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(54) SIMPLE APPROACH FOR PREPARING POST-TREATMENT-FREE SOLUTION PROCESSED NON-STOICHIOMETRIC NIOX NANOPARTICLES AS CONDUCTIVE HOLE TRANSPORT MATERIALS

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(57) ABSTRACT

High-quality non-stoichiometric NiO_x nanoparticles are synthesized by a facile chemical precipitation method. The NiO_x film can function as an effective p-type semiconductor or hole transport layer (HTL) without any post-treatments, while offering wide temperature applicability from room-temperature to 150° C. For demonstrating the potential applications, high efficiency is achieved in organic solar cells using NiO_x HTL. Better performance in NiO_x based organic light emitting diodes is obtained as compared to devices using PEDOT:PSS. The solution-processed NiO_x semiconductors at room temperature can favor a wide-range of applications of large-area and flexible optoelectronics.

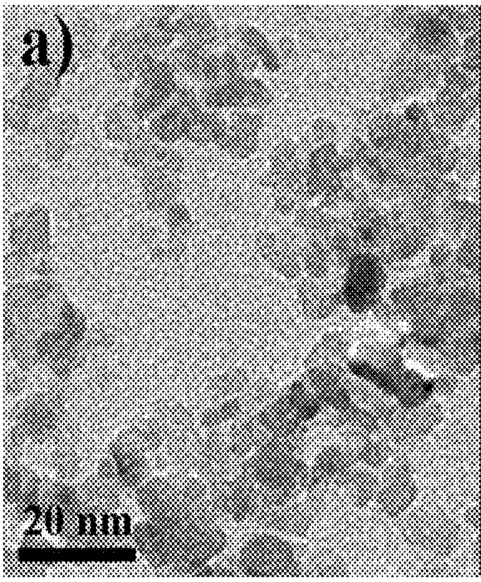


Figure 1(a)

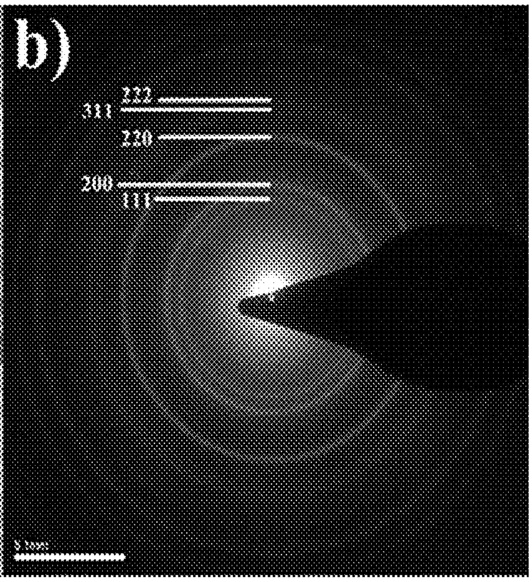


Figure 1(b)

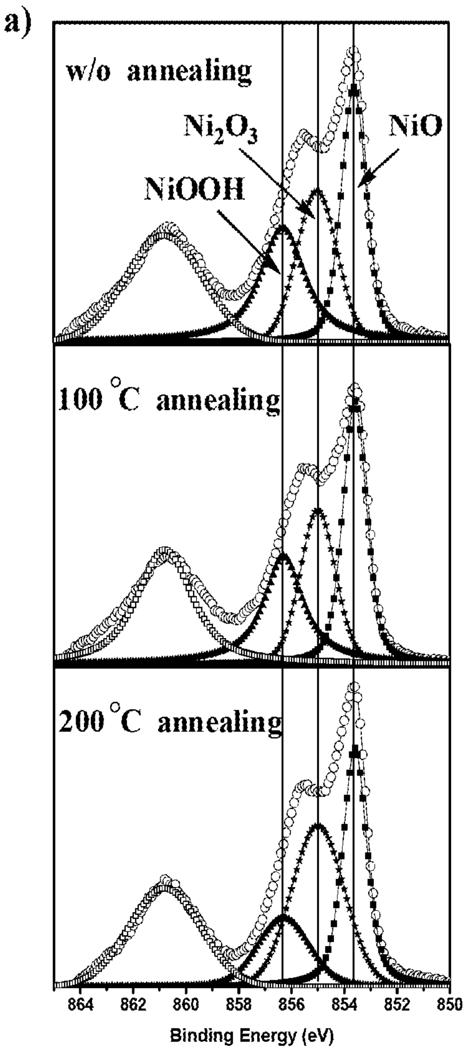


Figure 2(a)

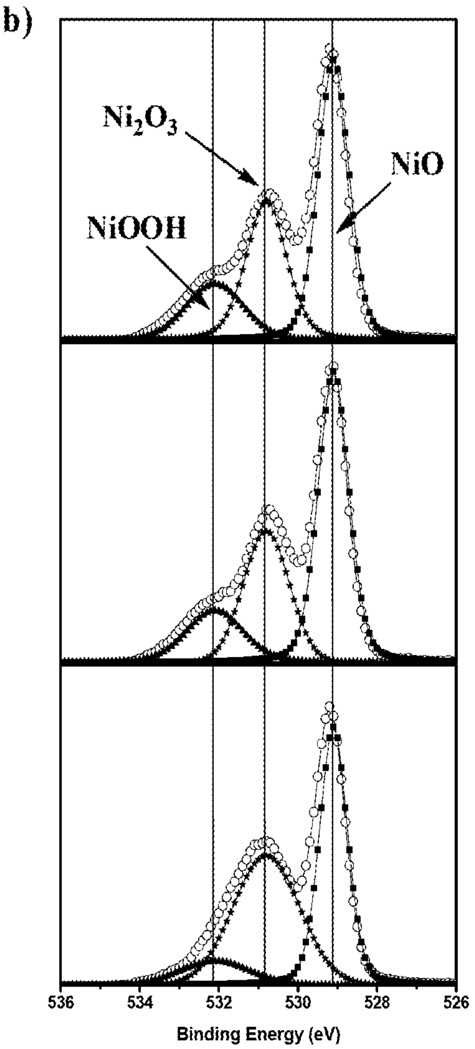


Figure 2(b)

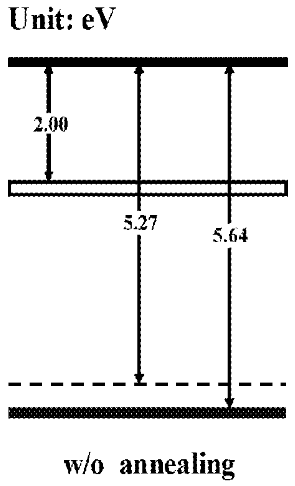


Figure 3(a)

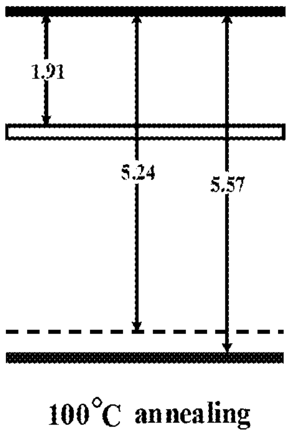


Figure 3(b)

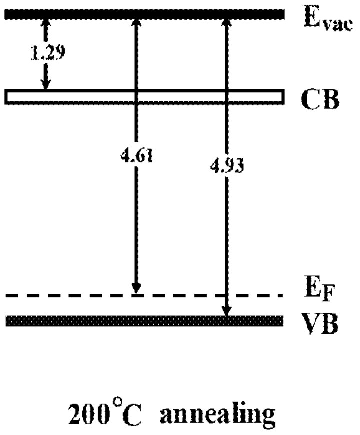


Figure 3(c)

Figure 4(a)

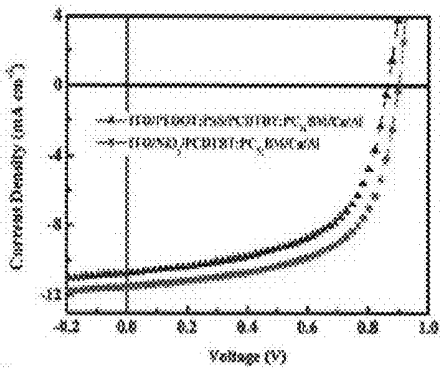
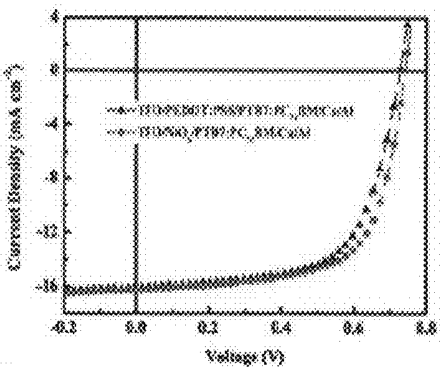


Figure 4(b)



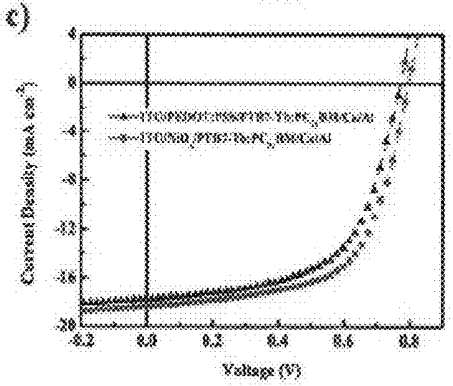


Figure 4(c)

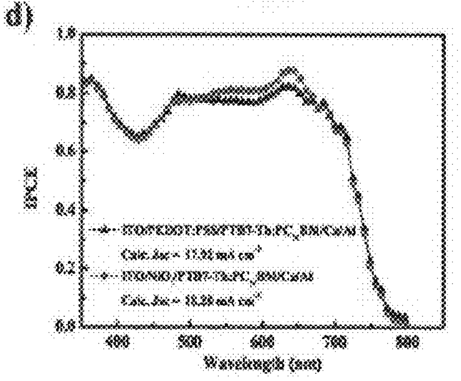


Figure 4(d)

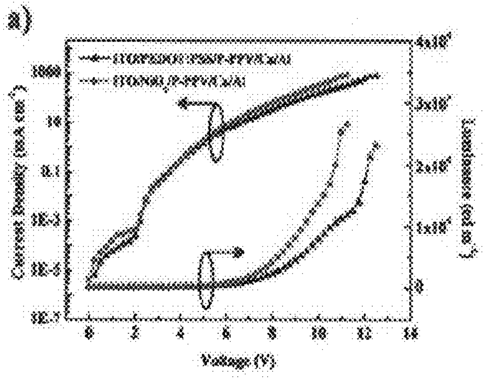


Figure 5(a)

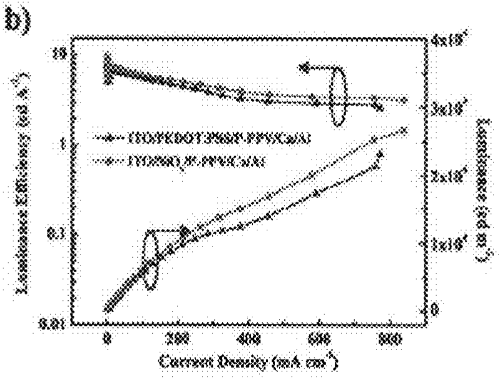


Figure 5(b)

SIMPLE APPROACH FOR PREPARING POST-TREATMENT-FREE SOLUTION PROCESSED NON-STOICHIOMETRIC NIOX NANOPARTICLES AS CONDUCTIVE HOLE TRANSPORT MATERIALS

FIELD OF THE INVENTION

[0001] The present invention relates to an improved method for providing hole transport layers for optoelectronic devices.

BACKGROUND OF THE INVENTION

[0002] Organic solar cells (OSCs) and organic light emitting diodes (OLEDs) have gained increasing attention owing to their superior advantages of low cost, light weight, and flexibility of a variety of optoelectronic applications. One of the critical aspects in fabricating highly efficient and stable optoelectronic devices is the design of the functional carrier transport layers between the organic active layer and the electrodes. Typically, effective hole transport layers (HTLs) in optoelectronic devices have to satisfy electrical and optical requirements of (1) high electrical conductivity, (2) good optical transparency with wide bandgap, (3) good electron blocking with efficient hole transport. Poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) with a work function (WF) of 5.10 eV has been widely used as HTL in optoelectronic devices, such as conventional organic optoelectronics. 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. Alternatively, stable transition metal oxides (TMOs) such as MoO_3, WO_3, V_2O_5 and NiO_x, 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 MoO_3, WO_3, and V_2O_5.

[0003] Differently, the valence band of NiO_x is well aligned with the highest occupied molecular orbital (HOMO) levels or valence band of many typical organic and inorganic semiconductors, respectively, for hole transport which is distinct from other typical oxide based HTL materials such as MoO_3, WO_3 and V_2O_5. 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 by a low temperature solution process still remains a great challenge. NiO_x is a cubic rock-salt structure with octahedral Ni^{2+} and O^{2-} sites. 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. Due to the positive charge compensation induced by thermodynamically favored cation vacancies, the non-stoichiometric NiOx shows a p-type conduction property.

[0004] The conventional ways of fabricating NiO_x usually involve thermal annealing processes and oxygen-plasma treatment, which hinders the applications of NiO_x in flexible optoelectronic devices (i.e. OLED/OSC).

BRIEF SUMMARY OF THE INVENTION

[0005] The present invention is directed to a chemical precipitation method for synthesizing NiO_x nanoparticles. The synthesized NiO_x can be used for producing NiO_x HTL film in a room temperature solution process without any post-treatments during device fabrication.

[0006] Embodiments of the subject invention are drawn to a new approach, i.e., a chemical precipitation and combustion method creating HTLs is achieved by forming non-stoichiometric NiO_x nanoparticles (NPs). The combustion in air promotes oxygen interactions with a nickel-deficient lattice, further forming different valence-state compositions, including NiO (Ni^{2+}), NiOOH (Ni^{3+}), and Ni_2O_3 (Ni^{3+}). The resultant nanoparticles are non-stoichiometric NiO_x nanoparticles, which are important due to their dispersion in water, reaching up to a high concentration of 50 mg L^{-1}. The dark-black NiO_x nanoparticles (powders) are very stable after 6 months during storage in an ambient environment, and the NiO_x nanoparticle dispersions are stable after 15 days, and are still well dispersed without any precipitation or aggregation.

[0007] In an embodiment, a new approach can be used to form a NiO_x HTL film through a room temperature solution process without any post-treatments including oxygen-plasma treatment and annealing treatment. The 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. The NiO_x NPs film has superior optical, electrical and surface properties, and the work function is well aligned with HOMO levels and the valence band of many typical p-type conjugated **4**polymers and inorganic semiconductors.

[0008] In another embodiment of the invention organic optoelectronic devices, using the NiO_x NPs film as HTLs and commercially available polymer/organic materials as the active layer of organic solar cells (OSC), high power conversion efficiency (PCE) of 9.16% with V_{OC} of 0.794 V, J_{SC} of 18.32 mA cm^{-2} and FF of 63.10% is achieved, which causes a noticeable enhancement compared with the control device using PEDOT:PSS as HTLs (PCE of 8.60%, V_{OC} of 0.782 V, J_{SC} of 18.03 mA cm $^{-2}$ and FF of 60.97%). The NiO_x NPs film can also function as HTLs in organic light emitting diodes (OLEDs) based on the use of commercially available polymer/organic materials as the active layer. The OLED devices have a turn-on voltage of 3.75 V, a maximum brightness of 26630 cd m^{-2} at 11.25 V, a current efficiency is 9.72 cd A^{-1}, which is higher than that of PEDOT:PSS-based devices with a maximum brightness of 23100 cd m^{-2} at 12.50 V and a current efficiency of 9.20 cd A^{-1}. The results reveal that both OLEDs and OSCs with efficient NiO_x HTLs can be comparable and competitive with that of PEDOT:PSS.

[0009] In a further embodiment, the synthesize method is a low cost process: no expensive and hi-tech equipment is required (only OSC and OLED devices fabrication is need), low cost materials (commercially available materials of $Ni(NO_3)_2 \cdot 6H_2O$ and NaOH), low energy consumption (low reaction time is only about five minutes, combustion process only needs 2 hours of energy consumption). In ambient environment, the NiO_x based OSC devices show much better stability compared to the devices using PEDOT:PSS as HTLs.

[0010] The room temperature process for the formation of conductive thin films according to the invention can be applicable to various substrates, including flexible substrates which will deform upon thermal annealing and are not compatible with high temperature processes.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] The foregoing and other objects and advantages of the present invention will become more apparent when considered in connection with the following detailed description and appended drawings in which like designations denote like elements in the various views, and wherein:

[0012] FIG. **1**(*a*) is a TEM image of non-stoichiometric NiO_x NPs with scale bar of 20 nm and FIG. **1**(*b*) is a X-ray diffractometry line broadening (XRD-LB) result of NiO_x;

[0013] FIG. **2**(*a*) is a XPS result of NiO_x films of Ni $2p_{3/2}$ core level peaks and FIG. **2**(*b*) is a XPS result of NiO_x films of O 1 s core level peaks;

[0014] FIGS. **3**(*a*), **3**(*b*) and **3**(*c*) is energy-level diagrams of the investigated NiO_x films (20 nm) with no annealing, 100° C. annealing and 200° C. annealing, respectively;

[0015] FIGS. **4**(*a*) to **4**(*c*) are current density-voltage (J-V) characteristics for PCDTBT, PTB7 and PTB7-Th, respectively, and FIG. **4**(*d*) is an IPCE curve for the same materials; and

[0016] FIG. **5**(*a*) is a J-V-L curve and FIG. **5**(*b*) is a LE-J-L curve of OLEDs, PEDOT:PSS and NiO_x.

DETAILED DISCLOSURE OF THE INVENTION

[0017] The subject invention relates to a new facile chemical precipitation and combustion method which is robust and simple for direct preparation of high quality non-stoichiometric NiO_x NPs. By using this method, NiO_x HTL film can be formed through a room temperature solution process without any post-treatments during device fabrication. Such a NiO_x HTL film can be used in many applications, including but not limited to flexible optoelectronics, organic solar cells, organic light emitting diodes, and organic photodetectors.

[0018] NiO_x NPs can be obtained by a chemical precipitation and combustion method using commercially available materials of $Ni(NO_3)_2{\cdot}6H_2O$ and NaOH. The raw materials are easily dissolved in deionized water. After dropwise adding NaOH, the clear green aqueous solution turns turbid. By accurately controlling the solution pH value to 10, a considerable yield of ultrafine nickel hydroxide $Ni(OH)_2$ is obtained. The obtained apple-green product is dried and calcined at 270° C. for two hours in air to decompose into dark-black NiO_x NPs. This calcination procedure is based on the thermal decomposition of $Ni(OH)_2$ aiming to produce non-stoichiometric NiO_x NPs. The dark-black NiO_x nanoparticles (powders) are very stable after 6 months during storage in an ambient environment, and the NiO_x nanoparticle dispersions are stable after 15 days, and are still well dispersed without any precipitation or aggregation.

[0019] Equations 1 and 2 illustrate the chemical reactions in this procedure of forming non-stoichiometric NiO_x NPs:

$$Ni(NO_3)_2 + NaOH \longrightarrow Ni(OH)_2 \downarrow + Na(NO_3)_2 \tag{1}$$

$$Ni(OH)_2 \longrightarrow NiO_x + H_2O \tag{2}$$

[0020] X-ray diffraction (XRD) to investigate the NiO_x crystal structure and dimensions reveals diffraction peaks which show the NiO_x as a cubic crystal structure. Three prominent characteristic diffraction peaks of NiO_x cubic structure appear at 2θ which equals 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 Debye-Scherrer equation: $D=0.89\lambda/(\beta \cos \theta)$, from which it can be determine that the average crystalline size is 4 nm. Meanwhile, as shown in the transmission electron microscopy (TEM) results of FIG. **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.

[0021] The optical, electrical and surface properties of the NiO_x thin films were examined by using different techniques. The NiO_x dispersion was prepared by dispersing the NiO_x NPs into water to a desired concentration from 5 mg ml^{-1} to 50 mg ml^{-1}. The NiO_x dispersion was spin-coated on pre-cleaned 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 were 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.

[0022] To demonstrate the capability of NiOx films to perform as highly efficient HTL over a wide range of temperatures, X-ray photoelectron spectroscopy (XPS) analysis was used to investigate the chemical composition of the NiO_x films processed under different temperatures. The Ni 2p 3/2 and O 1 s characteristic peaks of the NiO_x film in XPS spectra are shown in FIG. **2**. The decomposition of the XPS spectrum demonstrates 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 receives no annealing treatment or other UVO or O_2-plasma treatment, rather remarkable contributor peaks of Ni^{3+} state such as NiOOH (Ni 2p 3/2 at 856.3 eV and O 1 s at 532.1 eV), Ni_2O_3 (Ni 2p 3/2 at 855.0 eV and O 1 s 530.8 eV), and another Ni^{2+} state NiO (Ni 2p 3/2 at 853.6 eV and O 1 s 529.1 eV) appear. 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 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. Meanwhile, after 100° C. annealing treatment of the NiO_x film, no apparent shift or change of the dominant peaks in the Ni 2p 3/2 and O 1 s 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 are weakened and the Ni_2O_3 peaks are strengthened in the XPS spectra in FIGS. **2***a* and *b*. The variation in characteristic peaks by 200° C. annealing suggests a partial composition conversion from NiOOH to Ni_2O_3. Upon high temperature annealing, the change in the non-stoichiometric NiO_x film composition where excessive Ni_2O_3 is generated, can have a detrimental impact on the electrical properties and thus the device performance of the NiO_x HTL. As a result, in addition to room temperature, the NiO_x NPs are able to form effective and stable HTL over a wide range of annealing temperatures up to 150° C. without inducing detrimental changes in composition.

[0023] 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 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 FIG. **3**. The as-deposited NiO$_x$ films show an E_F of 5.25 eV. The appropriate E_F of post-treatment-free NiO$_x$ film favors ohmic contact formation to HOMO of donor materials in 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 is 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 is annealed at 200° C., the E_F of the NiO$_x$ significantly decreases from 5.25 eV to 4.61 eV. Both the CB and VB decrease to 1.33 eV and 4.97 eV respectively, which indicates 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. These results are consistent with the XPS results described previously, where the NiO$_x$ and oxidation states of the metal oxide are changed at relatively high temperature (over 200° C.).

[0024] To demonstrate that the NiOx film can function as an effective HTL, OSCs were fabricated and characterized. Four polymers with different bandgaps, P3HT, PCDTBT, PTB7 and PTB7-Th with HOMO energy levels of 5.00 eV, 5.30 eV, 5.14 eV and 5.22 eV respectively, were used to examine the effect of NiO$_x$ film as an efficient HTL. Device optimization was mainly focused on fine adjustment of the thickness and annealing temperature of the NiO$_x$ film. OSCs with conventional structure of ITO/NiO$_x$/Active layer/Ca (20 nm)/Al (100 nm) were fabricated. OSCs with PEDOT:PSS (34 nm) HTLs were also compared as a control. The current density-voltage (J-V) characteristics of P3HT devices using NiO$_x$ with different annealing temperatures were plotted in Table 1. 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 the XPS and UPS analytic results. Meanwhile, an annealing temperature over 200° C. significantly degrades the device performance due to a mismatch of WF of the NiO$_x$ to the HOMO of P3HT. The results demonstrate that the NiO$_x$ films in this work can function as effective HTLs without any post-treatment, as well as offer a wide temperature applicability from room-temperature to 150° C.

[0025] The optimized NiO$_x$ films were then applied to low bandgap polymers such as PCDTBT (E_{gap}=1.70), with a larger 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), which can enhance the hole extraction from the photoactive layer. A comparison of the illuminated current density-voltage (J-V) measurements for both NiO$_x$ and PEDOT:PSS based devices is presented in Table 2. The PCDTBT:PC$_{71}$BM 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 by 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 significant enhancement was mainly due to the ability of NiO$_x$ to form favorable energetic alignment with the active layer, as compared to the alignment formed with PEDOT:PSS. This result is comparable to some reported device performance in the literature for NiO$_x$ films prepared by other techniques. 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 PC$_{71}$BM (4.00 eV). This energetic orientation provides 1.75 eV to 2.15 eV energy barriers to electron collection at the anode and thus demonstrating effective electron-blocking properties of the NiO$_x$ which contributes to an increment in V_{OC} through reducing leakage current and photocurrent recombination 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 Ω cm^2 and 4.46 Ω cm^2, respectively. Improved contacts between active layer and anode, which facilitates free carriers extraction and transport, enhanced both J_{SC} and FF in the devices with NiO$_x$ HTLs.

[0026] To demonstrate the general viability of NiO$_x$ as an efficient HTL for low bandgap polymers, two PTB-derivatives, PTB7 (Egap=1.63 eV) and PTB7-Th (Egap=1.58 eV) were also selected to fabricate standard OSCs devices. FIG. **4*a*** shows the J-V curves PCDTBT. FIGS. **4*b*** and **4*c*** show the J-V curves of the PTB7 and PTB7-Th based BHJ OSCs with the PEDOT:PSS or NiO$_x$ HTLs, respectively. For PTB7:PC$_{71}$BM based devices, device performance with NiO$_x$ HTL has 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 is 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 show the same energy alignment ability with a low band gap polymer PTB7 based device. 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 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:PC$_{71}$BM based OSCs, the device with NiO$_x$ HTL has 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 has 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 Ω cm^2 and 3.37 Ω cm^2, respectively. Rationalized by a similar rule as noted above, the reduced R_S results in better electrical contact thus improved FF, which is beneficial for device performance. The OSCs with the 20 nm NiO$_x$ HTL shows higher IPCE at wavelengths of 500-700 nm compared with PEDOT:PSS HTL as shown in FIG. **4*d***. The IPCE maximum is 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 hole transport property of our low-temperature processing NiO$_x$ HTLs comparable to PEDOT:PSS is demonstrated with different bandgap polymeric donors in OSCs.

[0027] 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). OLEDs with PEDOT:PSS (34 nm) HTLs were also compared as a control. The current density-voltage-luminance density (J-V-L) characteristics and luminance efficiency-current density-luminance (LE-J-L) characteristics for devices are shown in FIGS. **5*a*** and **5*b***, respectively. The NiO$_x$ film based devices had a turn-on voltage of 3.75 V, a maximum brightness of 26630 cd m^{-2} at 11.25 V, a current efficiency of 9.72 cd A^{-1}, which is slightly higher than that of PEDOT:PSS-based devices with a maximum brightness of 23100 cd m^{-2} at 12.50 V, and a current efficiency of 9.20 cd A^{-1}. The results reveal that OLEDs with efficient NiO_x HTLs can be comparable and competitive with that of PEDOT:PSS HTLs.

[0028] Following are examples that illustrate the procedures for practicing the invention. These examples should not be construed as limiting.

EXAMPLE 1

[0029] The OSCs based on P3HT were fabricated by using the conventional structure of ITO/NiO_x/Active layer/Ca (20 nm)/Al (100 nm). With different annealing temperature of NiO_x film, the device performances of OSCs based on P3HT are summarized in Table 1.

TABLE 1

Device performance at different annealing temperatures for NiO_x based OSCs with conventional structure of ITO/NiO_x/P3HT:$PC_{61}BM$/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

EXAMPLE 2

[0030] The OSCs based on different bandgap polymers were fabricated by using the conventional structure of ITO/NiO_x/Active layer/Ca (20 nm)/Al (100 nm). The control OSCs were also fabricated by using PEDOT:PSS layer as comparisons. The device performance of OSCs based on different bandgap polymers with $PC_{71}BM$ were summarized in Table 2.

TABLE 2

Device performances of PEDOT:PSS or NiO_x based OSCs using different bandgap polymers with $PC_{71}BM$.

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

[0031] Based on these results it can be seen that the NiO_x nanoparticles are highly efficient hole transport layers in optoelectronic applications based on several donor polymers with different HOMO energy levels. Compared with conventional PEDOT:PSS-buffered devices, the NiO_x-buffered OSCs and OLEDs achieve improved or comparable device performances. The excellent optoelectronic performances can be realized at room temperature without any post-treatments to form the HTL films. Due to the desirable work function, NiO_x is a useful as an efficient HTL for high IP donor materials in order to maximize device performance. The NiO_x HTLs can be applied to various optoelectronic devices, including not only OSCs, but also OLEDs.

[0032] It should be understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application and the scope of the appended claims. In addition, any elements or limitations of any invention or embodiment thereof disclosed herein can be combined with any and/or all other elements or limitations (individually or in any combination) or any other invention or embodiment thereof disclosed herein, and all such combinations are contemplated with the scope of the invention without limitation thereto.

What is claimed is:

1. A method for preparing non-stoichiometric NiO_x nanoparticles, with a composition of NiO (Ni^{2+}), NiOOH (Ni^{3+}), and Ni_2O_3 (Ni^{3+}), wherein the method comprises:

using a base to react with Ni ions in water to form an electrically insulated and undispersed intermediate;

grinding the intermediate to form it into a uniform grain size;

combusting the intermediate in air to cause oxygen to interact with a nickel-deficient lattice and further form non-stoichiometric NiO_x nanoparticles.

2. The method of claim **1**, wherein the NiO_x nanoparticles have dark-black color or atrous color.

3. The method of claim **1**, wherein the NiO_x nanoparticles comprise vacancy-induced Ni^{2+} and Ni^{3+} composition.

4. The method of claim **1**, wherein the non-stoichiometric NiO_x nanoparticles contain nickel oxyhydroxide (NiOOH) which have a plurality of hydroxyl groups.

5. The method of claim **1**, wherein the step of using a base to form undispersed intermediate involves use of a dispersing agent that is water/methanol, water/ethanol, or water/other alcoholic solvents.

6. A non-stoichiometric NiO_xnanoparticle film, wherein the non-stoichiometric NiO_x nanoparticle film is produced by using the non-stoichiometric NiO_x nanoparticles according to claim **1**.

7. The non-stoichiometric NiO_x nanoparticle film of claim **6**, wherein the NiO_x nanoparticles film is formed through a room temperature solution process without any post-treatments.

8. The method of claim **7**, wherein said the NiO_x nanoparticle film has a work function of 5.25 eV, and possesses typical p-type semiconductor properties.

9. A method of claim **8**, wherein the NiO_x nanoparticle film is transparent and is placed on anITO/glass substrate and has an optical transparency of at least 85% when the film has a thickness of 30nm.

* * * * *

专利名称(译)	制备无处理后溶液的简单方法处理非化学计量的Niox纳米粒子作为导电空穴传输材料		
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其他公开文献	US10315929		
外部链接	Espacenet USPTO		

摘要(译)

通过简便的化学沉淀法合成高质量的非化学计量的NiO x 纳米粒子。NiO x 薄膜可以作为有效的p型半导体或空穴传输层（HTL），无需任何后处理，同时提供从室温到150°C的宽温适用性。用于演示在潜在的应用中，使用NiO x HTL在有机太阳能电池中实现了高效率。与使用PEDOT：PSS的器件相比，获得了基于NiO x 的有机发光二极管的更好性能。在室温下溶液处理的NiO x 半导体可以有利于大面积和柔性光电子的广泛应用。

$$Ni(NO_3)_2 + NaOH \longrightarrow Ni(OH)_2\downarrow + Na(NO_3)_2 \qquad (1)$$

$$Ni(OH)_2 \longrightarrow NiO_x + H_2O \qquad (2)$$