

Full paper

Pre- and post-treatments free nanocomposite based hole transport layer for high performance organic solar cells with considerably enhanced reproducibility



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ARTICLE INFO

Keywords:

Transition metal oxides
Post-treatment-free
Pre-treatment-free
Hole transport layer
Polymer/organic solar cells

ABSTRACT

In this work, we demonstrate a one-step room-temperature ethanol-processed nickel oxide (NiO_x):electron acceptor nanocomposite functioning as efficient hole transport layer (HTL). Specifically, one-step refers to the formation of the nanocomposite HTL films without extra steps of pre-treatments of ITO nor post-treatments of HTL films, and thus considerably reduce the fabrication complexity and cost. By varying the concentration of the electron acceptor, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ), the work function (WF) of the nanocomposite films can be widely tuned from 4.73 eV to 5.30 eV, which favors its use for photovoltaic applications of organic donor materials with different highest energy occupied molecular orbital (HOMO) energy levels. Organic solar cells (OSCs) have been fabricated by using the NiO_x:F4-TCNQ nanocomposite as HTL. The optimized average power conversion efficiency (PCE) of NiO_x:F4-TCNQ based OSCs can be 18% better than that of one-step prepared poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) based OSCs. Remarkably, NiO_x:F4-TCNQ based OSCs show better reproducibility as the deviation of PCE values can be improved by a greatest extent of 10 times. This work contributes towards simple and low-cost fabrication of high efficiency OSCs for practical photovoltaic applications.

1. Introduction

As a viable renewable energy source, organic solar cells (OSCs) have experienced a performance leap in the past decade. Interfacial layers, i.e. hole transport layer (HTL) and electron transport layer (ETL), have played important roles during this high-speed development [1–3]. However, during the formation of HTLs in normal OSCs, the pre-treatment of transparent indium tin oxide (ITO) substrates and post-treatment of HTLs are always necessary due to a series of reasons [4,5]. These pre-treatments and post-treatments increase the fabrication complexity and cost. Take the most commonly used HTL material for example, water-dissolved poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) faces the problem of wetting on pristine ITO. As a result, the underlying substrate needs to be ultraviolet-ozone (UVO) or oxygen-plasma treated to realize a good surface energy match with water-based PEDOT:PSS solution. Also, PEDOT:PSS needs thermal annealing after the film formation to remove the residual water. Otherwise, it will still re-absorb water if

the samples are not used immediately [6]. Elimination of these pre-treatments and post-treatments will influence the morphology of formed PEDOT:PSS films and degrade the device performance as a negative result.

Recently, stable and easily-synthesized metal oxides, including molybdenum oxide (MoO₃), tungsten oxide (WO₃), vanadium oxide (V₂O₅) and nickel oxide (NiO_x), have been developed as HTLs [7–9]. Among them, NiO_x shows advantages including p-type conductivity, better conductivity and good electron-blocking ability. Solution-processed NiO_x as HTL in OSCs was firstly developed by Olson's group through a precursor method [10–13]. This method needs post-treatment including annealing treatment at 300 °C and oxygen-plasma treatment. Later, Manders et al., Zhai et al. and Bai et al. developed other different precursor based method [14–16], in which post-treatment including UVO treatment or annealing treatment at different temperatures is needed after the film preparation. When using precursor based methods, the transition from precursor into oxide usually occurs after the film preparation, thus post-treatment is always

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inevitable. Nanoparticles (NPs) based method is another commonly used film formation method, which provides the advantage of decoupled particle synthesis and film formation [17]. Zhang et al. reported an annealing free NiO_x NPs for HTL application [18]. However, the oxygen-plasma treatment is still needed. Recently, Jiang et al. firstly demonstrated the solution-processed post-treatment-free NiO_x nanoparticles (NPs) which can be used as HTL in OSCs [19]. However, these NiO_x NPs is dispersed in water, which faces the same wetting issue with water-based PEDOT:PSS. The complex and power-consuming processes, including pre-treatment of substrates and post-treatment of NiO_x films, hinder their further applications in large-scale fabrication such as roll-to-roll (R2R) continuous processing on flexible substrates [20]. Thus, developing one-step prepared NiO_x based HTL could be of great interests to fully exploit the remarkable properties of NiO_x into economic and efficient production of OSCs. Specifically, one-step refers to the elimination of extra steps of pre-treatments of ITO and post-treatments of HTL films during the formation of HTL films.

In parallel, various kinds of organic donor materials have emerged in the past several years, which typically have different highest occupied molecular orbital (HOMO) values [21,22]. The most studied donor polymer, poly(3-hexylthiophene) (P3HT), has a HOMO energy level of around 5.00 eV [23]. Recently, conjugated polymers based on the backbone of alternating benzo[1,2-b;4,5-b']dithiophene (BDT) and thieno[3,4-b]thiophene (TT) building units contributes to high efficiency OSCs due to an extended light absorption for better short circuit current density (J_{SC}), and modulated HOMO energy level for better open circuit voltage (V_{OC}) [24]. Their HOMO values varies from 5.07 eV (PBDTTT-C) to 5.33 eV (PBDT-TS1) [25]. As the alignment of work function (WF) of HTL with donor's HOMO is a very important issue to prevent energy loss at the interface [26], developing WF tuning HTL becomes desirable [27–29].

In this work, we develop a new one-step room-temperature ethanol-based process to form NiO_x :electron acceptor nanocomposite HTL for high-efficiency OSCs. The judicious choosing of ethanol, which is low-cost, low-toxicity and shows good energy match with ITO, as the solvent can prevent any pre-treatment of ITO like UVO pre-treatment and oxygen-plasma pre-treatment. Through introducing a strong electron acceptor of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) into NiO_x , the WF of the metal oxide-electron acceptor nanocomposite films can be tuned from 4.73 eV to 5.30 eV (as wide as 0.57 eV), which can realize energy level match with most organic donor materials [30]. Although F4-TCNQ has been used as a p-type dopant of polymer materials [31–35], its successful application into inorganic p-type hole transport materials has never been explored to our knowledge. Also, such a wide continuous WF tuning of NiO_x has never been reported. By using P3HT and 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) [25] as the donor materials respectively, we have fabricated OSCs with NiO_x :F4-TCNQ as the HTL. The optimized average power conversion efficiency (PCE) of NiO_x :F4-TCNQ based OSCs can be 18% better than that of one-step prepared PEDOT:PSS based OSCs. Remarkably, our OSCs shows better reproducibility and the deviation of PCE values can be improved by a greatest extent of 10 times. Consequently, this work simultaneously contributes to efficient HTL for high efficiency OSCs and simple low-cost fabrication for practical photovoltaic production.

2. Experimental section

2.1. Materials

Nickel acetylacetonate ($\text{Ni}(\text{acac})_2$) was purchased from International Laboratory USA (99% purity), *tert*-butanol was purchased from International Laboratory USA (98% purity). F4-TCNQ was

purchased from Kintec. PEDOT:PSS (Baytron AL4083) was purchased from H.C. Starck GmbH, Germany. P3HT, [6,6]-phenyl- C_{61} -butyric acid methyl ester (PC_{61}BM), PTB7-Th and [6,6]-phenyl- C_{71} -butyric acid methyl ester (PC_{71}BM) were purchased from Solarmer Co., Ltd. 1,8-diiodooctane (DIO, >95.0%) DIO was purchased from Tokyo Chemical Industry Co., Ltd. (TCI). All chemicals were used as received.

2.2. Preparation of NiO_x :F4-TCNQ nanocomposite films

In a typical synthesis procedure, 0.13g (0.50 mmol) $\text{Ni}(\text{acac})_2$ was added into 14 mL *tert*-butanol (0.147 mol) followed by stirring at 700 rpm for 30 min until a turbid light green suspension formed. Then the suspension was transferred into a Teflon autoclave liner. The autoclave was placed into a muffle furnace followed by 220 °C treatment for 20 h. After cooling down, the resultant suspension was centrifuged at 15,000 rpm for 10 min. Supernatant was removed and the as-prepared yellow NiO_x powder was dried by vacuum treatment. Certain weight of NiO_x powder and corresponding amount of F4-TCNQ were dispersed into ethanol to form the NiO_x :F4-TCNQ solution. Usually, several drops of water needs to be added to realize a more stable solution. The NiO_x :F4-TCNQ nanocomposite films were prepared by spin-coating the NiO_x :F4-TCNQ solution onto ITO substrates. The thickness of the film resulted from a 5 mg mL^{-1} NiO_x solution was determined to be 17 nm by a spectroscopic ellipsometer (J.A. Woollam Co., Inc).

2.3. Characterization

Transmission electron microscope (TEM) was performed using a Philips Tecnai G2 20 s-TWIN. For the sample preparation, a drop of NiO_x solution was dropped onto copper grid and evaporated. Grazing incidence X-ray diffraction (GIXRD) pattern of the NiO_x powder was recorded using a Philips X'Pert X-ray diffractometer using Cu K α radiation ($\lambda=1.5406$ Å). X-ray photoelectron spectroscopy (XPS) of NiO_x films on ITO was measured in the ultrahigh vacuum environment using Physical Electronics PHI 5802 with a monochromatic Al K α X-ray source. Ultraviolet photoelectron spectroscopy (UPS) were characterized by using a He discharged lamp (He I 21.22 eV, Kratos Analytical). Height images were measured by using a tapping mode atomic force microscope (AFM, NT-MDT, Moscow, Russia).

2.4. Device fabrication of OSCs

For OSCs device fabrication, ITO-coated glass substrates with sheet resistance of 15 $\Omega \text{ sq}^{-1}$ were cleaned by a standard procedure with detergent, acetone and ethanol ultrasonic bath for each of 10 min. One-step prepared PEDOT:PSS was spin-coated with thickness of 34 nm without any post-treatments. P3HT: PC_{61}BM (20:20 mg mL^{-1} in DCB) were spin-coated on HTLs at 670 rpm followed by solvent annealing for one hour and thermal annealing at 130 °C for 10 min. The thickness of P3HT: PC_{61}BM about 220 nm. PTB7-Th: PC_{71}BM (10:15 mg mL^{-1} in CB, with addition of 3% volume ratio DIO) were spin-coated on HTLs at 2000 rpm. The thickness of PTB7-Th: PC_{71}BM is around 100 nm. DIO was removed by a reported methanol washing method [36,37]. Calcium (Ca, 20 nm)/Aluminium (Al, 100 nm) were thermally evaporated through a shadow mask as the top cathode, which defined the device area as 0.06 cm^2 . ZnO NPs in 1-butanol were synthesized according to a previously reported procedure [38]. Current density-voltage (J - V) characteristics were measured using a Keithley 2635 sourcemeter and ABET AM1.5G solar simulator.

3. Results and discussion

3.1. Preparation of NiO_x :F4-TCNQ nanocomposite films

In order to form the NiO_x :F4-TCNQ nanocomposites, NiO_x NPs are

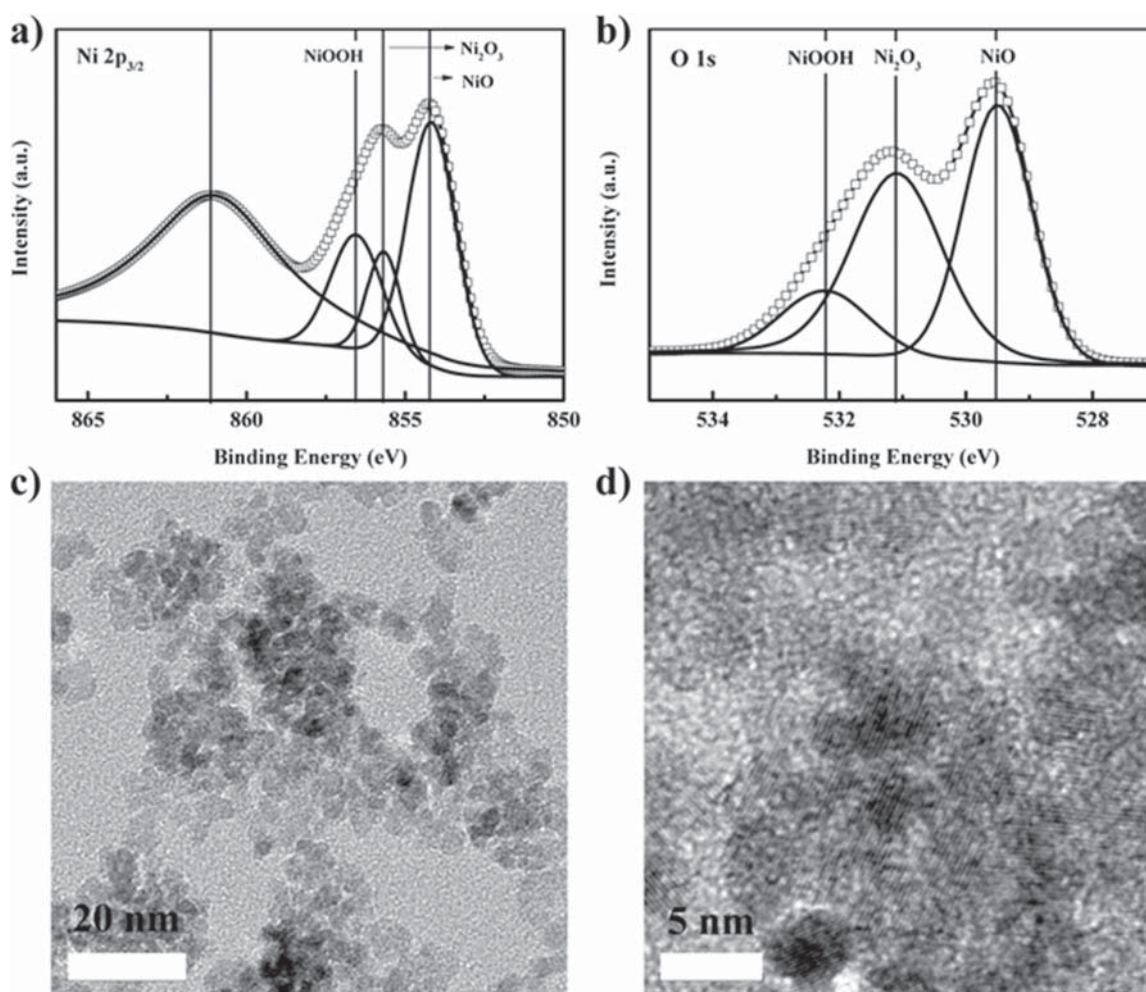


Fig. 1. XPS results of NiO_x films a) $\text{Ni } 2p_{3/2}$ and b) $\text{O } 1s$ core level peaks. c) TEM image of the NiO_x (scale bar: 20 nm) and d) HRTEM image of NiO_x NPs (scale bar: 5 nm).

synthesized firstly. Solvothermal reaction is a method to synthesize crystalline metal oxide NPs with the advantages of preventing the using of surfactant and good control over size, shape and agglomeration [39–41]. Here, we synthesize ethanol dispersible ultrasmall colloidal non-stoichiometric NiO_x NPs through a solvothermal method. After reaction at 220 °C for 20 h in a muffle oven, the products are dried through vacuum treatment and dispersed in ethanol. The resultant NiO_x NPs contain a certain concentration of Ni(III) species, as demonstrated in below, which are not yet reported to be synthesized by solvothermal method to our best knowledge and very important for the electrical properties of NPs to serve as effective HTL. Details of the synthesis of NiO_x NPs are described in Section 2. Fig. 1 shows X-ray photoelectron spectroscopy (XPS) results of synthesized NiO_x . The $\text{Ni } 2p_{3/2}$ characteristic peaks of NiO_x films are shown in Fig. 1a. The peak centered at 861.0 eV corresponds to a shake-up process in the cubic rocksalt structured NiO [42]. The main peak centered at 854.2 eV is ascribed to the standard Ni-O octahedral bonding configuration [43,44]. The peaks centered around 855–856 eV are ascribed to Ni^{2+} vacancy-induced Ni^{3+} state. These Ni^{2+} vacancies induce positive charge compensation, and result in the p-type conductivity property of NiO_x [45]. Typically, the peak centered at 856.4 eV corresponds to NiOOH species, while the peak centered at 855.5 eV corresponds to Ni_2O_3 species [11,19]. By analyzing the integral area in the $\text{Ni } 2p_{3/2}$ spectra, the concentration ratio of NiOOH , Ni_2O_3 , and NiO is 0.504:0.287:1. The atomic ratio of $\text{Ni}:\text{O}$ is determined to be 1:1.36 as a result, which deviates from 1:1 atomic ratio and favors a hole transport property [41]. Fig. 1b shows the spectrum of $\text{O } 1s$ state in NiO_x films. Similarly, the peak at 529.5 eV is indicative of Ni-O octahedral bonding in NiO [16,42]. The peak at

532.2 eV is ascribed to NiOOH and the peak at 531.1 eV is ascribed to the Ni_2O_3 species or hydroxyl groups absorbed on the surface [16]. Considering the insulating nature of stoichiometric NiO , the non-stoichiometric composition, determined from the XPS studies, endows prepared NiO_x hole transport ability.

Transmission electron microscope (TEM) results of NiO_x NPs are as shown in Fig. 1c and d. The particle size of as prepared NiO_x is around 4 nm, and shows a good uniformity. The X-ray diffraction (XRD) was also performed to investigate the crystal structure of NiO_x NPs. As shown in Fig. S1, three prominent characteristic peaks appear at 37.32°, 43.23° and 62.65°, respectively, which coincides with the electron diffraction pattern in Fig. S1b. The lattice fringe distances (Fig. 1d) and the electron diffraction patterns (Fig. S1) indicates the cubic rock salt structure of NiO_x synthesized NPs. The synthesized NiO_x NPs in ethanol (5 mg mL^{-1}), as shown in Fig. 2a, shows a clear and stable solution.

The photograph of F4-TCNQ in ethanol (5 mg mL^{-1}) is shown in Fig. 2a and its absorbance spectra is shown in Fig. S2. F4-TCNQ can be well dissolved into ethanol as well, which promises it as the dopant of the ethanol processed NiO_x NPs. By varying the concentration of F4-TCNQ from 0.05 to 0.5 mg mL^{-1} while fixing the concentration of NiO_x at 5 mg mL^{-1} , a series of well mixed NiO_x :F4-TCNQ solutions are prepared with their photograph shown in Fig. 2a. When the concentration of F4-TCNQ increases to 0.6 mg mL^{-1} or higher, the NPs tend to form precipitates. By simply spin-coating the NiO_x :F4-TCNQ solutions on ITO without any pre-treatments, the one-step prepared NiO_x :F4-TCNQ nanocomposite films have been prepared.

Due to the good surface energy match between ethanol and ITO, the

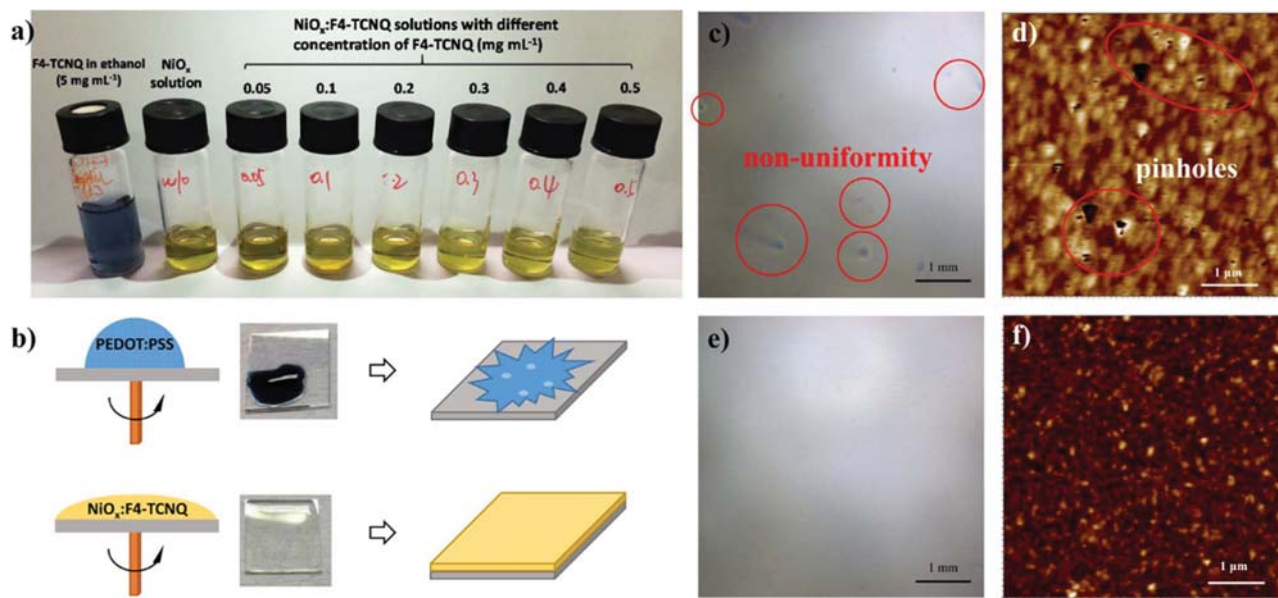


Fig. 2. a) Photograph of F4-TCNQ solution (5 mg mL⁻¹), NiO_x and NiO_x:F4-TCNQ solutions. b) Photograph of PEDOT:PSS and NiO_x:F4-TCNQ solutions (50 μL) on ITO substrates (1.7×1.7 cm²) without pre-treatments. c) Microscope characterization and d) AFM characterization of one-step prepared PEDOT:PSS film on ITO. e) Microscope characterization and f) AFM characterization of one-step prepared NiO_x:F4-TCNQ film (0.4 mg mL⁻¹) on ITO.

NiO_x:F4-TCNQ solution shows good wetting properties on pristine ITO even without any pre-treatments. As shown in Fig. 2b, only 50 μL NiO_x:F4-TCNQ solution can fully cover the pristine ITO substrate (1.7×1.7 cm²). As a comparison, 50 μL water-based PEDOT:PSS solution can hardly cover the pristine ITO substrate without any pre-treatments. To fully cover the substrate, 500 μL water-based PEDOT:PSS solution is needed to prepare the one-step prepared PEDOT:PSS films, which is very material-wasting. The surface morphology comparison between one-step prepared PEDOT:PSS and one-step prepared NiO_x:F4-TCNQ films on ITO have also been investigated by microscope characterization and AFM as shown in Fig. 2c–f. Due to the poor wetting properties of water on pristine ITO, the one-step prepared PEDOT:PSS shows non-uniformity and pinholes as shown in Fig. 2c and d. These non-uniformity and pinholes produce a negative influence on the one-step prepared PEDOT:PSS based devices and cause a poor reproducibility of the performance. Noteworthily, the one-step prepared NiO_x:F4-TCNQ film (with a concentration of 0.4 mg mL⁻¹ of F4-TCNQ, which is the optimized concentration for device fabrication) shows a uniform and pinhole-free morphology. AFM characterization of NiO_x:F4-TCNQ films with various concentration of F4-TCNQ are shown in Fig. S4. The root-mean-square (RMS) roughness slightly increases with the increasing of concentrations of F4-TCNQ. Considering the formation of films with well coverage and smoothness is fundamentally critical for the applications of interface materials in devices, the NiO_x:F4-TCNQ nanocomposite films are promising to serve as good HTLs for device applications.

3.2. Electrical and optical properties of NiO_x:F4-TCNQ nanocomposite films

Optical and electrical properties of one-step prepared NiO_x:F4-TCNQ HTL have been investigated and results are demonstrated as following. UPS is utilized to investigate the energy band structures of the ethanol processed NiO_x films. As shown in Fig. 3a, the secondary-electron cut-off ($E_{\text{cut-off}}$) at 16.52 eV indicates an effective WF of 4.70 eV. The valence band (VB) is 0.25 eV below the fermi level (E_F), indicating a p-type semiconducting property of the prepared NiO_x films. Optical constants, i.e. refractive index (n) and extinction coefficient (k), are obtained by ellipsometer, as shown in Fig. S5a. Optical band gap (E_{opt}), i.e. the energy difference between the conduc-

tion band (CB) and VB, is determined by the Tauc plot ($(\alpha h\nu)^{1/2} - h\nu$), as shown in Fig. S5b. The Tauc plot shows a linear relation in the energy range from 3.5 to 4.0 eV. Thus E_{opt} , the intersection of the extrapolated line of this linear part and the energy axis ($h\nu$), is determined to be 3.4 eV. As a result, the energy level diagram of NiO_x films can be demonstrated as Fig. 3b, which shows a p-type conductivity and a wide bandgap.

By varying the concentration of a strong electron acceptor, F4-TCNQ, in the NiO_x:F4-TCNQ solution, the WF of the one-step prepared NiO_x:F4-TCNQ nanocomposite films can be effectively tuned. The WF of NiO_x:F4-TCNQ films formed on ITO was determined by Kelvin-Probe measurement. For each sample, 200 points are collected, as shown in Fig. S6. The measured WF values are concluded in Table 1. WF of the pristine NiO_x film is determined to be 4.73 eV, which is comparable with the UPS results. When the added F4-TCNQ varies from 0.05 to 0.5 mg mL⁻¹, WF increases from 4.79 eV to 5.30 eV continuously. UPS spectra of NiO_x:F4-TCNQ films with different concentration of F4-TCNQ have also been characterized as shown in Fig. S6b. The extracted WF values are 4.80, 4.85, 4.98, 5.18, 5.26 and 5.30 eV respectively when the concentration of F4-TCNQ increases from 0.05 to 0.5 mg mL⁻¹. Considering the HOMO values of most donor materials used in OSCs vary from 5.0 eV to 5.5 eV, the NiO_x:F4-TCNQ films can serve as potential candidates of HTLs in OSCs.

The shift of WF can be explained by the theoretical model as following. According to the principle of Kelvin-Probe measurement, the potential difference between the sample and the reference tip is field free. F4-TCNQ is treated as a strong electron acceptor in films. Thus, the electrical potential $\phi(x)$ in the HTL follows the Poisson equation

$$\frac{d^2\phi}{dx^2} = \frac{e}{\epsilon_r\epsilon_0} [n(x) - p(x) + N_A] \quad (1)$$

with the boundary condition $d\phi/dx(L) = 0$, where $n(x)$ and $p(x)$ are the electron and hole densities in the CB and VB, respectively. N_A is the density of ionized F4-TCNQ acceptor molecules, x is the distance from the substrate. L is the layer thickness (determined to be 17 nm by ellipsometer) and relative permittivity $\epsilon_r = 12$ [46]. $n(x)$ and $p(x)$ are given by the convolution of Fermi-Dirac distribution and corresponding effective density of states distributions g_{CB} and g_{VB}

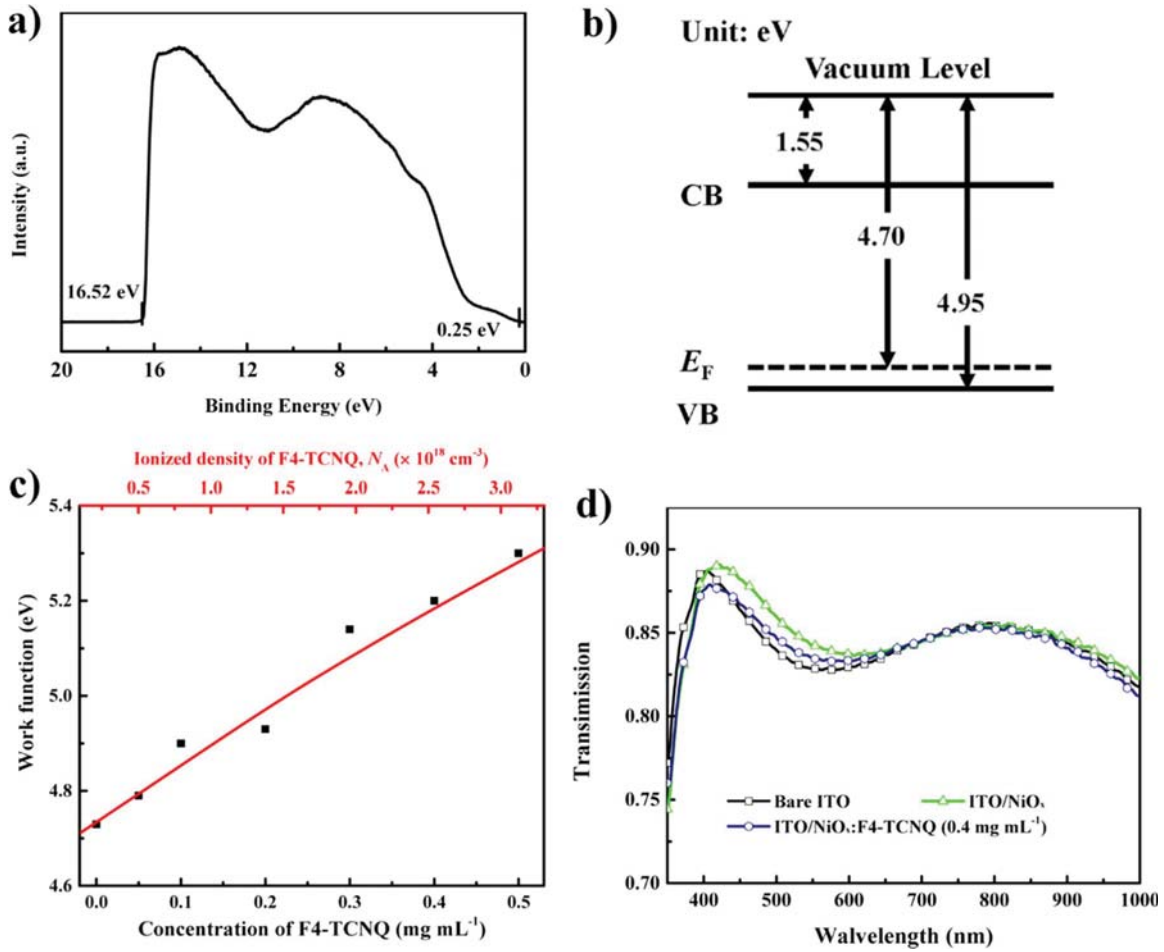


Fig. 3. a) UPS spectra of NiO_x films. b) Energy level diagram of the investigated NiO_x films. c) WF values determined by Kelvin-probe characterization of NiO_x:F4-TCNQ films versus concentrations of F4-TCNQ (dot) and theoretical WF values versus density of ionized F4-TCNQ molecules (line). d) Transmission spectra of bare ITO, ITO/NiO_x and ITO/NiO_x:F4-TCNQ (0.4 mg mL⁻¹) films.

Table 1

The WF variation of NiO_x:F4-TCNQ films with different concentrations of F4-TCNQ characterized by Kelvin-Probe measurements. ΔE_F is defined as the energy level offsets of the composite film and pristine film.

Concentrations of F4-TCNQ [mg mL ⁻¹]	WF [eV]	ΔE_F [eV]
w/o	4.73 ± 0.01	0
0.05	4.79 ± 0.01	0.06
0.1	4.90 ± 0.02	0.17
0.2	4.93 ± 0.01	0.20
0.3	5.14 ± 0.01	0.41
0.4	5.20 ± 0.01	0.47
0.5	5.30 ± 0.02	0.57

$$n(x) = \int_{-\infty}^{\infty} \frac{g_{CB}[E - e\phi(x)]}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)} dE \quad (2)$$

$$p(x) = \int_{-\infty}^{\infty} \frac{g_{VB}[E - e\phi(x)]}{1 + \exp\left(\frac{E_F - E}{k_B T}\right)} dE \quad (3)$$

WF at the HTL surface can be calculated by

$$\Phi_{HTL}(L) = \Phi_{Sub} - e\phi(L) \quad (4)$$

in which, Φ_{Sub} = 4.69 eV is the WF of ITO substrate. The relationship between $\Phi_{HTL}(L)$ and N_A turns out to be as shown in Fig. 3c. WF at the HTL surface increases with the density of ionized F4-TCNQ molecules, which is related to the concentration of F4-TCNQ in NiO_x:F4-TCNQ

solutions. The theoretical prediction of the WF variations is well coincident with the experimental results illustrated in Table 1. Detailed parameters and scheme of WF tuning can be found from Table S1 and Fig. S7.

Moreover, optical transparency is also an essential characteristic as a good HTL on ITO. Fig. 3d shows the optical transmission spectra of ethanol processed NiO_x:F4-TCNQ films (the thickness around 17 nm) on ITO substrates. The thickness of the NiO_x or NiO_x:F4-TCNQ films is the same as that used in OSCs discussed later. The concentration, 0.4 mg mL⁻¹, is the optimized concentration for device fabrication. The transmission spectra of all NiO_x:F4-TCNQ films is shown in Fig. S8. In the visible and near infrared (NIR) range, the NiO_x:F4-TCNQ films' transmission is over 83%. At the wavelength between 450 and 750 nm, which is the main absorption range of most organic donor materials, the ITO/NiO_x and ITO/NiO_x:F4-TCNQ (0.4 mg mL⁻¹) films are more transparent than bare ITO. This transmission enhancement phenomenon might be ascribed to interference effect at the interface. The results signify that NiO_x:F4-TCNQ nanocomposite films are decent HTL candidates in OSCs.

3.3. Device performances

To demonstrate the viability of NiO_x:F4-TCNQ films for photovoltaic applications in different donor polymer based bulk heterojunction (BHJ) systems, OSCs with P3HT:PC₆₁BM and PTB7-Th:PC₇₁BM as the active layers have been fabricated. The chemical structure of P3HT, PC₆₁BM, PTB7-Th and PC₇₁BM are as shown in Fig. S9. Device structure and the

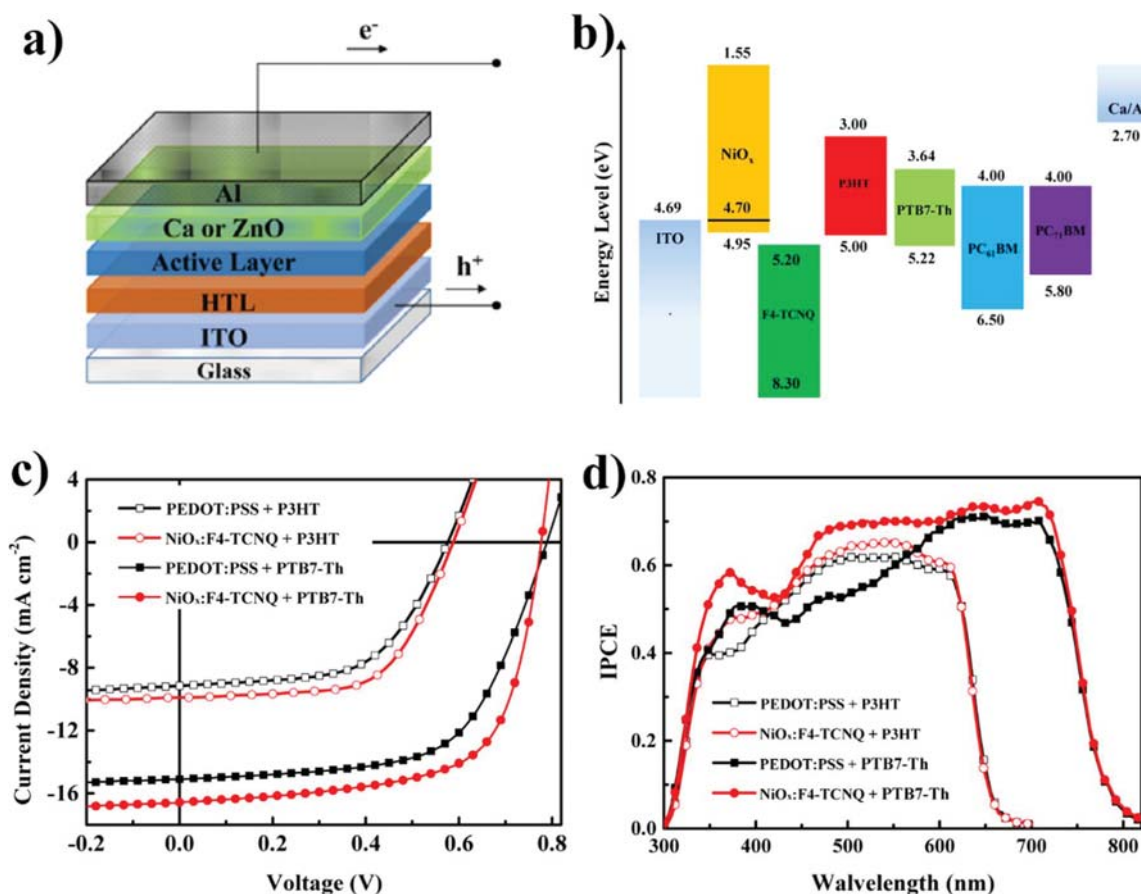


Fig. 4. a) Device structure of OSCs. b) Energy diagrams of OSCs. c) Representative current density-voltage (J - V) characteristics under AM 1.5G solar spectrum with a light intensity of 100 mW cm^{-2} . d) IPCE spectra of OSC with a structure of ITO/HTL (PEDOT:PSS or NiO_x :F4-TCNQ)/Active layer (P3HT:PC₆₁BM or PTB7-Th:PC₇₁BM) /Ca/Al.

energy levels of component materials are as shown in Fig. 4a and b. The concentrations of F4-TCNQ are varied from w/o to 0.5 mg mL^{-1} .

By changing the concentration of F4-TCNQ, device performances can be modified. The current density-voltage (J - V) characteristics are as shown in Fig. S10 and characteristic device parameters are summarized in Table 2. For P3HT:PC₆₁BM based OSCs, when the as prepared NiO_x (without F4-TCNQ) is used as HTL, the PCE is only

0.60%. This can be explained by the low WF of pristine NiO_x and the induced hole injection barrier at the interface [47,48]. Interestingly, when the concentration of F4-TCNQ increases from 0.05 to 0.4 mg mL^{-1} , J_{sc} , V_{oc} , and FF all increase and PCE increases to a best average value of 3.59%. The J - V characteristics of the optimized case is shown in Fig. 4c. The average PCE shows a 15.8% improvement compared with that of one-step prepared PEDOT:PSS based OSCs,

Table 2

Performance summary of OSCs with a structure of ITO/HTL/P3HT:PC₆₁BM/Ca/Al or ITO/HTL/PTB7-Th:PC₇₁BM/Ca/Al in which HTL is PEDOT:PSS or NiO_x :F4-TCNQ.

	Concentration of F4-TCNQ [mg mL^{-1}]	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF	PCE [%]
P3HT:PC ₆₁ BM	w/o	7.50 ± 0.44	0.34 ± 0.02	0.233 ± 0.012	0.60 ± 0.06
	0.05	8.99 ± 0.26	0.40 ± 0.01	0.290 ± 0.013	1.05 ± 0.09
	0.1	9.62 ± 0.20	0.48 ± 0.01	0.395 ± 0.019	1.83 ± 0.02
	0.2	9.61 ± 0.19	0.57 ± 0.01	0.571 ± 0.015	3.13 ± 0.04
	0.3	9.79 ± 0.19	0.59 ± 0.01	0.599 ± 0.009	3.46 ± 0.10
	0.4	9.89 ± 0.13	0.59 ± 0.01	0.616 ± 0.008	3.59 ± 0.04
	0.5	9.86 ± 0.11	0.59 ± 0.01	0.605 ± 0.009	3.52 ± 0.09
	PEDOT:PSS ^a	9.21 ± 0.35	0.58 ± 0.02	0.582 ± 0.047	3.10 ± 0.40
	w/o	16.43 ± 0.35	0.51 ± 0.01	0.454 ± 0.002	3.84 ± 0.11
	0.05	16.27 ± 0.21	0.60 ± 0.01	0.539 ± 0.008	5.29 ± 0.06
PTB7-Th:PC ₇₁ BM	0.1	16.40 ± 0.44	0.68 ± 0.01	0.571 ± 0.006	6.34 ± 0.19
	0.2	16.73 ± 0.18	0.74 ± 0.02	0.608 ± 0.006	7.48 ± 0.27
	0.3	16.78 ± 0.12	0.77 ± 0.01	0.623 ± 0.011	8.04 ± 0.22
	0.4	16.80 ± 0.23	0.78 ± 0.01	0.652 ± 0.010	8.59 ± 0.14
	0.5	16.60 ± 0.33	0.78 ± 0.01	0.644 ± 0.009	8.32 ± 0.11
	PEDOT:PSS ^a	15.15 ± 0.21	0.79 ± 0.00	0.606 ± 0.079	7.25 ± 0.97

^a One-step prepared PEDOT:PSS HTLs without any pre-treatment of ITO glasses or post-treatment.

Table 3Performance summary of the OSC devices (ITO/HTL/PTB7-Th:PC₇₁BM/ZnO/Al) based on PEDOT:PSS and NiO_x:F4-TCNQ.

HTL	J_{SC} [mA cm ⁻²]	V_{OC} [V]	FF	PCE (PCE _{max}) [%]
PEDOT:PSS ^a	16.54 ± 0.27	0.77 ± 0.02	0.630 ± 0.079	8.06 ± 0.72 (9.25)
NiO _x :F4-TCNQ ^b	18.29 ± 0.19	0.79 ± 0.01	0.660 ± 0.010	9.54 ± 0.20 (9.75)

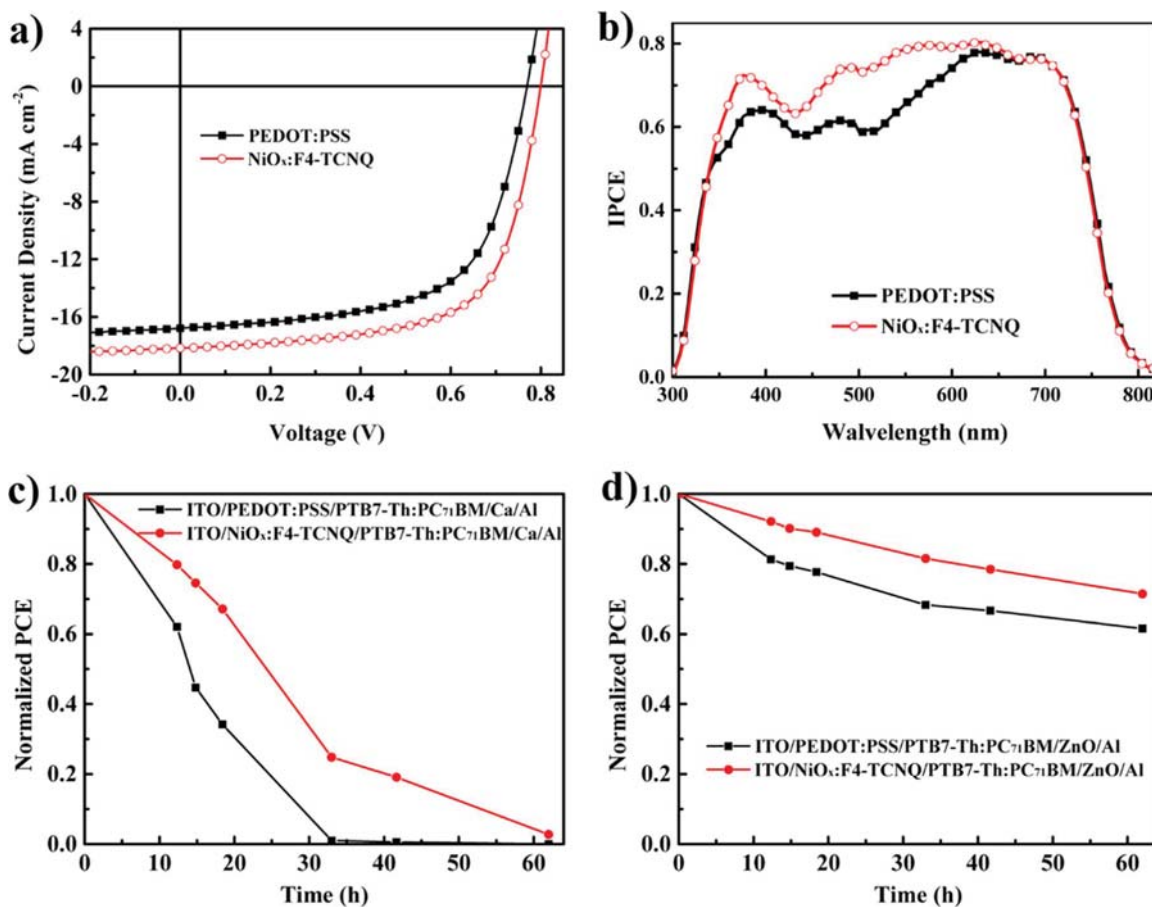
^a The PEDOT:PSS is one-step prepared without any pre- or post-treatment.^b The concentration of F4-TCNQ in NiO_x is 0.4 mg mL⁻¹.

Fig. 5. a) Representative current density-voltage (J - V) characteristics under AM 1.5G solar spectrum with a light intensity of 100 mW cm⁻². b) IPCE measurements for ITO/HTLs (PEDOT:PSS or NiO_x:F4-TCNQ)/PTB7-Th:PC₇₁BM/ZnO/Al, both HTLs are one-step prepared without any pre- or post-treatment. Changes of normalized PCE of devices with the structure of c) ITO/HTLs/PTB7-Th:PC₇₁BM/Ca/Al and d) ITO/HTLs/PTB7-Th:PC₇₁BM/ZnO/Al during exposure in air.

whose average PCE is only 3.10%. In addition, the performance deviation among the fabricated OSCs is remarkably improved, which indicates the one-step prepared NiO_x:F4-TCNQ based devices have a better reproducibility. As shown in Table 2, the deviation of final PCE values reduced by as much as 10 times from 0.40 (optimized PEDOT:PSS case) to 0.04 (optimized NiO_x:F4-TCNQ case), which is ascribed to the non-uniformity and pinholes of one-step prepared PEDOT:PSS films formed on pristine ITO.

The performance of PTB7-Th:PC₇₁BM based OSCs shows a similar trend of variation with the increasing of the F4-TCNQ concentration as that of P3HT:PC₆₁BM OSCs, as shown in Fig. S10b and Table 2. The highest efficiency is achieved when F4-TCNQ concentration is 0.4 mg mL⁻¹ with an optimized average PCE of 8.59% as shown in Table 2. The PCE outperforms that of the optimized OSCs based on one-step processed PEDOT:PSS by a 18.5% improvement. The optimized average PCE of the PEDOT:PSS case is only 7.25% due to the poor FF. Importantly, the deviation among the fabricated OSCs is remarkably improved again. The deviation of the optimized NiO_x:F4-TCNQ based devices (at F4-TCNQ concentration of 0.4 mg mL⁻¹) is

0.14 while that of the optimized PEDOT:PSS based devices is 0.97. The improvement is as large as about 7 times. Noteworthy, the V_{OC} of P3HT:PC₆₁BM based devices saturates at 0.59 V when F4-TCNQ's concentration is 0.3 mg mL⁻¹ while the V_{OC} of PTB7-Th:PC₇₁BM based devices saturates at 0.78 V when F4-TCNQ's concentration is 0.4 mg mL⁻¹. It should be noted that the average V_{OC} of PTB7-Th:PC₇₁BM based devices reduces to 0.77 V when the concentration of F4-TCNQ is 0.3 mg mL⁻¹. The V_{OC} loss is ascribed to energy loss caused by hole injection barrier (HIB), i.e. the offset between WF (5.14 eV) and HOMO energy level of PTB7-Th (5.22 eV). Considering P3HT and PTB7-Th have different HOMO energy levels of 5.00 eV and 5.22 eV respectively, the different V_{OC} variation with the concentration of F4-TCNQ certifies the effectiveness of WF tuning and the proposed NiO_x:F4-TCNQ can serve as effective HTL in OSCs based on different organic donor materials.

It should be noted that the J_{SC} improvement is confirmed by the incident photon-to-electron conversion efficiency (IPCE) spectra as shown in Fig. 4d, which shows obvious increment by replacing PEDOT:PSS with NiO_x:F4-TCNQ. For P3HT:PC₆₁BM based OSCs,

IPCE improves at the wavelength between 350 and 600 nm while for PTB7-Th:PC₇₁BM based OSCs, IPCE improves at wavelength between 350 and 700 nm. The integrated J_{SC} values for P3HT:PC₆₁BM based OSCs are 9.19 mA cm⁻² (one-step prepared PEDOT:PSS based device) and 9.52 mA cm⁻² (one-step prepared NiO_x:F4-TCNQ based device) respectively. For PTB7-Th:PC₇₁BM based OSCs, the integrated J_{SC} values are 14.96 mA cm⁻² (one-step prepared PEDOT:PSS based device) and 16.63 mA cm⁻² (one-step prepared NiO_x:F4-TCNQ based device). For all these devices, all the integrated J_{SC} values deduced from IPCE spectra matches well with values acquired from J - V measurements. This enhancement of IPCE is consistent with absorption spectra as shown in Fig. S11 and previous work on NiO_x as HTLs [14,16,18]. This phenomenon could be ascribed to different refractive indices between PEDOT:PSS and NiO_x:F4-TCNQ films and optical resonance in the devices [16]. Morphology of active layer on different underlying HTLs has also been investigated by AFM as shown in Fig. S12. The RMS values of active layer film on bare ITO and one-step prepared PEDOT:PSS are 2.15 nm and 1.87 nm respectively. After replacing PEDOT:PSS by NiO_x or NiO_x:F4-TCNQ (0.4 mg mL⁻¹), the RMS value slightly increases to 2.52 nm or 2.55 nm, which coincides with the properties of nanoparticle based HTLs.

Considering that parasitic absorption of Ca will cause negative influence on photocurrent generation [49], the ZnO has been widely used as a better choice in OSCs due to its optical spacer effect and better stability [50]. In conventional structured OSCs, the introduction of ZnO layer on active layer will modify the light distribution inside solar cells and thus optimize the absorption in active layer [51]. Photocurrent will be enhanced as a result. To realize a better performance, here, we use ZnO as ETL to further optimize the performance of OSCs with the structure of ITO/HTL/PTB7-Th:PC₇₁BM/ZnO/Al. The ZnO NPs in 1-butanol are synthesized by a former reported method [38]. The ZnO NPs solution (with a concentration of 16 mg mL⁻¹) is spin-coated onto the methanol washed active layer surface without any further treatment. The thickness of ZnO is determined to be 20 nm. The summary of resultant performance is concluded in Table 3, the J - V characteristics is as shown in Fig. 5a and the IPCE spectra is as shown in Fig. 5b. After using ZnO as ETL, the J_{SC} of one-step prepared PEDOT:PSS based devices increases from 15.15 mA cm⁻² to 16.54 mA cm⁻², and the J_{SC} of NiO_x:F4-TCNQ based devices increases from 16.80 mA cm⁻² to 18.29 mA cm⁻². The measured J_{SC} values, 16.54 mA cm⁻² and 18.29 mA cm⁻², matches well with integrated J_{SC} values, 16.72 mA cm⁻² (one-step prepared PEDOT:PSS based device) and 18.11 mA cm⁻² (one-step prepared NiO_x:F4-TCNQ based device), deduced from IPCE spectra as shown in Fig. 5b. Because of the significant enhancement of J_{SC} values, the average PCE increase from 7.25% to 8.06% and from 8.59% to 9.54% for one-step prepared PEDOT:PSS and NiO_x:F4-TCNQ based devices respectively. The performance of NiO_x:F4-TCNQ based OSCs outperforms PEDOT:PSS based OSCs by 18.4%. The PCE deviation among the fabricated OSCs improved from 0.72 (one-step prepared PEDOT:PSS based OSCs) to 0.20 (one-step prepared NiO_x:F4-TCNQ based OSCs) by 3.6 times.

Devices stability is also an important indicator of viability regarding OSCs' commercial application. Thus we have compared the stability of unencapsulated PEDOT:PSS and NiO_x:F4-TCNQ based devices stored in ambient environment as shown in Fig. 5c and d. When using Ca as ETL, the performance degrades fast due to its hygroscopic and easily-oxidized property. The PCE of PEDOT:PSS based devices degrade to zero after 33 h' storage while NiO_x:F4-TCNQ based devices exhibit a longer life, i.e. over 60 h. After replacing Ca with ZnO, the stability gets enhanced simultaneously. However, NiO_x:F4-TCNQ based devices continue to have a better stability as compared to PEDOT:PSS based OSCs. As shown in Fig. 5d, the PCE of NiO_x:F4-TCNQ based devices drop to about 71% of its original value while PEDOT:PSS based devices degrade to 62% of its original value after 62 h. The worse stability of PEDOT:PSS

based devices is ascribed to acidic and hygroscopic nature of PEDOT:PSS, which corrodes the ITO and the metal electrode.

4. Conclusion

In this work, we newly develop a one-step ethanol-processed NiO_x:F4-TCNQ nanocomposite HTLs without any pre-treatment of ITO glasses nor any post-treatment on the HTL for simple and efficient OSCs fabrication. By introducing the strong electron acceptor, F4-TCNQ, into ethanol dispersible NiO_x NPs, a continuously tunable WF has been demonstrated for NiO_x:F4-TCNQ nanocomposite films. The WF can be tuned from 4.73 eV to as high as 5.30 eV, which can align well with most organic donor materials. The continuous WF tuning range is as wide as 0.57 eV, which has never been reported in the case of NiO_x. Importantly, the ethanol-processed NiO_x:F4-TCNQ offers a much better wettability on ITO without UVO or oxygen-plasma pre-treatment compared with water based PEDOT:PSS. By using one-step pre- and post-treatment-free NiO_x:F4-TCNQ as HTL, average PCE of 3.59% has been realized in P3HT:PC₆₁BM based OSCs and 9.54% in PTB7-Th:PC₇₁BM based OSCs. The best PCE of NiO_x:F4-TCNQ based OSCs can reach at 9.75%. For the OSCs with different active layers studied in this work, the optimized average PCE of NiO_x:F4-TCNQ based OSCs can be 18% better than that of PEDOT:PSS based OSCs. Remarkably, the PCE deviation of devices can be improved by a largest extent of 10 times, which indicates a good reproducibility of the one-step prepared NiO_x:F4-TCNQ nanocomposite HTL. This NiO_x:F4-TCNQ nanocomposite HTL can provide great potential in the field of low cost and simple fabrication of high performance OSCs.

Acknowledgements

This work was supported by the University Grant Council of the University of Hong Kong (Grant 104003113), the General Research Fund (Grant HKU711813 and 17211916), the Collaborative Research Fund (Grants C7045-14E) from the Research Grants Council of Hong Kong Special Administrative Region, China, ECF Project 33/2015 from Environment and Conservation Fund, and Grant CAS14601 from CAS-Croucher Funding Scheme for Joint Laboratories.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2017.02.021.

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