Full paper

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


A R T I C L E   I N F O

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

A B S T R A C T

In this work, we demonstrate a one-step room-temperature ethanol-processed nickel oxide (NiOx):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 4.73eV 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 NiOx:F4-TCNQ nanocomposite as HTL. The optimized average power conversion efficiency (PCE) of NiOx: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, NiOx: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 (NiOx), have been developed as HTLs [7–9]. Among them, NiOx shows advantages including p-type conductivity, better conductivity and good electron-blocking ability. Solution-processed NiOx 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...
in inevitable. Nanoparticles (NPs) based method is another commonly used film formation method, which provides the advantage of de-coupled particle synthesis and film formation [17]. Zhang et al. reported an annealing free NiOx 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 NiOx nanoparticles (NPs) which can be used as HTL in OSCs [19]. However, these NiOx 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 NiOx 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 NiOx based HTL could be of great interests to fully exploit the remarkable properties of NiOx 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 (PBDDTT-T) to 5.33 eV (PBDD-TS) [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 F4–TCNQ: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. In a typical synthesis procedure, 0.13 g (0.50 mmol) Ni(acac)$_2$ was dispersed into ethanol to form the NiO$_x$:F4–TCNQ solution. Then the suspension was transferred into a Teﬂon autoclave. 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 was dispersed into ethanol to form the NiO$_x$:F4–TCNQ solution. Usually, several drops of water needs to 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 spectrophotometric ellipsometry. (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 Kα 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 Kα 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 microscopy (AFM, NT-MDT, Moscow, Russia).

### 2.4. Device fabrication of OSCs

For OSCs device fabrication, ITO-coated glass substrates with sheet resistance of 15 Ω sq$^{-1}$ were cleaned by a standard procedure with detergent, acetone and ethanol ultrasonic bath for each of 10 min. 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 after annealing [36,37].

### 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 purchased from Kintec. PEDOT:PSS (Baytron A14083) 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. and diocidoctadecane (DIO, > 95.0%) DIO was purchased from Tokyo Chemical Industry Co., Ltd. (TCI). All chemicals were used as received.
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 NiOx 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 NiOx 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 NiOx NPs are described in Section 2.

**Fig. 1.** XPS results of NiOx films a) Ni 2p3/2 and b) O 1s core level peaks. c) TEM image of the NiOx (scale bar: 20 nm) and d) HRTEM image of NiOx NPs (scale bar: 5 nm).

The peak centered 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 NiOx synthesized NPs. The synthesized NiOx 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 NiOx NPs. By varying the concentration of F4-TCNQ from 0.05 to 0.5 mg mL⁻¹ while fixing the concentration of NiOx at 5 mg mL⁻¹, a series of well mixed NiOx: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 NiOx:F4-TCNQ solutions on ITO without any pre-treatments, the one-step prepared NiOx:F4-TCNQ nanocomposite films have been prepared.

Due to the good surface energy match between ethanol and ITO, the
NiO$_2$:F4-TCNQ solution shows good wetting properties on pristine ITO even without any pre-treatments. As shown in Fig. 2b, only 50 μL NiO$_2$:F4-TCNQ solution can fully cover the pristine ITO substrate (1.7×1.7 cm$^2$). 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 concentrations 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 ($E_{cut-off}$) 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 ($E_{gap}$), i.e. the energy difference between the conduction band (CB) and VB, is determined by the Tauc plot ($\alpha(hv)^{1/2}$–hv), 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 (hv), 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 the HTL. From the boundary condition $\delta n(x)/\delta L = 0$, 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 $\varepsilon_r=12$ [46]. $n(x)$ and $p(x)$ are given by the convolution of Fermi-Dirac distribution and corresponding effective density of states distributions $\delta_{CB}$ and $\delta_{VB}$.

$$\frac{d^2 \phi}{dx^2} = \frac{e}{\varepsilon_0 k_0} [n(x) - p(x) + N_A]$$

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 $\varepsilon_r=12$ [46]. $n(x)$ and $p(x)$ are given by the convolution of Fermi-Dirac distribution and corresponding effective density of states distributions $\delta_{CB}$ and $\delta_{VB}$.
WF at the HTL surface can be calculated by

$$\Phi_{\text{HTL}}(L) = \Phi_{\text{sub}} - e\phi(L)$$  \hspace{1cm} (4)

in which, \(\Phi_{\text{sub}}=4.69\) eV is the WF of ITO substrate. The relationship between \(\Phi_{\text{HTL}}(L)\) 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 NiOx: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 NiOx:F4-TCNQ films (the thickness around 17 nm) on ITO substrates. The thickness of the NiOx or NiOx: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 NiOx:F4-TCNQ films is shown in Fig. S8. In the visible and near infrared (NIR) range, the NiOx: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/NiOx and ITO/NiOx: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 NiOx:F4-TCNQ nanocomposite films are decent HTL candidates in OSCs.

### 3.3. Device performances

To demonstrate the viability of NiOx: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

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**Table 1**

The WF variation of NiOx:F4-TCNQ films with different concentrations of F4-TCNQ characterized by Kelvin-Probe measurements. \(\Delta E_F\) is defined as the energy level offsets of the composite film and pristine film.

<table>
<thead>
<tr>
<th>Concentrations of F4-TCNQ [mg mL(^{-1})]</th>
<th>WF [eV]</th>
<th>(\Delta E_F) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/o</td>
<td>4.73 ± 0.01</td>
<td>0</td>
</tr>
<tr>
<td>0.05</td>
<td>4.79 ± 0.01</td>
<td>0.06</td>
</tr>
<tr>
<td>0.1</td>
<td>4.90 ± 0.02</td>
<td>0.17</td>
</tr>
<tr>
<td>0.2</td>
<td>4.93 ± 0.01</td>
<td>0.20</td>
</tr>
<tr>
<td>0.3</td>
<td>5.14 ± 0.01</td>
<td>0.41</td>
</tr>
<tr>
<td>0.4</td>
<td>5.20 ± 0.01</td>
<td>0.47</td>
</tr>
<tr>
<td>0.5</td>
<td>5.30 ± 0.02</td>
<td>0.57</td>
</tr>
</tbody>
</table>
energy levels of component materials are as shown in Fig. 4a and b. The concentrations of F4-TCNQ are varied from 0 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:PC$_{61}$BM 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.

![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:PC$_{61}$BM or PTB7-Th:PC$_{71}$BM) /Ca/Al.](image)

Table 2
Performance summary of OSCs with a structure of ITO/HTL/P3HT:PC$_{61}$BM/Ca/Al or ITO/HTL/PTB7-Th:PC$_{71}$BM/Ca/Al in which HTL is PEDOT:PSS or NiO$_x$:F4-TCNQ.

<table>
<thead>
<tr>
<th>Concentration of F4-TCNQ [mg mL$^{-1}$]</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>$V_{oc}$ [V]</th>
<th>FF</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT:PC$_{61}$BM</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>w/o</td>
<td>7.50 ± 0.44</td>
<td>0.34 ± 0.02</td>
<td>0.233 ± 0.012</td>
<td>0.60 ± 0.06</td>
</tr>
<tr>
<td>0.05</td>
<td>8.99 ± 0.26</td>
<td>0.40 ± 0.01</td>
<td>0.290 ± 0.013</td>
<td>1.05 ± 0.09</td>
</tr>
<tr>
<td>0.1</td>
<td>9.62 ± 0.20</td>
<td>0.48 ± 0.01</td>
<td>0.395 ± 0.019</td>
<td>1.83 ± 0.02</td>
</tr>
<tr>
<td>0.2</td>
<td>9.61 ± 0.19</td>
<td>0.57 ± 0.01</td>
<td>0.571 ± 0.015</td>
<td>3.13 ± 0.04</td>
</tr>
<tr>
<td>0.3</td>
<td>9.79 ± 0.19</td>
<td>0.59 ± 0.01</td>
<td>0.599 ± 0.009</td>
<td>3.46 ± 0.10</td>
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<td>0.4</td>
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<td>0.616 ± 0.008</td>
<td>3.59 ± 0.04</td>
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<tr>
<td>0.5</td>
<td>9.86 ± 0.11</td>
<td>0.59 ± 0.01</td>
<td>0.605 ± 0.009</td>
<td>3.52 ± 0.09</td>
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<tr>
<td>PEDOT:PSSa</td>
<td>9.21 ± 0.35</td>
<td>0.58 ± 0.02</td>
<td>0.582 ± 0.047</td>
<td>3.10 ± 0.40</td>
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<tr>
<td>PTB7-Th:PC$_{71}$BM</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>w/o</td>
<td>16.43 ± 0.35</td>
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<td>0.454 ± 0.002</td>
<td>3.84 ± 0.11</td>
</tr>
<tr>
<td>0.05</td>
<td>16.27 ± 0.21</td>
<td>0.60 ± 0.01</td>
<td>0.539 ± 0.008</td>
<td>5.29 ± 0.06</td>
</tr>
<tr>
<td>0.1</td>
<td>16.40 ± 0.44</td>
<td>0.68 ± 0.01</td>
<td>0.571 ± 0.006</td>
<td>6.34 ± 0.19</td>
</tr>
<tr>
<td>0.2</td>
<td>16.73 ± 0.18</td>
<td>0.74 ± 0.02</td>
<td>0.608 ± 0.006</td>
<td>7.48 ± 0.27</td>
</tr>
<tr>
<td>0.3</td>
<td>16.78 ± 0.12</td>
<td>0.77 ± 0.01</td>
<td>0.623 ± 0.011</td>
<td>8.04 ± 0.22</td>
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<td>16.80 ± 0.23</td>
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<td>0.652 ± 0.010</td>
<td>8.59 ± 0.14</td>
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<td>16.60 ± 0.33</td>
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<td>0.644 ± 0.009</td>
<td>8.92 ± 0.11</td>
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<tr>
<td>PEDOT:PSSa</td>
<td>15.15 ± 0.21</td>
<td>0.79 ± 0.00</td>
<td>0.606 ± 0.079</td>
<td>7.25 ± 0.97</td>
</tr>
</tbody>
</table>

a One-step prepared PEDOT:PSS HTLs without any pre-treatment of ITO glasses or post-treatment.
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 NiOx: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 NiOx: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 NiOx: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. Noteworthily, 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 NiOx: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 NiOx: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 PTHT:PC60BM 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 devices, all these 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 space 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 PTHT:PC60BM 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.

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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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