

Post-treatment-Free Solution-Processed Non-stoichiometric NiO_x Nanoparticles for Efficient Hole-Transport Layers of Organic Optoelectronic Devices

Fei Jiang, Wallace C. H. Choy,* Xinchun Li, Di Zhang, and Jiaqi Cheng

Organic solar cells^[1] (OSCs) and organic light-emitting diodes^[2] (OLEDs) have gained increasing attention owing to their superior advantages of low-cost, light weight, and flexibility for a variety of optoelectronic applications. One of the critical aspects in fabricating highly efficient and stable optoelectronic device is the design of functional carrier-transport layers between the organic active layer and the electrodes. Typically, effective hole-transport layers (HTLs) suitable for OSC and OLED have to satisfy electrical and optical requirements of i) high electrical conductivity, ii) good optical transparency with wide bandgap, iii) good electron blocking with efficient hole transport.^[3] Poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) with a work function (WF) of 5.10 eV has been widely used as an HTL in conventional organic optoelectronics.^[4] However, there are some issues of its electrical and physical inhomogeneity, such as the long-standing acidic nature of PSS regarding the poor stability and severe degradation of organic optoelectronic devices.^[5] Alternatively, stable transition metal oxides (TMOs) such as MoO₃,^[6] WO₃,^[7] V₂O₅,^[8] and NiO_x^[9] stand out as promising candidates for efficient HTLs. It is essential to develop a wide range of efficient and low-cost TMOs to serve as functional HTLs. Until now, low-temperature solution-processed approaches have been demonstrated for MoO₃,^[6c] WO₃,^[7a] and V₂O₅.^[8]

Differently, the valence band of NiO_x is well aligned with the highest occupied molecular orbital (HOMO) levels of many typical p-type conjugated polymers^[9b,c] for hole transport which is distinct from other typical oxide-based HTL materials, such as MoO₃, WO₃, and V₂O₅. Besides, NiO_x offers promising characteristics as an anode interlayer with wide-bandgap semiconductor properties, good electron blocking, and optical transparency. However, the fabrication of highly efficient NiO_x HTLs from low temperature solution process still remains a great challenge. NiO_x is a cubic rock-salt structure with octahedral Ni²⁺ and O²⁻ sites.^[10] Pure stoichiometric nickel oxide is an excellent insulator with conductivity of 10⁻¹³ S cm⁻¹, while non-stoichiometric NiO_x is a wide-bandgap p-type semiconductor.^[11] The p-type conductivity of NiO_x originates from two positive charge compensation which favored Ni²⁺ vacancies.^[12]

In the early stage, Marks and co-workers^[13] reported a striking performance improvement of OSCs by replacing PEDOT:PSS with NiO_x film using a pulsed-laser deposition technology. From then on, NiO_x HTLs have been reported for organic optoelectronics by various preparation methods, such as thermal evaporation,^[14] sputtering,^[9a] and solution process.^[9d,15] Among them, solution process method is desirable for low-cost, large-scale and roll-to-roll production. Olson and co-workers^[16] proposed a solution-processed NiO_x film as highly efficient HTL in OSCs. The functional NiO_x HTL was fabricated through annealing the precursor film at a temperature of 275 °C. So and co-workers^[17] also presented a NiO_x film by using monoethanolamine (MEA) to react with Ni in ethanol solution followed by thermally converting (275 °C) coordination complexes ions [Ni(MEA)₂(OAc)]⁺ into high-quality NiO_x. Meanwhile, solution-processed NiO_x at 150 °C has also been realized. Ma and co-workers^[18] reported a solution-processed NiO_x film for OSCs using oxygen-plasma treatment and annealing treatment simultaneously. Zhang et. al. reported that the colloidal NiO nanoparticles are used as the anode buffer layer in OSCs without high temperature post-annealing to induce decomposition and crystallization.^[9f] For a long period, the studies of NiO_x HTLs were focused on utilizing sol-gel methods with thermally converting the precursor solution to NiO_x thin films. In the process of device fabrications, thermal annealing process and oxygen-plasma treatment may be simultaneously required, which hinders the applications of NiO_x in flexible optoelectronic devices. Instead of precursor method, an approach to significantly reduce the processing temperature of TMO HTLs is to directly use high-quality colloidal nanoparticles (NPs). Jin and co-workers demonstrated a facile and general strategy based on ligand protection for the synthesis of unstable colloidal NiO nanocrystals.^[19] Fattakhova-Rohlfing and co-workers described the preparation of ultrasmall, crystalline, and dispersible NiO nanoparticles, which are promising candidates as catalysts for electrochemical oxygen generation.^[9e]

Herein, we will demonstrate a facile chemical precipitation method which is robust and simple for direct preparation of high-quality non-stoichiometric NiO_x NPs. Remarkably, by using this method, NiO_x HTL film can be formed through a room-temperature solution process without any post-treatments during device fabrication. Interestingly, our results show that the NiO_x NPs film can function as effective HTLs over a wide range of annealing temperatures from room temperature to 150 °C. Very good optoelectronic performances utilizing the NiO_x NPs film as HTLs have been demonstrated in both OSCs and OLEDs. High power conversion efficiency (PCE) of 9.16% (best 9.28%) was achieved in OSCs using NiO_x

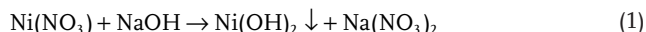
Dr. F. Jiang, Dr. W. C. H. Choy, X. Li,
Dr. D. Zhang, J. Cheng
Department of Electrical and Electronic Engineering
The University of Hong Kong
Pokfulam Road, Hong Kong, PR China
E-mail: chchoy@eee.hku.hk



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HTL. For an OLED device using the NiO_x HTL, better performance was also observed compared with the device using the conventional PEDOT:PSS as the HTL. Consequently, the capability to form solution-processed NiO_x HTLs at room temperature can favor wide-range applications of large-area and flexible optoelectronics.

NiO_x NPs were obtained by a chemical precipitation method using commercially available materials of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NaOH . The raw materials were easily dissolved in deionized water. After dropwise adding NaOH , the clear green aqueous solution turned turbid. Through accurately controlling the solution pH value to 10, ultrafine nickel hydroxide $\text{Ni}(\text{OH})_2$ was obtained in a considerable yield. The obtained apple-green product was dried and calcined at 270 °C for 2 h in air to decompose into dark-black NiO_x NPs. This calcination procedure was based on the thermal decomposition of $\text{Ni}(\text{OH})_2$ aiming to produce non-stoichiometric NiO_x NPs. The detailed synthesis procedure can be found in Experimental Section. Reaction 1 and 2 illustrate the chemical reactions in this procedure of non-stoichiometric NiO_x NPs:



It is worth mentioning that when the calcination temperature is below 270 °C nickel hydroxide ($\text{Ni}(\text{OH})_2$) will not be completely decomposed. Since $\text{Ni}(\text{OH})_2$ is electrically insulated and not easily dispersed in solvent, the products are not likely to form effective HTL. On the contrary, when the temperature is above 270 °C, the high temperature calcined crystalline NiO_x cannot form uniform films owing to the very poor ability to disperse in solvent. Therefore, in the synthesis procedure of NiO_x NPs, the calcination temperature was kept at 270 °C. The product of NiO_x NPs and corresponding dispersion are shown in Figure S1 in the Supporting Information. The NiO_x NPs dispersion exhibits remarkable stability. Figure S2 in the Supporting Information shows the dispersion in ambient environment for 15 d, which is still well dispersed without any precipitation.

X-ray diffraction (XRD) was performed to investigate the NiO_x crystal structure and dimension (see Figure S1, Supporting Information). The diffraction peaks reveals NiO_x as a cubic crystal structure. Three prominent characteristic diffraction peaks of NiO_x cubic structure appears at 2θ which equals to 37.11°, 43.08°, and 62.25°, respectively. Among them, the strongest diffraction peak is observed when 2θ is 43.08°, which demonstrates that the NiO_x NPs have already crystallized. The diameter (D) of the NiO_x NPs is calculated by the Debye–Scherrer equation, $D = 0.89\lambda/(\beta\cos\theta)$,^[20] from which we can determine that the average crystalline size is 4 nm. Meanwhile, as shown in the transmission electron microscopy (TEM) results of Figure 1, the NiO_x nanoparticles with a good uniformity can be obtained. The particle size is about 3–5 nm, which is consistent with the X-ray diffractometry line broadening (XRD-LB) results, and the TEM image in Figure S3 in the Supporting Information shows that there was no obvious change of the 4 nm NiO_x nanoparticles after stored in the ambient environment over 120 d.

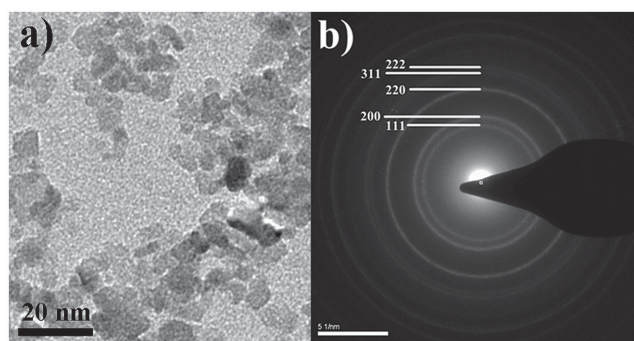


Figure 1. a) TEM image of non-stoichiometric NiO_x NPs with scale bar of 20 nm. b) XRD-LB of NiO_x .

The optical, electrical, and surface properties of NiO_x thin films were studied by using different techniques. The NiO_x dispersion was prepared by dispersing the NiO_x NPs into water to a desired concentration from 5 to 50 mg mL⁻¹. The NiO_x dispersion was spin-coated on precleaned indium tin oxide (ITO) glass. The resultant NiO_x films were annealed at different temperatures (from no annealing to 300 °C) under ambient environment. The thicknesses of corresponding NiO_x films are ca. 4 nm (5 mg mL⁻¹), 12 nm (15 mg mL⁻¹), 20 nm (30 mg mL⁻¹), and 32 nm (50 mg mL⁻¹), which were measured by ellipsometry. Optical transparency is an essential characteristic to determine if the NiO_x film is suitable for a good HTL. Even the 32-nm NiO_x film can reach a transparency over 83%, as shown in Figure S4 in the Supporting Information. We also measured the optical constants (refractive index (n) and extinction coefficient (k)) of the NiO_x film obtained by fitting spectroscopic ellipsometry data, as shown in Figure S5 in the Supporting Information. The optical bandgap (E_{opt}) for NiO_x film derived by following Tauc's formula (Figure S6, Supporting Information) is about 3.64 eV, which is consistent with the commonly reported values.^[13,16] Meanwhile, atomic force microscopy (AFM) analysis was also investigated in Figure S7 in the Supporting Information with a slightly increased root-mean-square roughness of 3.61 nm.

To demonstrate the NiO_x film's properties to perform as highly efficient HTL over a wide range of temperatures, X-ray photoelectron spectroscopy (XPS) analysis was used to investigate the chemical component of the NiO_x films processed under different temperatures. The Ni 2p_{3/2} and O 1s characteristic peaks of the NiO_x film in XPS spectra were shown in Figure 2 and Figure S8 in the Supporting Information. The background was subtracted from the XPS spectra by using a Shirley-type background subtraction. The decomposition of the XPS spectrum demonstrated that the Ni 2p spectrum can be well fitted by two different oxidation states (Ni^{2+} and Ni^{3+}) in the form of a Gaussian function. When the NiO_x film received no annealing treatment and other UVO or O₂-plasma treatment, rather remarkable contributor peaks of Ni^{3+} state such as NiOOH (Ni 2p_{3/2} at 856.3 eV and O 1s at 532.1 eV), Ni_2O_3 (Ni 2p_{3/2} at 855.0 eV, and O 1s 530.8 eV), and another Ni^{2+} state NiO (Ni 2p_{3/2} at 853.6 and O 1s 529.1 eV) appeared. As calculated from the integral area in the Ni 2p spectrum, the three composition concentration ratio of NiOOH , Ni_2O_3 , and NiO is about 1.13:1.22:1 and the atomic ratio between Ni and

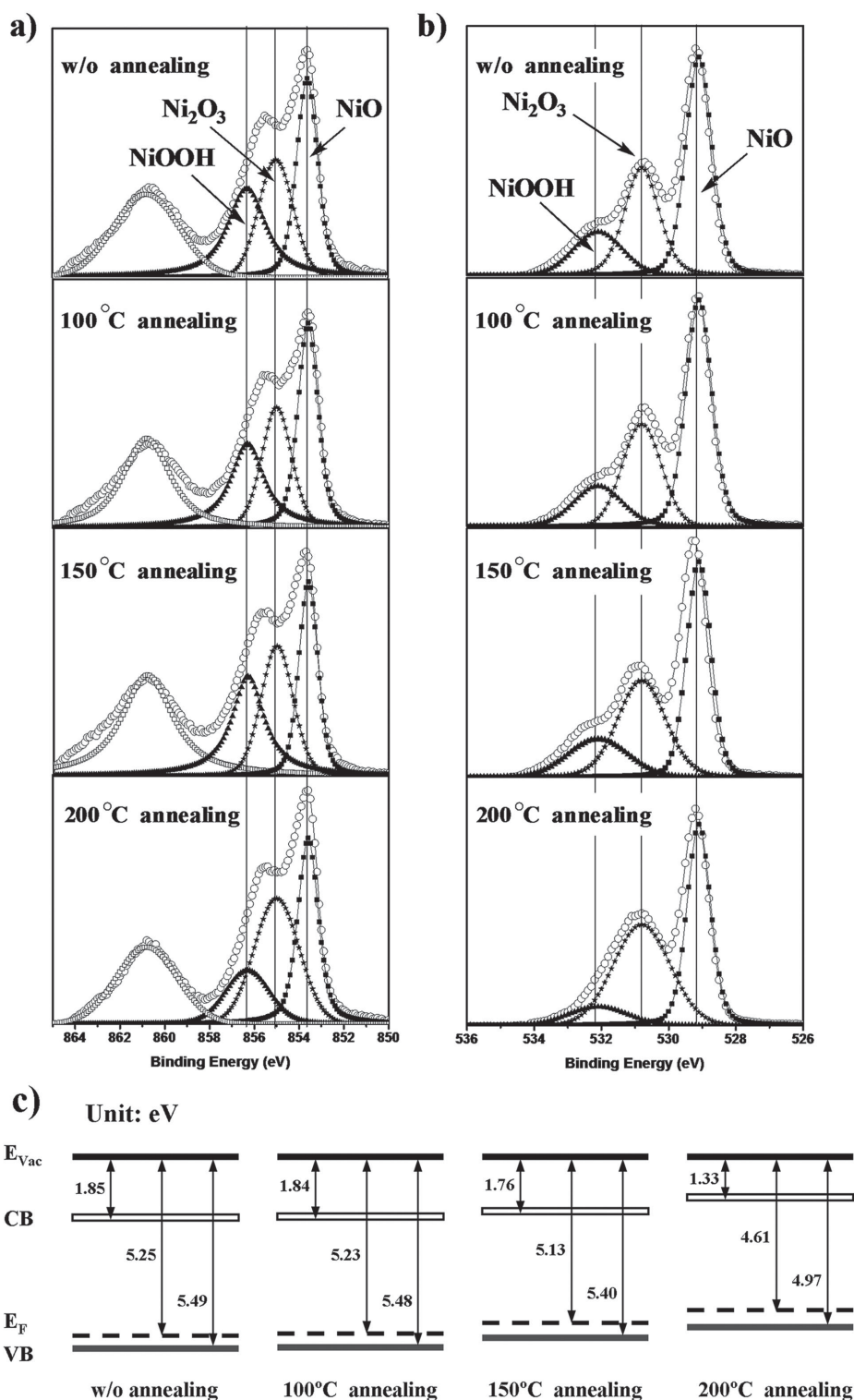


Figure 2. XPS results of NiO_x films a) Ni $2p_{3/2}$, b) O $1s$ core level peaks. c) Energy-level diagrams of the investigated NiO_x films (20 nm) under different processing temperatures.

O is about 1:1.14, which illustrates that the composition of the nickel oxide is non-stoichiometric. The result is completely different from the previously reported ones that only additional

simultaneous O_2 -plasma or UVO treatment or annealing treatment can lead to the formation of Ni^{3+} state in NiOOH species.^[10,21] Meanwhile, after 100 °C annealing treatment of the

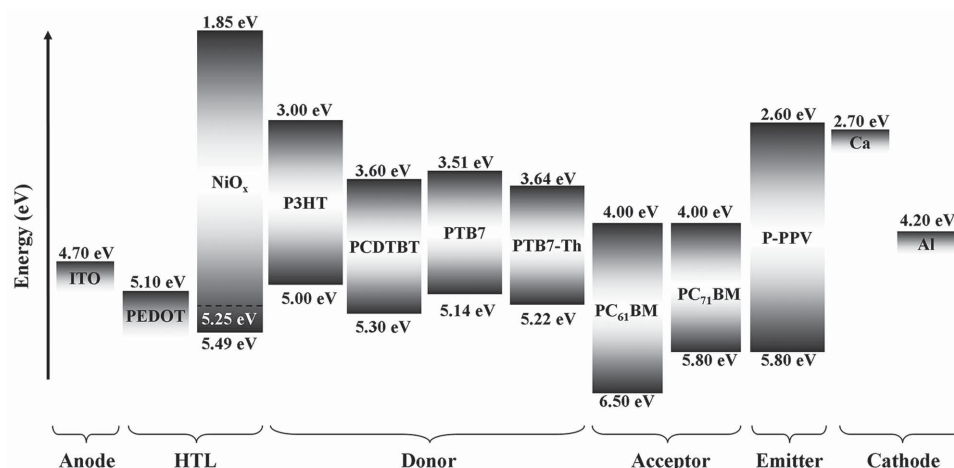


Figure 3. Detailed energy levels of different materials used in OSCs and OLEDs.

NiO_x film, no apparent shift or change of the dominant peaks in the Ni 2p_{3/2} and O 1s spectra was observed, which indicates that the major composition of the NiO_x thin films remains unchanged. However, when the annealing temperature is above 200 °C, the composition of NiO_x film changes such that NiOOH peaks will be weakened and the Ni₂O₃ peaks will be strengthened in the XPS spectra in Figure 2a,b. The variation in characteristic peaks by 200 °C annealing suggests a partial composition conversion from NiOOH to Ni₂O₃. Upon high-temperature annealing, the change in the non-stoichiometric NiO_x film composition where excessive Ni₂O₃ is generated can have a detrimental impact on the electrical properties and thus the device performance of the NiO_x HTL (as will be discussed later). As a result, in addition to room temperature, our NiO_x NPs are capable to form effective and stable HTL over a wide range of annealing temperatures up to 150 °C without inducing detrimental changes in composition.

Ultraviolet photoelectron spectroscopy (UPS) was utilized to investigate the energy band structures of the as-deposited and annealed NiO_x films at different temperatures. As shown in Figure S9 in the Supporting Information, it can be observed from the UPS results that the NiO_x film secondary-electron cut-off edges strongly depended on the annealing temperature. This indicated that the Fermi level (E_F) of NiO_x film is related to the annealing temperature. As calculated from the UPS results, the band diagram parameters including vacuum level (E_{vac}), conduction band (CB), E_F , and valence band (VB) are shown in Figure 2c. The as-deposited NiO_x films gave an E_F of 5.25 eV. The appropriate E_F of post-treatment-free NiO_x film favors Ohmic contact formation to the HOMO of donor materials in a bulk heterojunction (BHJ). The CB of NiO_x, which is 1.85 eV from vacuum level, allows NiO_x to serve as an effective electron blocking layer to suppress electron recombination at the anode. The VB is 0.24 eV below the E_F , indicating that NiO_x is a typical p-type semiconductor. After 150 °C annealing treatment, the E_F of the film was slightly changed to 5.13 eV, accompanied with CB of 1.76 eV and VB of 5.40 eV, which was almost the same with the as-deposited NiO_x film. However, when the NiO_x film was annealed at 200 °C, the E_F of the NiO_x significantly decreased from 5.25 to 4.61 eV. Both the CB and VB

decreased to 1.33 and 4.97 eV, respectively, which indicated that the electrical properties of the film have been modified. Due to the larger energy mismatch with the HOMO of the donor materials (usually above 5.0 eV), the NiO_x film annealed at 200 °C can no longer function as an effective HTL (as will be verified by device characterization later). These results are consistent with the XPS results described previously, where the NiO_x and oxidation states of the metal oxide have been changed at relatively high temperature (over 200 °C). The E_F changes of the NiO_x films were also reconfirmed by Kelvin probe measurement results. The WF variation along with annealing temperature from no annealing to 300 °C annealing treatment of the films is plotted in Figure S10 in the Supporting Information. The hole mobility of NiO_x film of $3.75 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was also investigated and shown in Figure S11 in the Supporting Information.

To demonstrate that the NiO_x film can function as an effective HTL, OSCs have been fabricated and characterized with the structures shown in Figure S12 in the Supporting Information. As plotted in Figure 3, four polymers with different bandgaps, P3HT, PCDTBT, PTB7, and PTB7-Th with HOMO energy levels of 5.00, 5.30, 5.14, and 5.22 eV, respectively, were used to examine the effect of NiO_x film as an efficient HTL. The molecular structures of polymers were drawn in Figure S13 in the Supporting Information. Device optimization was mainly focused on fine adjustment of the thickness and annealing temperature of the NiO_x film. The robust polymer P3HT ($E_{gap} = 2.00 \text{ eV}$) was selected as the donor material to investigate these two parameters. OSCs with conventional structure of ITO/NiO_x/P3HT:PC₆₁BM (220 nm)/Ca (20 nm)/Al (100 nm) were fabricated. OSCs with PEDOT:PSS (34 nm) HTLs were also compared as control. The thickness of the NiO_x film was adjusted by spin-coating NiO_x with different concentrations (from 5 to 50 mg mL⁻¹). In Table S1 and Figure S14 in the Supporting Information, the NiO_x-buffered OSCs with an optimized thickness of 20 nm showed an average J_{SC} of 9.67 mA cm⁻², V_{OC} of 0.588 V, and a FF of 67.20% to yield a PCE of 3.81%, which is comparable with the device performances by PEDOT:PSS HTLs (J_{SC} 9.36 mA cm⁻², V_{OC} of 0.620 V, FF of 65.04%, and PCE of 3.78%). The V_{OC} of the NiO_x-based devices slightly decreased 0.03 V, which may be caused by the energy level difference

Table 1. Device performance of different annealing temperatures of NiO_x-based OSCs with conventional structure of ITO/NiO_x/P3HT:PC₆₁BM/Ca/Al.

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

of 0.25 eV between the work function of NiO_x layer and the HOMO of P3HT.^[22] The device performance of NiO_x HTLs was compensated by an offset of lower series resistance (*R_s*) compared with the PEDOT:PSS HTLs. The slightly increased *J_{SC}* and FF may be ascribed to lower *R_s* and enhanced conductivity. Thus, the overall PCE of the NiO_x-based devices is comparable with that of PEDOT:PSS-based devices. Note that the optimized NiO_x thickness of 20 nm was thicker than that the commonly reported thickness of optimized NiO_x film of 5–10 nm,^[13,17] which indicated that our NiO_x film has superior electrical conductivity and optical transparency. We have also investigated the stability of the NiO_x-based OSCs. As shown in Figure S15 in the Supporting Information, NiO_x-based OSCs indicate the improved stability compared with PEDOT:PSS-based devices.

The current density–voltage (*J*–*V*) characteristics of P3HT devices using NiO_x with different annealing temperatures were plotted in Table 1 and Figure S16 in the Supporting Information. It can be clearly seen that all the devices show similar performances from w/o annealing to 150 °C. The results confirm that the film has mostly the same composition and WF below 150 °C annealing temperature, which is consistent with XPS and UPS analytic results. Meanwhile, annealing temperature over 200 °C significantly degrades the device performance due to the mismatch of WF of the NiO_x to the HOMO of P3HT. Our results demonstrate that the NiO_x films in this work can function as effective HTLs without any post-treatment, as well as offer a widely temperature applicability from room temperature to 150 °C.

The optimized NiO_x films were then applied to low-bandgap polymers such as poly[*N*-9'-heptadecan-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] PCDTBT (*E_{gap}* = 1.70),^[23] with a large *V_{OC}* due to the ionization potential (IP) higher than P3HT, to demonstrate its applicability to work

as efficient HTL for low-bandgap polymers. The WF of NiO_x (5.25 eV) is very close to the HOMO level of the donor polymer PCDTBT (5.30 eV), as seen in Figure 3, which can enhance the hole extraction from the photoactive layer. A comparison of the illuminated *J*–*V* measurements for both NiO_x and PEDOT:PSS-based devices is presented in Table 2 and Figure 4a. The PCDTBT:PC₇₁BM devices employing PEDOT:PSS HTL exhibited an average *V_{OC}* of 0.878 V, *J_{SC}* of 10.81 mA cm⁻², and FF of 57.52% to yield a PCE of 5.45%. While utilizing the NiO_x thin film as HTLs, a remarkable 17.8% increment in device performance accompanied with an average *V_{OC}* of 0.906 V, *J_{SC}* of 11.36 mA cm⁻², FF of 62.35%, and PCE of 6.42% was realized. The incident photon-to-current conversion efficiency (IPCE) of PCDTBT-based devices were plotted in Figure S17 in the Supporting Information. The significant enhancement was mainly due to the ability of NiO_x to form favorable energetic alignment with the active layer, as compared with the alignment formed with PEDOT:PSS. This result is comparable with some reported device performance in the literature for NiO_x films prepared by other techniques.^[18,19] In addition, different from PEDOT:PSS, the *E_{opt}* of the NiO_x is 3.64 eV, indicating that the conduction band is 1.85 eV above the LUMO of the donor PCDTBT (3.60 eV) and acceptor PC₇₁BM (4.00 eV). This energetic orientation provides 1.75–2.15 eV energy barriers to electron collection at the anode and thus demonstrating effective electron-blocking properties of the NiO_x,^[16] which contributes to an increment in *V_{OC}* through reducing leakage current and photocurrent recombination^[24] at the anode. The series resistance for the devices with NiO_x HTLs and the PEDOT:PSS reference devices was calculated to be 2.65 and 4.46 Ω cm², respectively. Improved contacts between active layer and anode, which facilitates free carriers extraction and transport therefore enhanced both *J_{SC}* and FF in the devices with NiO_x HTLs.^[16,25]

Table 2. Device performances of PEDOT:PSS or NiO_x-based OSCs using different-bandgap polymers with PC₇₁BM.

Device structures	V _{OC} [V]	J _{SC} [mA cm ⁻²]	FF [%]	R _s [Ω cm ²]	PCE [%]
PEDOT:PSS/PCDTBT	0.878 ± 0.003	10.81 ± 0.22	57.52 ± 0.79	4.46 ± 0.10	5.45 ± 0.18
NiO _x /PCDTBT	0.906 ± 0.002	11.36 ± 0.31	62.35 ± 0.72	2.65 ± 0.06	6.42 ± 0.20
PEDOT:PSS/PTB7	0.735 ± 0.003	15.84 ± 0.30	63.63 ± 1.05	2.62 ± 0.09	7.41 ± 0.16
NiO _x /PTB7	0.744 ± 0.004	16.10 ± 0.27	66.42 ± 0.66	1.74 ± 0.05	7.96 ± 0.20
PEDOT:PSS/PTB7-Th	0.782 ± 0.003	18.03 ± 0.21	60.97 ± 0.60	3.37 ± 0.08	8.60 ± 0.16
NiO _x /PTB7-Th	0.794 ± 0.002	18.32 ± 0.17	63.10 ± 0.45	2.20 ± 0.10	9.16 ± 0.12

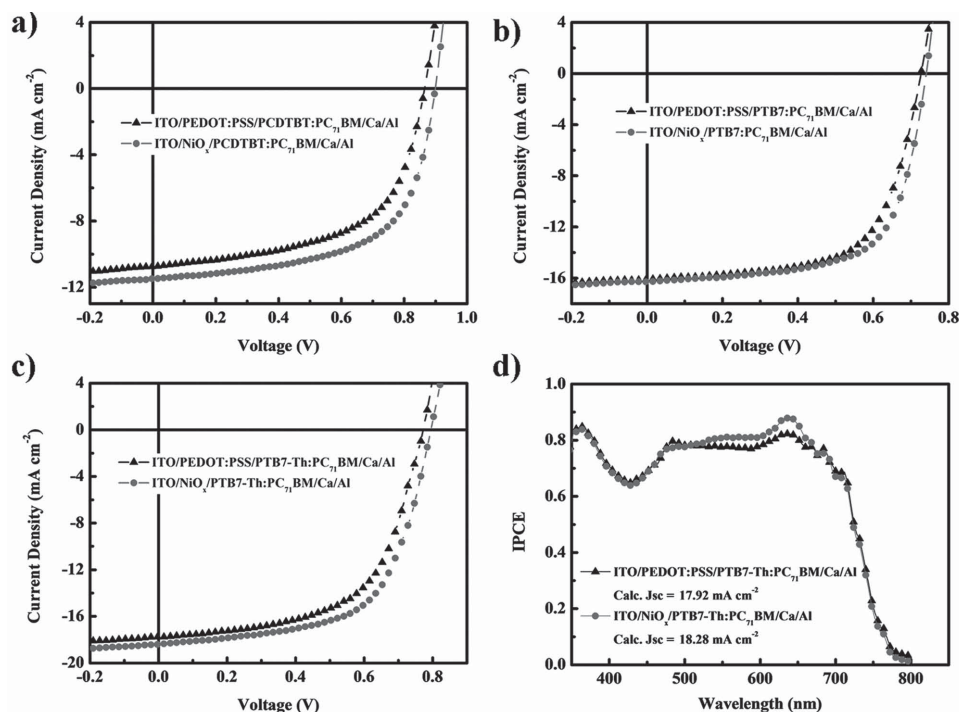


Figure 4. Representative current density–voltage (J – V) characteristics under AM 1.5G solar spectrum with a light intensity of 100 mW cm^{-2} for OSCs. The device structures are a) ITO/ NiO_x or PEDOT:PSS/PCDTBT:PC₇₁BM/Ca/Al; b) ITO/ NiO_x or PEDOT:PSS/PTB7:PC₇₁BM/Ca/Al; c) ITO/ NiO_x or PEDOT:PSS/PTB7-Th:PC₇₁BM/Ca/Al; d) IPCE measurements for ITO/ NiO_x or PEDOT:PSS/PTB7-Th:PC₇₁BM/Ca/Al.

To demonstrate the general viability of NiO_x as efficient HTL for low-bandgap polymers, two PTB-derivatives, PTB7 ($E_{\text{gap}} = 1.63 \text{ eV}$) and PTB7-Th ($E_{\text{gap}} = 1.58 \text{ eV}$) were also selected to fabricate standard OSCs devices. Figure 4b,c showed the J – V curves of the PTB7 and PTB7-Th-based BHJ OSCs with the PEDOT:PSS or NiO_x HTLs, respectively. For PTB7:PC₇₁BM-based devices, device performance with NiO_x HTL had a V_{OC} of 0.744 V , J_{SC} of 16.10 mA cm^{-2} , FF of 66.42% , and PCE of 7.96% , which was slightly higher than PEDOT:PSS devices (V_{OC} of 0.735 V , J_{SC} of 15.84 mA cm^{-2} , FF of 63.63% , and PCE of 7.41%). The results showed the same energy alignment ability with low-bandgap polymer PTB7-based device as confirmed. The IPCE curves based on PTB7 devices were plotted in Figure S18 in the Supporting Information. The NiO_x HTL calculated J_{SC} (16.05 mA cm^{-2}) from the IPCE spectra matched well with the J_{SC} (16.10 mA cm^{-2}) recorded from the current density–voltage (J – V) curves. The maximum IPCE spectrum in NiO_x devices is over 70% , indicative of highly efficient photon-to-electron conversion. For PTB7-Th:PC₇₁BM-based OSCs, the device with NiO_x HTL had an average PCE of 9.16% with V_{OC} of 0.794 V , J_{SC} of 18.32 mA cm^{-2} , and FF of 63.10% , which had a noticeable enhancement compared with the PCE of the control device using PEDOT:PSS (PCE of 8.60% with a V_{OC} of 0.782 V , J_{SC} of 18.03 mA cm^{-2} and FF of 60.97%). The R_s with NiO_x HTLs and PEDOT:PSS devices were 2.20 and $3.37 \Omega \text{ cm}^2$, respectively. Rationalized by a similar rule as noted above, the reduced R_s resulted in better electrical contact thus improved FF, which was beneficial for the device performance. The OSCs with the 20 nm NiO_x HTL showed higher IPCE at wavelengths of 500 – 700 nm compared with PEDOT:PSS HTL, as shown in

Figure 4d. The IPCE maximum was over 80% , indicating an effective charge-carrier generation and collection property. The calculated J_{SC} 18.28 mA cm^{-2} from the IPCE spectra is consistent with the J_{SC} 18.32 mA cm^{-2} recorded from the J – V measurements. Consequently, the efficient HTL property of our low-temperature processing NiO_x comparable with PEDOT:PSS has been demonstrated with different-bandgap polymeric donors in OSCs.

Finally, OLEDs employing solution-processed NiO_x as HTLs were fabricated with a conventional structure of ITO/ NiO_x /emission layer (80 nm)/Ca (20 nm)/Al (100 nm), where the emission layer is poly[2-(4-(3',7'-dimethyloctyloxy)-phenyl)-p-phenylene-vinylene] (P-PPV).^[26] OLEDs with PEDOT:PSS (34 nm) HTLs were also compared as a control. The energy levels of different materials in the OLEDs are plotted in Figure 3. A detailed description of the device fabrication was provided in the Experimental Section. The current-density–voltage–luminance density (J – V – L) characteristics and luminance–efficiency–current density–luminance (LE – J – L) characteristics for devices were shown in Figure 5a,b, respectively. The NiO_x films-based devices had a turn-on voltage of 3.75 V , a maximum brightness of $26\,630 \text{ cd m}^{-2}$ at 11.25 V , a current efficiency was 9.72 cd A^{-1} , which was slightly higher than that of PEDOT:PSS-based devices with a maximum brightness of $23\,100 \text{ cd m}^{-2}$ at 12.50 V , a current efficiency was 9.20 cd A^{-1} . Our results revealed that OLEDs with efficient NiO_x HTLs can be comparable and competitive with that of PEDOT:PSS HTLs.

In conclusion, NiO_x NPs have been demonstrated as highly efficient HTLs in optoelectronic applications based on several

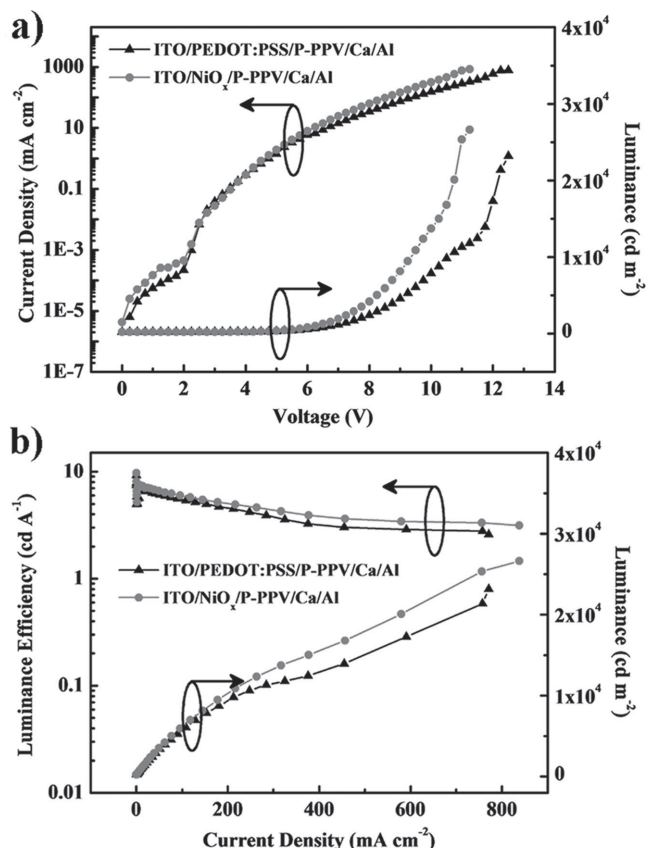


Figure 5. Representative a) J - V - L and b) LE - J - L characteristics of OLEDs, triangle markers for PEDOT:PSS device, circle markers for NiO_x device.

donor polymers with different HOMO energy levels. Compared with conventional PEDOT:PSS-buffered devices, the NiO_x -buffered OSCs and OLEDs achieved improved or comparable device performances. The excellent optoelectronic performances in our work can be realized by a room-temperature process without any post-treatments for forming the HTL films. Owing to the desirable WF, NiO_x is therefore a promising candidate as an efficient HTL for high IP donor materials in order to maximize device performances. The NiO_x HTLs can be applied to various optoelectronic devices, including not only OSCs but also OLEDs. The NiO_x HTLs demonstrate in this work can pave the way toward industrial scalable roll-to-roll manufacturing of optoelectronics.

Experimental Section

Non-stoichiometric NiO_x NPs Synthesis: $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mol) (Aladdin Reagent) was dispersed in 100 mL deionized water to obtain a dark green solution. The pH of the solution was adjusted to 10 by adding a NaOH solution (10 mol L^{-1}). After stirring for 5 min, the colloidal precipitation was thoroughly washed with deionized water twice, and dried at 80°C for 6 h. The obtained green powder was then calcined at 270°C for 2 h to obtain a dark-black powder. The 4-nm sized NPs were dispersed in deionized water to desired concentrations.

Materials: All the chemicals and materials were purchased and used as received unless otherwise noted. PEDOT:PSS (Baytron A1 4083) was purchased from H. C. Starck GmbH, Germany. P3HT, PC_{61}BM , and

PC_{71}BM were purchased from Solarmer Co., Ltd. PCDTBT, PTB7, and PTB7-Th were purchased from 1-Materials Co., Ltd, and P-PPV was purchased from Canton Oledking Optoelectronic Materials Co., Ltd.

Device Fabrication of OSCs and OLEDs: For OSCs device fabrications, ITO-coated glass substrates with sheet resistance of $15 \Omega \text{ sq}^{-1}$ were cleaned and then ultraviolet-ozone treated for 15 min. PEDOT:PSS (Baytron A1 4083) was spin-coated with thickness of 34 nm and then dried at 120°C for 20 min. The NiO_x was spin-coated with different concentrations (from 5 to 50 mg mL^{-1}) to obtain different thickness of NiO_x film. The NiO_x films were then annealed from w/o treatment to 300°C , respectively for 10 min on a hotplate in air. For P3HT: PC_{61}BM (1:1, 40 mg mL^{-1} in 1,2-dichlorobenzene (DCB)) as active layer with a thickness about 220 nm, solvent annealing was conducted and then the samples were annealed at 130°C for 10 min. For PCDTBT: PC_{71}BM (1:4, 35 mg mL^{-1} in DCB) as active layer, it has a thickness about 80 nm; for PTB7 or PTB7-Th: PC_{71}BM (1:1.5, 25 mg mL^{-1} in CB, with addition of 3% 1,8-diiodooctane (DIO) in volume concentration), the active layer has a thickness about 100 nm. For OLEDs, 80 nm P-PPV layer (7 mg mL^{-1} in toluene) was spin-coated on top of the PEDOT:PSS or NiO_x buffer layer. Ca. (20 nm)/Al (100 nm) were finally thermally evaporated as the cathode with a device area of 6 mm^2 defined by a shadow mask.

Characterizations: XPS measurement was carried out using a Physical Electronic 5600 multitechnique system. All the spectra were adjusted according to the standard value of C 1s peak at $(284.6 \pm 0.1) \text{ eV}$. UPS were obtained using a He discharged lamp (He I 21.22 eV , Kratos Analytical) with an experimental resolution of 0.025 eV . AFM was measured by using NanoScope III (Digital Instrument) in the tapping mode. Transmission electron microscopy (TEM) was performed using a Philips Tecnai G2 20 S-TWIN. Transmittance measurement was performed under a dark ambient environment by using spectroscopic ellipsometry (Woollam). Current density-voltage (J - V) characteristics were obtained by using a Keithley 2635 source meter and Newport AM 1.5G solar simulator with 100 mW cm^{-2} illumination. The J - V and luminance-voltage (L - V) data of the prepared devices were measured with a Keithley 2400 and a calibrated Si photodiode.

Supporting Information

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

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