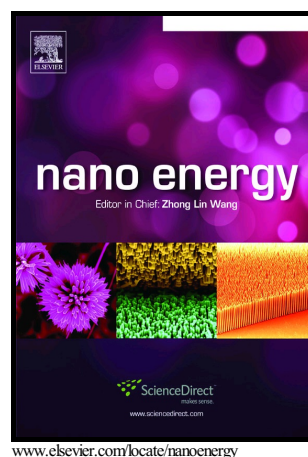


All-Room-Temperature Solution-Processed New Nanocomposites Based Hole Transport Layer from Synthesis to Film Formation for High-Performance Organic Solar Cells Towards Ultimate Energy-Efficient Fabrication

Zhanfeng Huang, Jiaqi Cheng, Xingang Ren, Jiaqing Zhuang, Vellaisamy A.L. Roy, Jeffrey Mark Burkhartsmeyer, Kam Sing Wong, Wallace C.H. Choy



PII: S2211-2855(18)30086-7
DOI: <https://doi.org/10.1016/j.nanoen.2018.02.019>
Reference: NANOEN2506

To appear in: *Nano Energy*

Received date: 2 January 2018
Revised date: 3 February 2018
Accepted date: 8 February 2018

Cite this article as: Zhanfeng Huang, Jiaqi Cheng, Xingang Ren, Jiaqing Zhuang, Vellaisamy A.L. Roy, Jeffrey Mark Burkhartsmeyer, Kam Sing Wong and Wallace C.H. Choy, All-Room-Temperature Solution-Processed New Nanocomposites Based Hole Transport Layer from Synthesis to Film Formation for High-Performance Organic Solar Cells Towards Ultimate Energy-Efficient Fabrication, *Nano Energy*, <https://doi.org/10.1016/j.nanoen.2018.02.019>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting galley proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

All-Room-Temperature Solution-Processed New
Nanocomposites Based Hole Transport Layer from
Synthesis to Film Formation for High-Performance
Organic Solar Cells Towards Ultimate Energy-Efficient
Fabrication

*Zhanfeng Huang[†], Jiaqi Cheng[†], Xingang Ren[†], Jiaqing Zhuang[‡], Vellaisamy A. L. Roy[‡], Jeffrey
Mark Burkhartsmeyer[§], Kam Sing Wong[§], Wallace C. H. Choy^{*†}*

[†] Department of Electrical and Electronic Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, China.

[‡] Department of Physics and Materials Science and Centre for Functional Photonics (CFP), City University of Hong Kong, Kowloon, Hong Kong, China

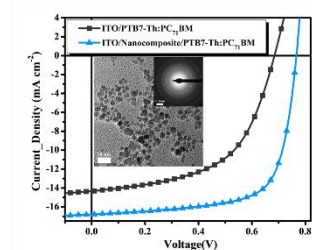
[§] Department of Physics, Hong Kong University of Science and Technology, Kowloon, Hong Kong, China

ABSTRACT

It is an ultimate goal of energy-efficient fabrication that photovoltaic devices only need low energy consumption processes covering both synthesis of material and fabrication of device. Regarding to charge transport layer, it is worthwhile to synthesize nanomaterials and deposit films all at room temperature while still have good electrical properties. Meanwhile, there are very limited studies on room temperature solution approaches for modification on nanocrystal colloidal for facilely forming high quality film with tunable electrical properties. In this work, we propose and demonstrate a new nanocomposites of maghemite and iron hydroxide through a low energy consumption approach which is all room-temperature solution processes from the synthesis of the nanocomposites to the formation of high quality hole transport layer (HTL). Strategically adjustment of acidity for the conversion of prepared precipitation is demonstrated to achieve a component controllable maghemite and iron hydroxide nanocomposites which contributes to in-situ tunable work function of the nanocomposites HTL from 4.70 eV to 5.16 eV. Simultaneously, since the nanocomposites synthesized from this approach have the features of ultra-small size of 6-10 nm and surfactant-free, high quality and efficient HTL films can be formed at room temperature. For organic solar cells using nanocomposite as HTL, the power conversion efficiency can be significantly improved by as much as 80% as compared with the optimized devices without HTL. Besides, both the efficiency and stability of the nanocomposite based organic solar cells are better than that of devices using poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS). Consequently, the work contributes to the fabrication of simple, low-cost, and stable optoelectronics promoting green photovoltaics and flexible electronics.

GRAPHICAL ABSTRACT

Energy-Efficient Fabrication from Synthesis to Film Formation is demonstrated on preparing maghemite/iron hydroxide nanocomposite as efficient hole transport layer. Since the nanocomposite is surfactant-free and ultra-small nanocrystal, high quality film with tunable work function can be formed for fabrication higher performance organic solar cells



KEYWORDS: maghemite and iron hydroxide, nanocomposite, tunable work function, hole transport layer, polymer/organic solar cells.

INTRODUCTION

To realize large scale application of photovoltaic devices, besides efficiency, the cost and stability are also critical topics. To achieve cost effective organic solar cells (OSCs), different strategies have been investigated in developing potential lower cost materials such as transparent electrode of metal [1-5] and graphene [6], non-fullerene acceptor [7-9]. Regarding carrier (electron and hole) transport layers, in the early stage, high energy consumption techniques (e.g. thermal evaporation under high vacuum, pulsed-laser deposition, radio frequency magnetron sputtering) are generally used to demonstrate a metal oxide, such as V_2O_5 , MoO_3 , NiO_x and CrO_x , as efficient hole transport layer (HTL) [10-12]. Meanwhile, solution process techniques have also been intensively studied on HTL [13-18]. Among them, precursor approach generally performs under ambient condition but typically needed post-treatment such as thermal annealing and ultraviolet-ozone [16-19]. In addition, the HTL prepared from oxide nanocrystal colloidal is typically energy-consuming either the synthesis processes of the nanomaterials or post-treatments of films [14, 15, 20]. However, the ultimate goal of energy-efficient or cost-effective fabrication for photovoltaic devices is low energy consumption covering both synthesis of material and film formation. Moreover, extra treatments and processes (which needed additional power consumption) are typically used to make the film with good electrical properties for functioning as effective HTL [21-24]. Consequently, it is desirable to achieve all room temperature solution process from synthesis of nanomaterials to film formation for HTL which can simultaneously offer decent electrical properties.

OSCs based on varied photoactive layer which typically consists of different donor and acceptor materials require tunable electrical properties of HTL. Choy and coworker demonstrated a simple cesium intercalation method to tune the work function of metal oxide for

efficient HTL [25]. Cheng J. et al. also utilized a composite scheme to develop efficient nanocomposite HTL with tunable work function via controlling the dopant concentration in the nanocrystal colloidal solution[20]. Besides, Wang, Y., et al. reported a mixed solution of poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate) (PEDOT:PSS) and graphene oxide to minimize the energy loss at the interface via tuning work function [26] and Lee and coworkers used perfluorinated ionomer to tailor the energy level for band alignment to reduce interface energy offset and charge recombination thus achieving high performances [27]. Modification on the nanocrystal colloidal rather than post-treatment, is a promising approach to simply deposit HTL with desirable electrical properties in low cost and large scale. Hence, to favor OSCs fabrication in large scale and cater different application occasions, it is very deserved to investigate other different techniques for modification on nanocrystal colloidal for facilely depositing efficient HTL.

In this work, we demonstrate a new nanocomposites of maghemite and iron hydroxide by a low energy consumption method, i.e., all room-temperature solution process from the synthesis of maghemite and iron hydroxide nanocomposites to the formation of efficient HTL. To be more specific, by using room temperature chemical precipitation method and controlling the pH condition for conversion, a component controllable maghemite and iron hydroxide nanocomposite colloidal is prepared. Simultaneously, the ratio between maghemite and iron hydroxide in the deposited nanocomposite films can be adjusted for realizing in-situ work function tuning by around 0.46 eV. Additionally, the produced nanocomposites are ultra-small nanoparticles and surfactant free that favoring the formation of high quality HTL film. To demonstrate the effectiveness as HTL material for high efficient OSC, three representative bulk heterojunction active layers have been investigated, namely the blends of poly(3-hexylthiophene-

2,5-diyl) (P3HT) with [6,6]-Phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM), 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) with [6,6]-Phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) and the non- fullerene material system of poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione))] (PBDB-T) with small molecular compound 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno [2,3- d:2',3'-d']-s-indaceno[1,2-b:5,6-b'] dithiophene) (ITIC). The power conversion efficiency (PCE) of P3HT:PC₆₁BM and PTB7-Th:PC₇₁BM devices are remarkably enhanced with the introduction of nanocomposite comparing with the optimized devices without HTL. In addition, the nanocomposite based devices show better stability in comparison with device fabricated from PEDOT:PSS. Consequently, this new all room temperature processed maghemite and iron hydroxide nanocomposites based HTL contributes to low-cost and high performance OSCs for photovoltaic applications.

1. EXPERIMENTAL SECTION

2.1 Chemicals.

FeCl₃, FeCl₂, Methanol and 28-30 % Ammonium hydroxide solution in water were purchased from Aladdin. PEDOT:PSS (Baytron A14083) was purchased from H.C. Starck GmbH, Germany. P3HT, [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM), PTB7-Th, [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM), PBDB-T and ITIC were purchased from Solarmer Co., Ltd. 1,8-diiodooctane (DIO, > 95.0%) DIO was purchased from Tokyo Chemical Industry Co., Ltd. (TCI). 1,2-Dichlorobenzene (DCB) and Chlorobenzene (CB) in extra dry grade were purchased from Acros. All chemicals were used as received.

2.2 Preparation of maghemite and iron hydroxide nanocomposites.

A typical chemical precipitation method was used and accompanied with phase conversion under acid condition to prepare iron oxide/hydroxide nanocomposites. Typically, an iron salt with $\text{Fe}^{3+}/\text{Fe}^{2+}$ aqueous solution was prepared by dissolving 1.3g FeCl_3 and 0.5g FeCl_2 into 95 mL deionized (DI) water with continually stirring. Around 5 mL 28-30 % Ammonium hydroxide solution was added into the prepared $\text{Fe}^{3+}/\text{Fe}^{2+}$ aqueous solution under vigorous stirring, black precipitate producing instantly. The black product were separated by a magnetic field when it was stirred another 10 minutes after adding ammonium hydroxide. Then, the black precipitate was washed three time by DI water and finally dispersed in DI water with adjusted pH value under around 30 minutes ultrasonic treatment. The well dispersed colloidal was further stirred overnight in ambient condition, which results in a maghemite and iron hydroxide nanocomposite colloidal solution with a color of burgundy. The concentration was determined by weighting the powder obtained by drying certain amount corresponding solution.

2.3 Nanocomposite Characterization.

Transmission electron microscope (TEM) was performed using a Philips Tecnai G2 20 s-TWIN. For the sample preparation, a small amount nanocomposite solution was dropped onto a carbon coated copper grid and evaporated. The grazing incidence X-ray diffraction (GIXRD) pattern of the nanocomposite film was recorded using a Rigaku SmartLab 9kW diffractometer with a copper rotating anode ($\text{K}\alpha_1$ 1.54059 Å) rated at 200 mA/ 45 kV. X-ray photoelectron spectroscopy (XPS) of nanocomposite films on ITO was measured in the ultrahigh vacuum environment using Physical Electronics PHI 5802 with a monochromatic Al $\text{K}\alpha$ X-ray source.

2.4 Device fabrication.

ITO-coated glass substrates with sheet resistance of $\sim 15 \text{ } \Omega/\text{sq}$ were cleaned by a typical procedure in ultrasonic bath with DI water, acetone, and ethanol for each of 10 minutes and dried with nitrogen gas. For PEDOT:PSS device, it was spin-coated on the clean and 15 min ultraviolet-ozone (UVO) treated ITO substrates with thickness around 40 nm and then annealed at $150 \text{ } ^\circ\text{C}$ for 10 min. The maghemite and iron hydroxide nanocomposite based HTL were prepared by spin-coating nanocomposite colloidal solution with certain concentration onto the cleaned ITO at 2000 rpm for 40s at room temperature while the same amount of DI water was spun on substrate for the devices without HTL. The P3HT:PC₆₁BM layer with a thickness around 220 nm (20:20 mg/mL in DCB) was spin-coated on HTL at 670 rpm for 42s followed by solvent annealing for one hour and thermal annealing at $130 \text{ } ^\circ\text{C}$ for 10 minutes. The active layer (around 100 nm) of low bandgap polymer was prepared from PTB7-Th:PC₇₁BM solution (10:15 mg/mL in CB, with addition of 3 vol% DIO) by spin-coating at 1600 rpm at room temperature. Methanol washing method was performed to remove the high-boiling-point DIO as reported [28-30]. For non-fullerene OSCs, the procedure is referred to the reference [8]. Typically, 20 mg PBDB-T:ITIC (1:1 weight ratio) was dissolved in 1 mL CB:DIO (99.5:0.5 volume ratio) solution. A thickness of 100 nm film was deposited by spin-coating with $120 \text{ } ^\circ\text{C}$ thermal treatment for 20 minutes. Device fabrication was completed by thermal evaporating around 40 nm calcium and a 100 nm aluminum cathode with area of 0.06 cm^2 defined by a shadow mask.

2.5 Device characterization.

J-V characteristics were measured using a Keithley 2635 sourcemeter and ABET AM1.5G solar simulator which was calibrated with a standard silicon solar cell. The IPCE measurement of OSCs was taken by a home-built IPCE measurement system with a Newport xenon lamp, a monochromator, a preamplifier, and a lock-in amplifier.

2. RESULTS AND DISCUSSION

3.1 Synthesis and properties of maghemite and iron hydroxide nanocomposites

To obtain maghemite and iron hydroxide nanocomposite in energy-efficient manner, the chemical precipitation method from previous references [31, 32] was modified to obtain black magnetic product. We use the pH method to adjust the condition for the conversion of black resultant to nanocomposite at room temperature, since the Fe^{2+} and Fe^{3+} cation on octahedral and tetrahedral site can be control via tuning ratio of H^+/OH^- [33]. This method produced ultra-small nanoparticles without the assistance of surfactant. Notably, high temperature annealing is generally needed to remove surfactant. Differently, since surfactant-free ultra-small nanocomposite is achieved in our method and the particle size is small (6-10 nm as described later), we can achieve room-temperature processed high quality film (as shown in supporting information, **Figure S1**). In addition, work function of thin film deposited from the prepared nanocomposites can be easily controlled by adjusting the conversion pH value during the synthesis process which will favor the band alignment and thus uses in various OSCs with different donor HOMO.

Grazing incidence X-ray diffraction (GIXRD) was performed to characterize the nanocrystalline dimension and material phases of the nanoparticles obtained under conversion pH=2. Typically, the pattern of sample from pH=2 as shown in **Figure 1a**, consists of five main diffraction peaks locating at 2θ around 30.2° , 35.5° , 43.2° , 57.2° and 62.9° respectively, indicating that the obtained oxide is well crystallized. These diffraction peaks can match well with three possible material phases, namely maghemite ($\gamma\text{-Fe}_2\text{O}_3$), magnetite (Fe_3O_4) and iron hydroxide ($\text{Fe}(\text{OH})_3$). Since these phases have similar main peaks location, it is difficult to exactly determine what the components are only from XRD pattern. However, three phases can

be identified from the results, suggesting that the prepared oxide can be a composite of these possible phases. Besides, from Debye–Scherrer equation[14]: $D = 0.89\lambda/(\beta\cos\theta)$, diameter (D) of the oxide nanocrystals is estimated to have average of 7.5 nm from three strongest peaks. Meanwhile, as shown in **Figure 1b**, the transmission electron microscopy (TEM) and the selected area electron diffraction (SAED) results show that the oxide nanocomposites have good uniformity and crystallization with the size about 6-10 nm, which are consistent with the calculated results from XRD.

In order to identify the chemical components of the nanocomposites with the measured phases, X-ray photoelectron spectroscopy (XPS) measurement was conducted with samples on the ITO glass. **Figure S2a** shows the full spectra from 0 to 1400 eV of sample prepared from pH=2. Apart from the characteristic peaks from oxide sample, there are some peaks detected from ITO glass, such as indium and tin. The narrow scanned Fe 2p and O1s characteristic peaks in **Figure 2** were calibrated by the standard C 1s peak value of 284.8 eV. Both spectra of Fe 2p doublet composed of two main peaks are observed. These peaks at 724.4 eV and 710.8 eV with a spin-orbital coupling separation of 13.6eV are identified as the signal from the Fe-O bond with Fe 2p_{1/2} and Fe 2p_{3/2} respectively [34, 35]. These are the characteristic binding energies of Fe³⁺, while peaks of Fe²⁺ are not observed[36, 37]. Moreover, two satellite peaks at around 719 eV and 731 eV (see **Figure 2a**) manifests that iron in the sample is at high oxidation state (Fe³⁺) rather than low oxidation state (Fe²⁺). **Figure 2b** corresponds to XPS spectra of O 1s, which can be deconvoluted into two peaks at around 530.1 eV and 531.6 eV coinciding with the species of O²⁻ and OH⁻ [38, 39]. The detected signal of OH⁻ indicates the existence of iron hydroxide that may come from the precipitation reaction of the iron salt and ammonium hydroxide. Consequently, from the XRD and XPS analysis results, it can be inferred that the prepared

sample mainly consists of maghemite and iron hydroxide, while the magnetite with low oxidation state iron can be excluded from the XRD results. The ratio between these two component (O^{2-} and OH^-) was calculated by the integral area of O 1s spectrum to be 2.15. The spectrum of samples obtained by other pH conditions are given in Supporting Information (**Figure S2b**) and the ratio are calculated to be 2.45, 1.90 and 1.68 for pH=1, 3 and 4 respectively.

As measured from XPS, the ratio between maghemite and iron hydroxide varies with the conversion pH values. The contained hydroxide in nanocomposite would cause variation of work function, which have been studied in NiO_x [40]. Different work function of the thin films prepared by spin-coating the nanocomposite colloidal onto ITO glass are obtained by Kelvin Probe measurement as listed in the **Table 1**. When the pH value reduces from 4 to 2, the amount of hydroxide was gradually reduced. As we know, the maghemite have a spinal structure with Fe^{3+} ion in tetrahedral and octahedral sites while there are cation vacancies in octahedral sites to keep charge neutrality [41]. When the acidity increase, more maghemite tends to produce [33, 42]. Consequently, in the maghemite and iron hydroxide nanocomposite, when the pH value decreases from 4 to 1, the ratio of maghemite in the nanocomposite will gradually increase which will induce the increase of cation vacancy density. As reported, the increase of cation vacancy density in the oxide effectively make the materials more p-type [43], which agrees well with our experimental results that work function increases from 4.70 eV to 5.16 eV. However, when pH value is adjusted to 1, the work function does not increase further, which might be the detrimental impact of anion from addition for adjusting pH. The highest work function 5.16 eV obtained from the sample prepared with pH=2 is slightly higher than PEDOT:PSS (5.08 eV). Consequently, a new class of maghemite and iron hydroxide nanocomposites with in-situ tuning

work function from 4.70 eV to 5.16 eV has been obtained for forming effective HTL as described below.

3.2 Device Performances

To evaluate the maghemite and iron hydroxide nanocomposite based HTL, OSCs with a structure of ITO/HTL/P3HT:PC₆₁BM/Ca/Al have been fabricated. Devices optimization is conducted by adjusting the pH values for the conversion and the concentration of the nanocomposites which leads to different film thicknesses. The current density (J) vs voltage bias (V) characteristics are shown in the **Figure 3a** and device parameters are summarized in the **Table 2**. When work function increases from 4.70 eV (pH=4) to 5.16 eV (pH=2), open circuit voltage (V_{OC}) gradually goes up from 0.56 to 0.60. The V_{OC} loss at low work function devices is ascribed to decreased work function difference between anode and cathode contact[44]. Apart from the pH value, the impact of the thickness of HTL prepared by different concentrations of the nanocomposites were investigated including 0mg/mL, ~6 mg/mL, ~12 mg/mL and ~18 mg/mL. **Figure 3b** presents J - V characteristics of OSCs and **Table 3** listed the parameters of these devices. With the introduction of nanocomposite, a good interfacial layer is gradually formed to improve the energetic contact between active layer and ITO anode electrode. The steady V_{OC} up to 0.60 V is observed when the concentration up to 12 mg/mL, which can be ascribed to the formation of the nanocomposite HTL favoring effective hole extraction from active layer to ITO substrate. However, when the concentration is further increased to 18 mg/mL, short circuit current (J_{SC}) decreases from the peak value to 8.78 mA/cm² without clear change of V_{OC} and FF . This can be explained by the high in series resistance induced by the increase of thickness. However, the anode of devices without maghemite and iron hydroxide nanocomposite interface layer exhibits a low work function (~4.78 eV) which induces hole

extraction barrier at the interface, resulting in poor performance with average V_{OC} and PCE only 0.525 V and 2.65%. In comparison, the device with nanocomposite prepared at pH=2 as HTL offers good band alignment and improves PCE to the value of 3.84% (by around 45% improvement as compared to the case of no HTL) as shown in **Figure 4a** and **Table 4**. Similar enhancement is also observed in the solar cells devices using narrow-bandgap polymer PTB7-Th:PC₇₁BM. Only 5.02% of average PCE is achieved without HTL with J_{SC} , V_{OC} and FF only 14.07 mA/cm², 0.663 V and 0.539 respectively. With the optimized HTL incorporation, the average PCE reaches as high as 9.04% (by around 80% improvement from no HTL case), resulting from increased J_{SC} (16.94 mA/cm²), V_{OC} (0.775 V) and FF (0.689). Consequently, the all room temperature prepared maghemite and iron hydroxide nanocomposite HTL offers very good hole extraction properties for achieving high efficiency OSCs.

To compare with commercial PEDOT:PSS, the optimized thin film formed from the nanocomposite prepared at pH=2 and with a concentration of around 12 mg/mL is used to serve as HTL in the P3HT:PC₆₁BM, narrow-bandgap polymer PTB7-Th:PC₇₁BM and non-fullerene material system PBDB-T:ITIC solar cells. The characteristic J - V curve and devices performance parameters are presented in Figure 4a-c and Table 4. Comparing to the PEDOT:PSS devices, the improved performances are mainly the results of enhanced J_{SC} and FF . Specifically, for P3HT:PC₆₁BM devices, an enhanced PCE of 3.84% is realized by employing maghemite and iron hydroxide nanocomposite as HTL with average J_{SC} of 9.58 mA/cm², V_{OC} of 0.602 V and FF of 0.667 while the PEDOT:PSS based devices have lower average J_{SC} of 9.08 mA/cm² and FF of 0.660 resulting average PCE of 3.62%. In PTB7-Th:PC₇₁BM based OSCs, higher average J_{SC} (16.94 mA/cm²) and FF (0.689) of devices using nanocomposite (16.37 mA/cm² and 0.670 for J_{SC} and FF of PEDOT:PSS devices) are realized which contribute to an average PCE of 9.04%.

Additionally, non- fullerene OSCs (PBDB-T:ITIC) have also been fabricated with two kinds of HTLs. Similarly, higher average J_{SC} (17.12 mA/cm²) and FF (0.696) contribute to surpassed average PCE (10.75%) with highest PCE reaching 10.94% while only average 10.17% from PEDOT:PSS devices. The incident photon-to-current efficiency ($IPCE$) of different devices has also been measured in 5 nm interval as shown in the **Figure 4d-f**. The photocurrent integrated from $IPCE$ are 8.03 mA/cm², 8.96 mA/cm² and 9.44 mA/cm² of P3HT: PC₆₁BM, 14.07 mA/cm², 15.96 mA/cm² and 16.58 mA/cm² of PTB7-Th:PC₇₁BM for no HTL, PEDOT:PSS and nanocomposite based devices and 16.34 mA/cm² and 16.69 mA/cm² for non-fullerene devices, which is in good agreement with the measured J_{SC} from the J - V curve. In order to understand the enhancement of J_{SC} and FF , the surface properties of the nanocomposite have been investigated via SEM, AFM and contact angle as shown in supporting information Figure S1 and **Figure S3**. Good surface coverage by the nanocomposite film was realized as observed in the SEM and AFM, which can effectively block the leakage current. The contact angle of DI water on prepared nanocomposite film is larger than that of PEDOT:PSS. This implies that the nanocomposite film is more hydrophobic that favors the spread of dichlorobenzene and chlorobenzene solution and promotes to form smoother active layer (as compared to the case of PEDOT:PSS) as shown in **Figure S4**. The slightly lower in-series resistance (R_s) of nanocomposite based devices may be ascribed to the better film formation on hydrophobic HTL and better band alignment which can contribute to increased J_{SC} and FF . Additionally, we employ a numeral simulation using transfer matrix method [45], to investigate optical properties and light harvesting of our nanocomposite in P3HT:PC₆₁BM based OSCs. The used optical parameters of refractive index (n) and extinction coefficient (k) are measured from ellipsometer shown in the supporting information **Figure S5**. As shown electric field intensity distribution in

Figure 5 and the electric field of typical wavelength (550 nm) across the whole device in **Figure S6a**, higher intensity electric field distribution in active layer of nanocomposite based devices are observed. As a result, nanocomposite based device show improved absorption of active layer in the range of 438 nm to 630nm (**Figure S6b** which is in accordance with the experiment results as illustrated in the **Figure S7**. Overall, the improved device performance of OSCs with maghemite and iron hydroxide nanocomposite as HTL is ascribed to the slightly lower device in-series resistance and the higher active layer absorption resulting from the adjusted electric field distribution.

Apart from device efficiency, stability is also of vital importance to practical applications. As shown in the **Figure 6a**, the degradation of devices performance has been investigated in ambient condition (around 40% humidity under room temperature) without encapsulation. In P3HT:PC₆₁BM devices, nanocomposite-based device using calcium/aluminum as top electrode can last longer than 11 days while still keep more than 50% of its initial performance while the devices using PEDOT:PSS can keep half of its initial performance within only two days and completely loss its function in around 11 days. Regarding to the low bandgap polymer devices, the stability is in general not as good as P3HT:PC₆₁BM devices. Interestingly, our nanocomposite based devices show better stability than the devices using PEDOT:PSS as shown in **Figure 6b**. Overall, compared to nanocomposite based devices, PEDOT:PSS-based devices without encapsulation show poor stability in ambient condition which may ascribed to the hygroscopic and long-standing acidic nature that have detrimental effect on the interfaces[46].

3. CONCLUSION

In conclusion, we have successful demonstrated a low energy consumption method to develop new nanocomposites of maghemite and iron hydroxide by all room-temperature solution

process from the synthesis to the formation of efficient HTL. By modifying the conversion pH values, a component controllable maghemite and iron hydroxide nanocomposites colloidal is prepared. As a result, work function of this nanocomposite based HTL can be in situ tuned from 4.70 eV to 5.16 eV without assistance from any additional dopant. Additionally, since the iron oxide nanocomposites are surfactant free and with a small particle size of 6-10 nm, high quality HTL film are achieved at room temperature process and without post-treatment. By using the nanocomposite as HTL, the PCE can be significantly improved by as much as 80% improvement as compared to control device without HTL. Additionally, the devices using nanocomposite show obviously better performance than PEDOT:PSS in both PCE and stability. The success of using the maghemite and iron hydroxide nanocomposites as HTL contribute to achieving low cost, high performance, flexible and stable OSCs.

ACKNOWLEDGMENT

This work was supported by the University Grant Council of the University of Hong Kong (Grant 201611159194 and 201511159225), 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

References

- [1] L. Yang, T. Zhang, H. Zhou, S.C. Price, B.J. Wiley, W. You, ACS Appl. Mater. Interfaces 3 (2011) 4075-4084.
- [2] Z. Yu, L. Li, Q. Zhang, W. Hu, Q. Pei, Adv. Mater. 23 (2011) 4453-4457.
- [3] J. Lee, I. Lee, T.S. Kim, J.Y. Lee, Small 9 (2013) 2887-2894.
- [4] H. Lu, D. Zhang, X. Ren, J. Liu, W. C. H. Choy, ACS Nano. 8 (2014) 10980-10987.
- [5] H. Lu, D. Zhang, J. Cheng, J. Liu, J. Mao, W.C.H. Choy, Adv. Funct. Mater. 25 (2015) 4211-4218.
- [6] H. Kim, J. Byun, S.-H. Bae, T. Ahmed, J.-X. Zhu, S.-J. Kwon, Y. Lee, S.-Y. Min, C. Wolf, H.-K. Seo, J.-H. Ahn, T.-W. Lee, Adv. Energy Mater. 6 (2016) 1600172.
- [7] Y. Zhong, M.T. Trinh, R. Chen, W. Wang, P.P. Khlyabich, B. Kumar, Q. Xu, C.Y. Nam, M.Y. Sfeir, C. Black, M.L. Steigerwald, Y.L. Loo, S. Xiao, F. Ng, X.Y. Zhu, C. Nuckolls, J. Am. Chem. Soc. 136 (2014) 15215-15221.
- [8] W. Zhao, D. Qian, S. Zhang, S. Li, O. Inganas, F. Gao, J. Hou, Adv. Mater. 28 (2016) 4734-4739.
- [9] S. Holliday, R.S. Ashraf, A. Wadsworth, D. Baran, S.A. Yousaf, C.B. Nielsen, C.H. Tan, S.D. Dimitrov, Z. Shang, N. Gasparini, M. Alamoudi, F. Laquai, C.J. Brabec, A. Salleo, J.R. Durrant, I. McCulloch, Nat. Commun. 7 (2016) 11585.
- [10] V. Shrotriya, G. Li, Y. Yao, C.-W. Chu, Y. Yang, Appl. Phys. Lett. 88 (2006) 073508.
- [11] M.D. Irwin, D.B. Buchholz, A.W. Hains, R.P.H. Chang, T.J. Marks, PNAS 105 (2008) 2783-2787.
- [12] P. Qin, G. Fang, N. Sun, X. Fan, Q. Zheng, F. Chen, J. Wan, X. Zhao, Thin Solid Films 519 (2011) 4334-4341.
- [13] F. Xie, W.C. Choy, C. Wang, X. Li, S. Zhang, J. Hou, Adv. Mater. 25 (2013) 2051-2055.
- [14] F. Jiang, W.C. Choy, X. Li, D. Zhang, J. Cheng, Adv. Mater. 27 (2015) 2930-2937.
- [15] T. Stubhan, N. Li, N.A. Luechinger, S.C. Halim, G.J. Matt, C.J. Brabec, Adv. Energy Mater. 2 (2012) 1433-1438.
- [16] X. Tu, F. Wang, C. Li, Z.a. Tan, Y. Li, J. Phys. Chem. C 118 (2014) 9309-9317.
- [17] Z.a. Tan, L. Li, F. Wang, Q. Xu, S. Li, G. Sun, X. Tu, X. Hou, J. Hou, Y. Li, Adv. Energy Mater. 4 (2014) 1300884.
- [18] Q. Xu, F. Wang, Z. Tan, L. Li, S. Li, X. Hou, G. Sun, X. Tu, J. Hou, Y. Li, ACS Appl. Mater. Interface 5 (2013) 10658-10664.
- [19] S. He, S. Li, Z.a. Tan, H. Zheng, J. Lin, S. Hu, J. Liu, Y. Li, Journal of Physics D: Appl. Phys. 47 (2014) 505101.
- [20] J. Cheng, X. Ren, H.L. Zhu, J. Mao, C. Liang, J. Zhuang, V.A.L. Roy, W.C.H. Choy, Nano Energy 34 (2017) 76-85.
- [21] J. Wang, V. Ibarra, D. Barrera, L. Xu, Y.J. Lee, J.W. Hsu, J. Phys. Chem. Lett. 6 (2015) 1071-1075.
- [22] J. Wang, Y.-J. Lee, J.W.P. Hsu, J. Mater. Chem. C 4 (2016) 3607-3613.
- [23] E.L. Ratcliff, J. Meyer, K.X. Steirer, A. Garcia, J.J. Berry, D.S. Ginley, D.C. Olson, A. Kahn, N.R. Armstrong, Chem. Mater. 23 (2011) 4988-5000.
- [24] X. Li, W.C. Choy, F. Xie, S. Zhang, J. Hou, J. Mater. Chem. A 1 (2013) 6614-6621.
- [25] X. Li, F. Xie, S. Zhang, J. Hou, W.C.H. Choy, Adv. Funct. Mater. 24 (2014) 7348-7356.
- [26] Y. Wang, H. Wang, J. Xu, B. He, W. Li, Q. Wang, S. Yang, B. Zou, Polym. Composite DOI: 10.1002/pc.24311(2017).
- [27] K.-G. Lim, S. Ahn, Y.-H. Kim, Y. Qi, T.-W. Lee, Energy Environ. Sci. 9 (2016) 932-939.

- [28] H. Zhou, Y. Zhang, J. Seifert, S.D. Collins, C. Luo, G.C. Bazan, T.Q. Nguyen, A.J. Heeger, *Adv. Mater.* 25 (2013) 1646-1652.
- [29] Z. Xiao, Y. Yuan, B. Yang, J. VanDerslice, J. Chen, O. Dyck, G. Duscher, J. Huang, *Adv. Mater.* 26 (2014) 3068-3075.
- [30] L. Zhao, S. Zhao, Z. Xu, Q. Yang, D. Huang, X. Xu, *Nanoscale* 7 (2015) 5537-5544.
- [31] Y.S. Kang, S. Risbud, J.F. Rabolt, P. Stroeve, *Chem. Mater.* 8 (1996) 2209-2211.
- [32] I. Martínez-Mera, M. Espinosa-Pesqueira, R. Pérez-Hernández, J. Arenas-Alatorre, *Mater. Lett.* 61 (2007) 4447-4451.
- [33] S.Z.H. Shah, U. Khan, S. Riaz, S. Naseem, *Materials Today: Proceedings*, 2 (2015) 5214-5219.
- [34] R. Guo, L. Fang, W. Dong, F. Zheng, M. Shen, *J. Mater. Chem.* 21 (2011) 18645-18652.
- [35] M. Kaloti, A. Kumar, *J. Phys. Chem. C* 120 (2016) 17627-17644.
- [36] T. Fujii, F. De Groot, G. Sawatzky, F. Voogt, T. Hibma, K. Okada, *Phys. Rev. B* 59 (1999) 3195.
- [37] K. Song, Y. Lee, M.R. Jo, K.M. Nam, Y.-M. Kang, *Nanotechnology* 23 (2012) 505401.
- [38] V. Shubina, L. Gaillet, S. Ababou-Girard, V. Gaudefroy, T. Chaussadent, F. Farças, T. Meylheuc, C. Dagbert, J. Creus, *Appl. Surf. Sci.* 351 (2015) 1174-1183.
- [39] M. Outirite, M. Lagrenée, M. Lebrini, M. Traisnel, C. Jama, H. Vezin, F. Bentiss, *Electrochim Acta.* 55 (2010) 1670-1681.
- [40] M.T. Greiner, M.G. Helander, Z.-B. Wang, W.-M. Tang, Z.-H. Lu, *J. Phys. Chem. C* 114 (2010) 19777-19781.
- [41] R. Grau-Crespo, A.Y. Al-Baitai, I. Saadoun, N.H. De Leeuw, *Journal of Physics: Condensed Matter.* 22 (2010) 255401.
- [42] H. Park, P. Ayala, M. Deshusses, A. Mulchandani, H. Choi, N. Myung, *Chem. Eng. J.* 139 (2008) 208-212.
- [43] H. Raebiger, S. Lany, A. Zunger, *Phys. Rev. B* 76 (2007).
- [44] H. Frohne, S.E. Shaheen, C.J. Brabec, D.C. Müller, N.S. Sariciftci, K. Meerholz, *Chemphyschem* 3 (2002) 795-799.
- [45] G.F. Burkhard, E.T. Hoke, M.D. McGehee, *Adv. Mater.* 22 (2010) 3293-3297.
- [46] Y. Sun, C.J. Takacs, S.R. Cowan, J.H. Seo, X. Gong, A. Roy, A.J. Heeger, *Efficient, Adv. Mater.* 23 (2011) 2226-2230.



Zhanfeng HUANG received his bachelor degree in the School of Material Science and Technology from Huazhong University of Science and Technology in 2015. Currently, he is studying Ph.D. program in department of Electrical and Electronic Engineering in The University of Hong Kong. His current research interests including device engineering and carrier transport layer materials of photovoltaic devices.



Jiaqi Cheng received his bachelor degree in the Department of Polymer Science and Engineering from Zhejiang University in 2013. Currently, he is studying Ph.D. program in department of Electrical and Electronic Engineering in The University of Hong Kong. His current research interests include device engineering and carrier transport layer materials of organic solar cells.



Xingang Ren received the B.S. in Mathematics and Applied Mathematics and M.S. in Electromagnetic Field and Microwave Technology from Anhui University, Hefei, China in 2009 and 2012, respectively. He received his Ph.D. degree from the Department of Electrical and Electronic Engineering (EEE), the University of Hong Kong (HKU). His research interests include the nano optics and physics of organic optoelectronics.



Jiaqing Zhuang received his B.Sc. in materials chemistry from China University of Geosciences, Beijing (CUGB) in 2012 and M.Sc. in materials engineering and nanotechnology from City University of Hong Kong in 2013. He is currently a doctoral candidate in the Department of Physics and Materials Science at City University of Hong Kong.



Vellaisamy A. L. Roy obtained his Ph.D. degree from Nagpur University in 2004. Dr. Vellaisamy started his research on light emitting materials during his Ph.D., mainly on Electron Spin Resonance analysis of organic materials and was working on the growth of wide band gap nano-structures. Currently, he is an associate professor at the Department of Physics and Materials Science, City University of Hong Kong. His research interests are design, synthesis, and charge transport analysis of self-assembled nanostructures and functional materials for sensors, thin film transistors and floating gate flash memories. Dr. Vellaisamy received the TRIL Fellowship awarded by UNESCO in 2003 and an Excellent Product Award for his project prototypes on Sensors and Memories at China Hitech-Fair for three consecutive years since 2002. He has published over 80 papers in international SCI journals, including *Advanced Materials*, *Angewandte Chemie International Edition*, *Nano Letters*, *ACS Nano* and his papers have been cited more than 1800 times.

Jeffrey Burkhardtmeier currently works at the Department of Physics, The Hong Kong University of Science and Technology. His research interest is in Biophysics.



Kam Sing Wong received his DPhil degree at the Clarendon Laboratory, University of Oxford in 1987. He is now a professor in department of physics, HKUST. His research interests cover ultrafast laser spectroscopy, nonlinear optical properties of semiconductors and polymers, fabrication and applications of photonic crystals and plasmonic nanostructures, photo-physics of organic and inorganic materials. He has published more than 170 journal articles and more than 80 refereed conference articles and edited one book chapter “Fabrication of Photonic Crystals using Holographic Lithography” in Organic and Hybrid Photonic Crystals, in Springer (2015). He is serving as journal editor of International Journal of Spectroscopy and Journal of Infrared and Millimeter Waves (1999-2003).



Wallace C.H. Choy received his Ph.D. Degree in Electronic Engineering from University of Surrey, UK in 1999. He is now a Professor in Department of EEE, HKU. His research interests cover organic/inorganic optoelectronic devices, plasmonic structures, metal oxides, and nanomaterial devices. He has published more than 170 peer-reviewed papers, a number of book chapters, patents, and edited one book published in Springer. He was recognized as the Top 1% of most-cited scientists in Thomson Reuter's Essential Science Indicators from 2014 to 2016. He is serving as editorial board member of NPG Scientific Reports and IOP J Physics D, topical editor of OSA JOSA B, and senior editor of IEEE Photonic Journals. He is an elected fellow of OSA.

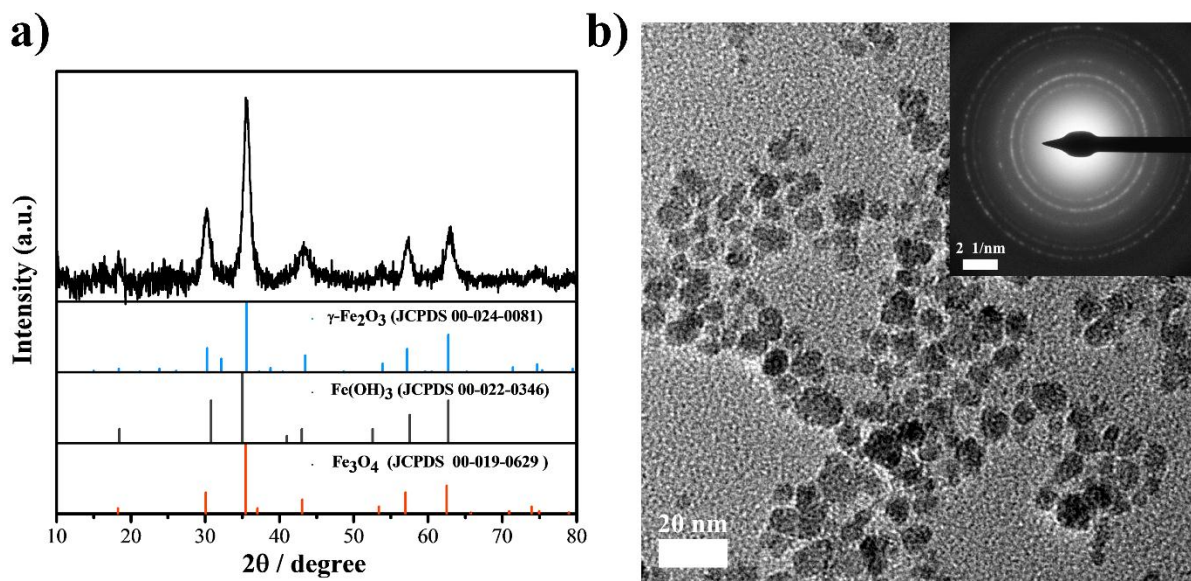


Figure 1. a) GIXRD pattern of representative maghemite and iron hydroxide nanocomposite with conversion pH=2 and the standard peaks of maghemite ($\gamma\text{-Fe}_2\text{O}_3$), iron hydroxide ($\text{Fe}(\text{OH})_3$) and magnetite (Fe_3O_4); b) the TEM image of nanoparticles with scale bar of 20 nm, the inset up-right corner is the electron diffraction pattern of the nanoparticles.

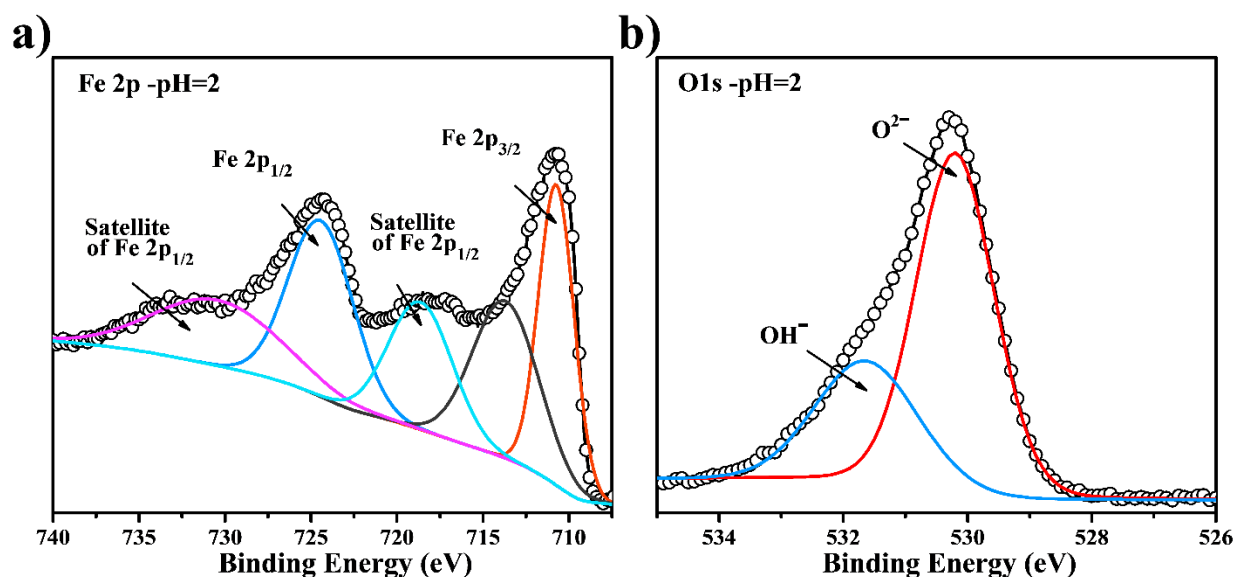


Figure 2. XPS results of maghemite and iron hydroxide nanocomposite prepared with pH=2, narrow scan a) of Fe 2p, b) of O 1s, the peak at around 715 eV of Sn 3p is from the indium tin oxide substrate.

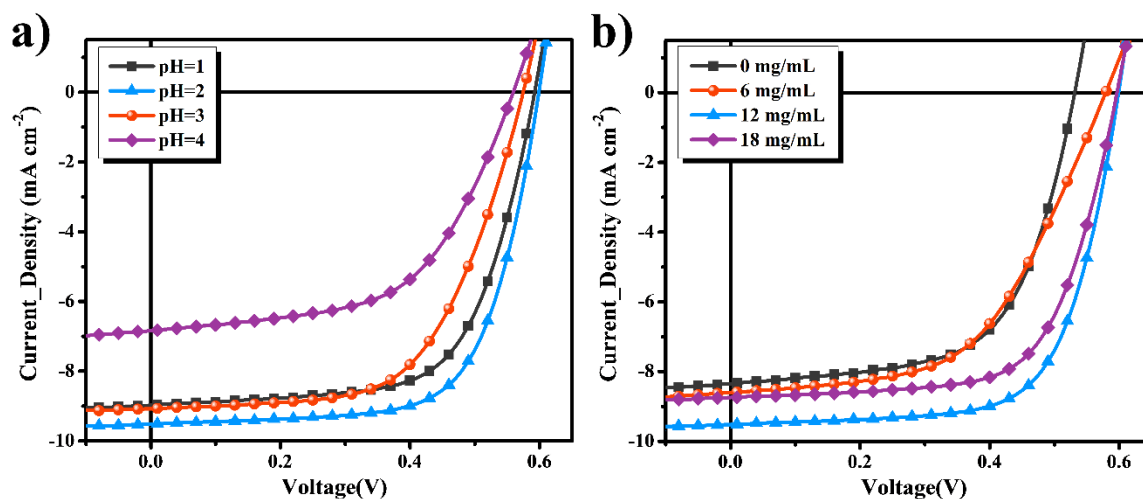


Figure 3. Representative current density–voltage (J – V) characteristics under AM 1.5G solar spectrum with a light intensity of 100 mW cm^{-2} for P3HT: PC₆₁BM based OSCs, a) using different pH prepared nanocomposites; b) using different concentration of maghemite and iron hydroxide nanocomposite prepared at pH=2.

Table 1. Work Function of bare ITO, films of maghemite and iron hydroxide nanocomposites prepared under different pH values and PEDOT:PSS spin-coated on ITO, measured in air using Kelvin Probe (KP) system.

Sample	WF by KP [eV]
pH=1	5.05 ± 0.05
pH=2	5.16 ± 0.03
pH=3	4.95 ± 0.10
pH=4	4.70 ± 0.08
ITO	4.78 ± 0.03
PEDOT	5.08 ± 0.04

Table 2. Average device performance of ten devices from different pH prepared nanocomposite based HTL with conventional structure of ITO/HTL/P3HT:PC₆₁BM/Ca/Al.

Samples	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	PCE [%]
pH=1	8.97	0.59	0.66	3.47
pH=2	9.58	0.60	0.67	3.84
pH=3	9.07	0.57	0.60	3.12
pH=4	6.83	0.56	0.56	2.14

Table 3. Average device performance of ten devices from different concentration nanocomposite colloidal with conventional structure of ITO/HTL/P3HT:PC₆₁BM/Ca/Al

Samples	J_{SC} [mA cm ⁻²]	V_{oc} [V]	FF	PCE [%]
0mg/mL	8.46	0.53	0.60	2.65
6mg/mL	8.60	0.58	0.54	2.67
12mg/mL	9.58	0.60	0.67	3.84
18mg/mL	8.78	0.60	0.66	3.44

Accepted manuscript

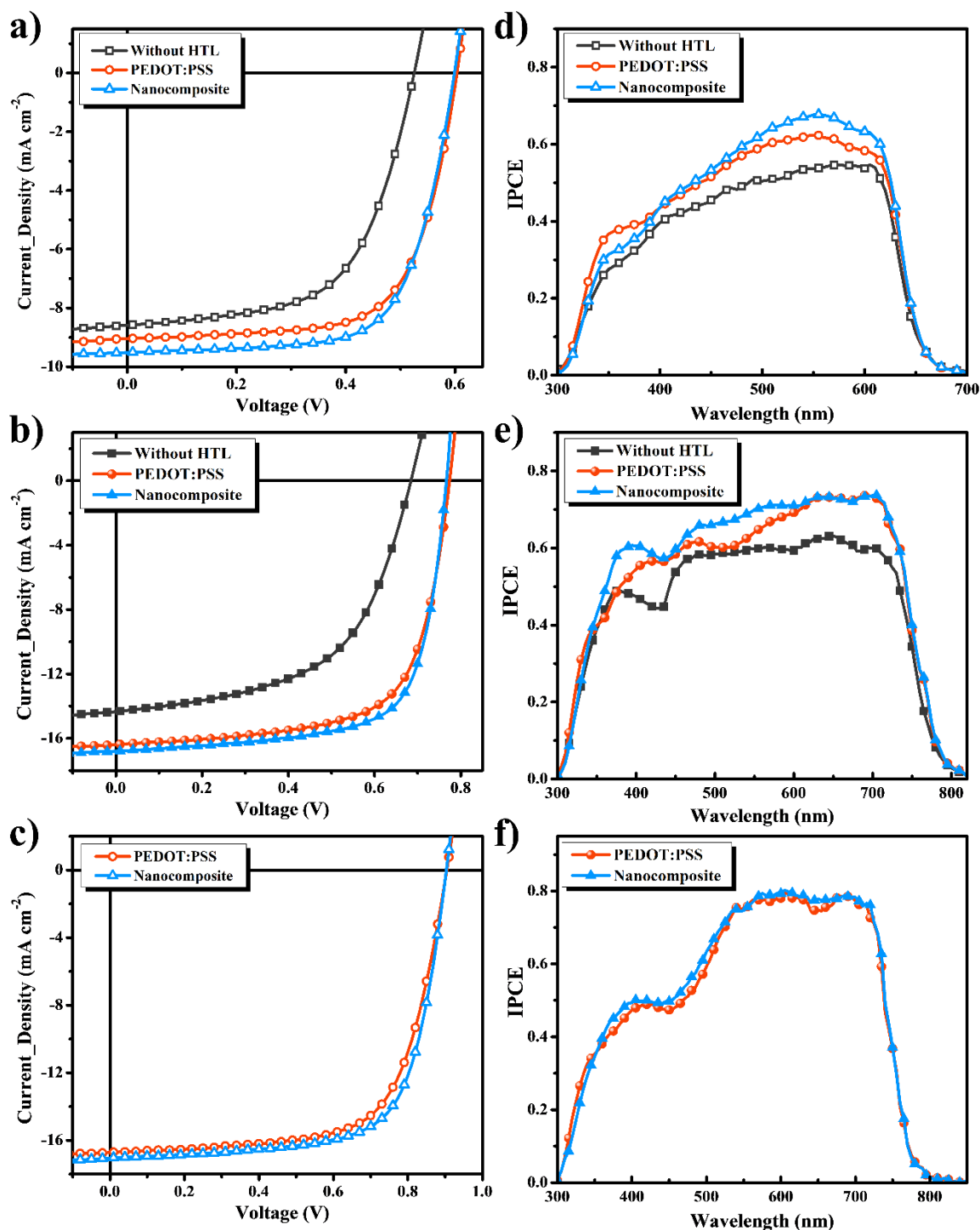


Figure 4. a-c) Representative current density–voltage (J – V) characteristics of optimized devices with the structure of ITO/HTL/Active Layer/Ca/Al, using different HTL in P3HT:PC₆₁BM, PTB7-Th:PC₇₁BM and PBDB-T:ITIC system respectively; d-f) the IPCE spectrum of optimized device with the structure of ITO/HTL/PTB7-Th:PC₇₁BM/Ca/Al, using different HTL in P3HT:PC₆₁BM, PTB7-Th:PC₇₁BM and PBDB-T:ITIC system respectively.

Table 4. Average Device performances of ten devices from PEDOT:PSS or nanocomposite-based OSCs with different polymers, using Ca/Al as top electrode. In-series resistance (R_s) is calculated from representative devices at around V_{OC} .

Device structures		J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF	R_s [ohmcm ⁻²]	PCE [%]
ITO/P3HT:PC ₆₁ BM/Ca/Al	Average	8.46±0.11	0.525±0.010	0.596±0.020		2.65±0.08
	Champion	8.35	0.530	0.615		2.72
ITO/PEDOT:PSS/P3HT:PC ₆₁ BM/Ca/Al	Average	9.08±0.26	0.604±0.005	0.660±0.013	6.30±0.41	3.62±0.05
	Champion	9.37	0.600	0.660		3.72
ITO/Nanocomposite/P3HT:PC ₆₁ BM/Ca/Al	Average	9.58±0.19	0.602±0.006	0.667±0.011	5.71±0.28	3.84±0.10
	Champion	9.69	0.600	0.679		3.95
ITO/PTB7-Th:PC ₇₁ BM/Ca/Al	Average	14.07±0.72	0.663±0.020	0.539±0.020		5.02±0.34
	Champion	14.97	0.670	0.556		5.58
ITO/PEDOT:PSS/PTB7-Th:PC ₇₁ BM/Ca/Al	Average	16.37±0.23	0.778±0.006	0.670±0.010	3.32±0.27	8.59±0.14
	Champion	16.39	0.780	0.684		8.74
ITO/Nanocomposite/PTB7-Th:PC ₇₁ BM/Ca/Al	Average	16.94±0.32	0.775±0.009	0.689±0.010	3.09±0.38	9.04±0.09
	Champion	16.87	0.790	0.691		9.20
ITO/PEDOT:PSS/PBDB-T:ITIC/Ca/Al	Average	16.75±0.16	0.902±0.004	0.674±0.004	6.83±0.09	10.17±0.13
	Champion	16.88	0.900	0.675		10.25
ITO/Nanocomposite/PBDB-T:ITIC/Ca/Al	Average	17.12±0.18	0.902±0.004	0.696±0.004	5.67±0.12	10.75±0.10
	Champion	17.31	0.900	0.703		10.94

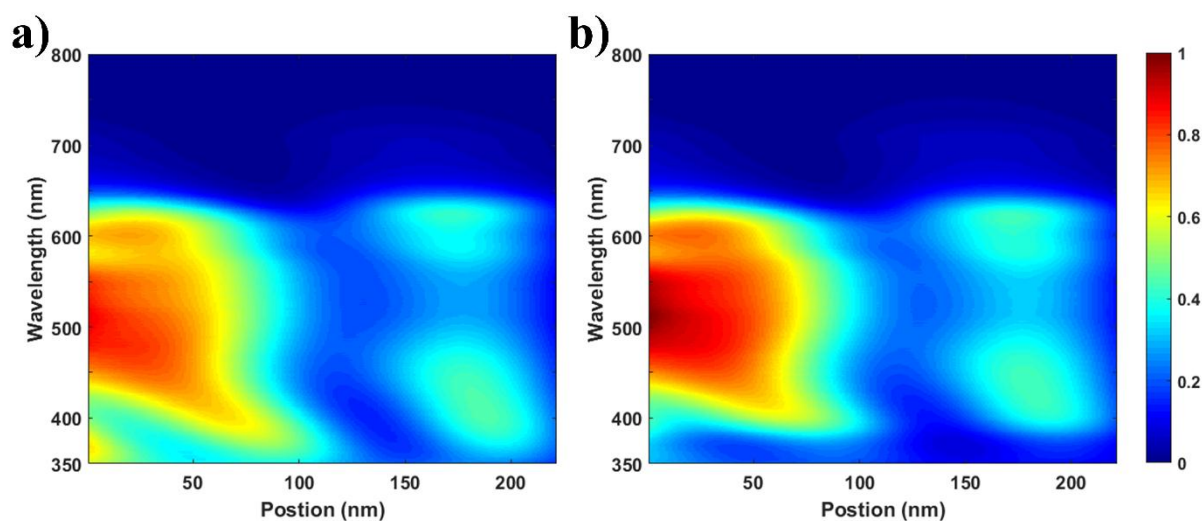


Figure 5. calculated electric field intensity to wavelength in different position of active layer (P3HT:PC₆₁BM) in the device using a) PEDOT:PSS, b) maghemite and iron hydroxide nanocomposite as HTL.

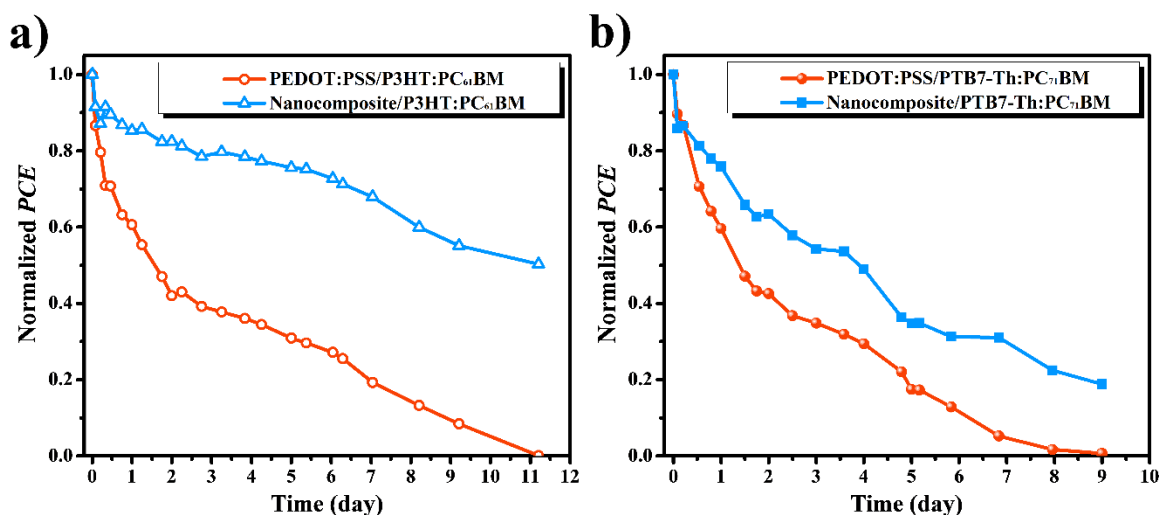


Figure 6. The change in normalized PCE of maghemite and iron hydroxide nanocomposite or PEDOT:PSS based devices with Ca/Al as top electrode, for a) P3HT: PC₆₁BM or b) PTB7-Th:PC₇₁BM, recording in ambient condition without encapsulation (humidity around 40% under room temperature).

Highlights

- All-room-temperature solution-processed method was demonstrated to develop maghemite and iron hydroxide nanocomposites as new hole transport layer
- Tunable work function (WF) from 4.70 eV to 5.16 eV achieved by tuning pH.
- The nanocomposite significantly improved the PCE as much as 80% improvement as compared to control device without HTL.
- Enhanced performance in both efficiency and stability compared to PEDOT:PSS based devices.