₂SO₄ (98%, 25 mL) under ice bath. Then 3 g KMnO₄ was slowly added into the mixture to prevent a rapid rise of temperature. After stirring under ice bath for 2 h, the reaction mixture was heated to 35 °C for 1 h. The slurry was quenched by a mixture of 200 mL deionized (DI) water and 10 mL concentrated H₂SO₄. Finally, 10 mL H₂O₂ was added to form the L-GO dispersion. The dispersion was centrifuged at 6000 rpm for 10 min. The precipitate was washed by DI water and ethanol for 3 times, respectively. Finally, the precipitate was dispersed into ethanol to get the L-GO in ethanol. For the H-GO synthesis, 1 g graphite was ultrasonic treated with 7.5 mL concentrated H₂SO₄ for 8 h. The pre-oxidized graphite was washed by water and dried before conducting the same reaction process of L-GO to get the H-GO in ethanol. NiO_x NPs were synthesized as reported.^[30,31] The GO and NiO_x solution were blended according to respective ratio. XPS was measured in the ultrahigh vacuum environment using Physical Electronics PHI 5802 with a monochromatic Al K α X-ray source. UPS was characterized by using a He discharged lamp (He I 21.22 eV, Kratos Analytical). AFM was measured by using a tapping mode atomic force microscope (AFM, NT-MDT, Moscow, Russia). Conductivity was extracted by a former reported method.^[45] TEM images were measured by using a Philips CM100 transmission electron microscope. SEM images were measured by using a Hitachi S-4800 FEG scanning electron microscope. Kelvin-probe measurements were conducted by using a SKP5050 Scanning Kelvin Probe System (KP Technology Ltd.) with a resolution 1–3 meV and a fresh highly oriented pyrolytic graphite (HOPG) surface as the reference. 500 points were collected from each sample.

Device Fabrication: For OSCs device fabrication, ITO-coated glass substrates with sheet resistance of 15 Ω sq⁻¹ were cleaned by a standard procedure with detergent, acetone, and ethanol ultrasonic bath for each of 10 min. ZnO was prepared according to a reported sol–gel method.^[46] Sol–gel ZnO solution was spin coated on cleaned ITO at 3000 rpm and then annealed at 200 °C for 1 h in the air. PTB7-Th:PC₇₁BM (10:15 mg mL⁻¹ in CB, with addition of 3% volume ratio DIO) were spin coated on ZnO at 2000 rpm. The thickness of PTB7-Th:PC₇₁BM

was around 100 nm. DIO was removed by a reported methanol washing method.^[47] PBDB-T:ITIC (10:10 mg mL⁻¹ in CB, with addition of 0.5% DIO) and PBDB-T:IT-M (10:10 mg mL⁻¹ in CB, with addition of 1% DIO) was spin coated on ZnO at 2500 rpm followed by annealing at 160 °C for 30 min. GO and GO:NiO_x solution were spin coated onto active layer to form the solution-processed HTLs. Finally, Ag (100 nm) were thermally evaporated through a shadow mask as the top cathode, which defined the device area as 0.06 cm². For GO and GO:NiO_x based devices, GO and GO:NiO_x solution were spin coated on cooled down active layer at 4000 rpm to form the solution-processed HTLs.

Device Characterization: *J*–*V* characteristics were measured using a Keithley 2635 sourcemeter and ABET AM 1.5G solar simulator. The IPCE measurement of OSCs was taken by a home-built IPCE measurement system with a Newport xenon lamp, a monochromator, a preamplifier, and a lock-in amplifier. The diffuse reflection and transmission spectra were measured using a goniometer combined with a charge coupled device spectrometer and integrating sphere. The impedance spectroscopy results were measured by a computer-controlled potentialstat (Autolab PGSTAT320N) from 100 Hz to 1 MHz. A small voltage perturbation (20 mV rms) was applied. Measurements were carried out under 1 sun light intensity illumination at 0.8 V DC bias voltage. The measured data was fitted by Z-view to extract the resistance values. TPC measurements were conducted with a 532 nm 6 ps pulse width laser (130 μ J per pulse at 100 Hz) and recorded by a 4 GHz Keysight MSO9404A digital oscilloscope. TPV measurements were conducted by using the same laser and oscilloscope under illumination with different intensity of light. Lifetime values were extracted by using an exponential decay fitting.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

hole transport layers, non-fullerene solar cells, organic solar cells, quasi-3D nanocomposite, stability

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