

Synergic Effects of Randomly Aligned SWCNT Mesh and Self-Assembled Molecule Layer for High-Performance, Low-Bandgap, Polymer Solar Cells with Fast Charge Extraction

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Currently, most of the promising organic solar cells (OSCs) are based on low bandgap polymer donors with deep-lying highest occupied molecular orbit (HOMO) levels, which impose the challenges for device architecture design. In terms of fast charge extraction and suppression of bimolecular recombination, elaborate interface design in low bandgap OSCs is of significance to further boost their ultimate efficiency. In this work, a facile solution-processed functionalized single wall carbon nanotube (f-SWCNT) mesh/self-assembled molecule (SAM) hybrid structure is reported as hole transport layer (HTL) in low bandgap OSCs. The effectiveness of such hybrid HTL originates from two aspects: (i) SAM layer can effectively realize Ohmic contact between f-SWCNT and low bandgap polymer donors with deep-lying HOMO levels due to the reduction of interface energy barrier; (ii) f-SWCNT mesh can provide fast hole extraction pathways to quickly sweep out photogenerated charges. As a consequence of synergic effects of such hybrid HTL, both photocurrent and fill factor are greatly enhanced due to the reduced bimolecular recombination. Together with careful light management by using ZnO optical spacer, a high efficiency of 10.5% has been achieved. This work offers an excellent choice for large-scale processable and effective HTL toward the application in low bandgap OSCs with deep-lying energy levels.

photovoltaic technology to meet the increasing demand of renewable and green energy sources.^[1–6] The power conversion efficiency (PCE) of state-of-the-art BHJ OSCs has been rapidly boosted with a record value of over 10%,^[7–9] representing the bright future of such kind of cells. The charge generation and extraction are considered as two key steps for photon–electron conversion in BHJ OSCs. For the purpose of generating more charge carriers with large potential, the state-of-the-art polymeric donors have been designed by featuring a low bandgap and deep-lying highest occupied molecular orbit (HOMO) level.^[10–16] In addition, many other strategies, such as light trapping,^[17–25] and morphology control in active layer have also been used.^[26–34] On the other hand, the generated charges are required to be quickly extracted by electrodes; otherwise they will be lost through a bimolecular recombination channel. In this regard, finely electrode/active layer interface design for efficient charge extraction is of significance to enhance the PCE of OSCs up to their application levels.

1. Introduction

Bulk heterojunction (BHJ) conjugated polymer based organic solar cells (OSCs) featuring low cost, mechanical flexibility, and scalable manufacture hold the promise of next-generation

Currently, the most promising OSCs are based on low bandgap polymer donors with deep-lying HOMO levels. By adopting traditional device architecture with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) as hole transport layer (HTL), high performance OSCs can be achieved after finely tailoring the morphology.^[11,35,36] In these OSCs, the negligible electrical field dependence of charge generation indicated the suppressed geminate recombination, while bimolecular recombination is likely the main energy loss channel.^[37–39] From the perspective of interface engineering, the PEDOT:PSS layer with moderate work function (WF) might not offer energy matched interface with BHJ active layer bearing deep-lying HOMO level donors. In addition, PEDOT:PSS layer is a source of device instability due to its hygroscopic and acidic nature.^[40] Although diverse high-WF metal oxides such as MoO₃, V₂O₅, and NiO have proved their effectiveness in classic wide bandgap OSCs,^[41–47] only

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few of them have succeeded in specific low bandgap systems.^[46,47] In addition, intrinsically low charge mobility in high-WF metal oxide layers might compromise the charge extraction, and simultaneously impose the challenges for large-scale processing.

Single-wall carbon nanotubes (SWCNTs) exhibit intrinsic fast charge carrier mobility of up to $10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature, excellent chemical stability, and mechanical robustness.^[48–50] More importantly, random network of SWCNTs can be solution deposited at large scale by existing low-cost techniques such as gravure, inkjet printing, and roll-to-roll processing.^[51,52] Several works have demonstrated SWCNT networks as HTL in OSCs based on shallow-lying HOMO level polymer donors.^[53,54] However, the study on SWCNT network application in OSCs with promising low bandgap and deep-lying HOMO donors still lags behind although it looks promising. The moderate WF of SWCNT networks might be the main concern for their extensive application. On the other hand, the detailed role of SWCNT network in charge extraction is still not clear. Therefore, it is essential to further exploit the potential of SWCNT network in newly emerged low bandgap OSCs with deep-lying energy level and uncover the underlying mechanism of efficient charge extraction.

In this work, we explored the feasibility of using functionalized SWCNT (f-SWCNT) mesh as hole transport layer in low bandgap polymer OSCs with deep-lying HOMO levels and discussed the mechanism for charge extraction. A promising polymer based on benzodithiophene (BDT)-thieno[3,4-b]thiophene (TT) backbone (PBDT-TS1) with a bandgap of 1.55 eV and a HOMO level of -5.33 eV was used as polymer donor in this study.^[11] Compared to the traditional poly(3-hexylthiophene)(P3HT)/[6,6]-phenyl C61-butyric acid methyl ester (PCBM) system, the device results indicated that the direct contact of f-SWCNT mesh with PBDT-TS1/[6,6]-phenyl C₇₁-butyric acid methyl ester (PC₇₀BM) active layer would form interface energy barrier, which results in inefficient charge extraction and reduced open-circuit voltage. By using a self-assembled molecule (SAM) layer to modify f-SWCNT mesh, the energy barrier was removed and consequently the device performance was greatly improved. The effectiveness of this hybrid HTL has been proved to originate from two factors: (i) SAM layer effectively modifies the WF of anodic electrode to realize Ohmic contact at anode interface for reducing charge extraction barrier, and (ii) f-SWCNT mesh provides fast hole extraction pathways to quickly enable the sweep-out of photogenerated charges. The synergic effects of such hybrid HTL offer the enhancement of both photocurrent and fill factor due to the reduced bimolecular recombination. After careful optimizing electromagnetic field spatial distribution by using ZnO optical spacer in the optimized hybrid HTL based OSCs, the highest PCE of 10.5% is achieved, which is one of the best results for a single-junction OSCs. It should be noted that the proposed hybrid HTL here may be adaptive to various polymer systems with diverse energy levels because of the synergistic effect by SAM layer and f-SWCNT mesh. Our research has great application for producing highly efficient and stable OSCs with low cost.

2. Results and Discussions

2.1. Morphological and Optical Property of f-SWCNT Mesh

The purified SWCNTs are functionalized with carboxylic acid (f-SWCNTs) and dispersed in dimethylformamide (DMF) solvent with concentrations of 0.05, 0.15, 0.25, and 0.5 mg mL^{-1} . The Raman spectrum of f-SWCNT mesh was recorded at an excitation laser of wavelength 514 nm, as shown in Figure S1a in the Supporting Information. Dominant features at 1590 and 1572 cm^{-1} , which was assigned to the photon transition within 1D SWCNTs, were observed, indicating the absence of other carbon-based species. The transmission electron microscopy (TEM) of f-SWCNT was carried out and demonstrated in Figure S1b in the Supporting Information, also indicating the sample was mainly f-SWCNT but not other carbon-based species. The morphology of f-SWCNTs on indium tin oxide (ITO) substrate was studied by scan electron microscopy (SEM) and corresponding results are displayed in Figure 1a–d. The well-dispersed f-SWCNTs are randomly aligned on ITO substrate with lengths ranged from 0.3 to $5 \mu\text{m}$ and diameters ranged from 2 to 26 nm. The coverage of f-SWCNTs on top of ITO substrates gradually increases as the concentration of solution increases from 0.05 to 0.5 mg mL^{-1} . The lateral conductivity of f-SWCNT mesh was measured by using four-point probe station and no signal was detected, which indicates the f-SWCNT meshes did not form percolated networks for lateral electrical conduction. The surface topography of f-SWCNTs mesh spin-coated from 0.25 mg mL^{-1} solution on ITO substrate was investigated by atomic force microscopy (AFM) as shown in Figure S1c in the Supporting Information. The f-SWCNT coated ITO is rough with a root mean square (RMS) roughness of 4.2 nm. As a result, the relatively rough f-SWCNT mesh can increase the contact area between active layer and electrode, which may be beneficial for charge extraction. In addition, the f-SWCNT meshes exhibit high transparency of 93% (Figure S1d, Supporting Information), which guarantees it as an effective optical window for incident solar light.

2.2. The Interplay between f-SWCNT Coverage, WF, and Device Performance

In this section, we aim for applying f-SWCNT meshes as HTL in regular-structure OSCs with Ca/Al cathode. The rough surface of f-SWCNT mesh is embedded at transparent ITO electrode/active layer interface for photogenerated hole extraction. The classic P3HT and low bandgap PBDT-TS1 are used as polymer donors to constitute active layer for light harvest (Figure S2a, Supporting Information). The current density–voltage (J – V) characteristics of P3HT/PCBM and PBDT-TS1/PC₇₀BM based solar cells with different coverage f-SWCNT meshes as HTLs are shown in Figure 2a,b and corresponding photovoltaic parameters are listed in Table 1. For P3HT/PCBM solar cells, the device performance shows strong dependence on the coverage of f-SWCNT meshes. The best P3HT/PCBM OSCs are obtained using the f-SWCNT mesh from 0.25 mg mL^{-1} solution, exhibiting average V_{OC} of 0.581 V, J_{SC} of 11.0 mA cm^{-2} , fill factor (FF) of 66%, and overall PCE of 4.22%. The resulted

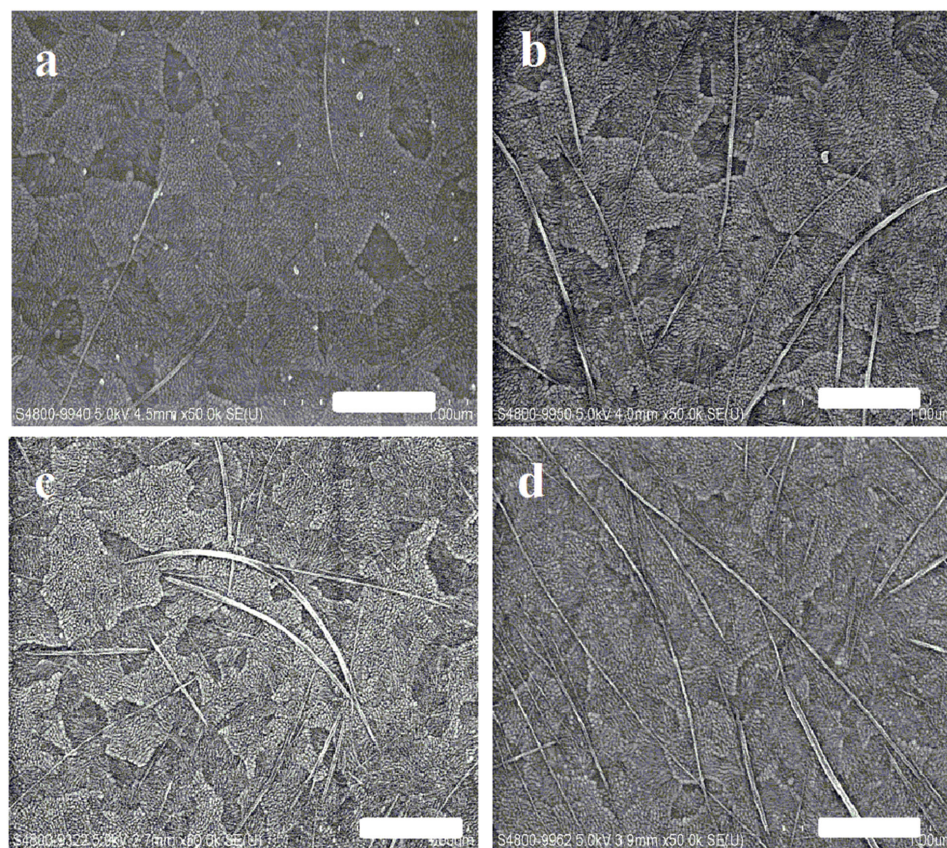


Figure 1. The SEM images of SWCNT meshes processed from DMF solution with a) 0.05 mg mL^{-1} , b) 0.15 mg mL^{-1} , c) 0.25 mg mL^{-1} , and d) 0.5 mg mL^{-1} . Scale bar: 500 nm.

efficiency even surpasses that of PEDOT:PSS-based reference solar cells with average PCE of 3.66%. This result indicates that the embedded f-SWCNT mesh is capable to deliver more efficient hole extraction than PEDOT:PSS layer.

PBDT-TS1/PC₇₀BM OSCs with 0.25 mg mL^{-1} f-SWCNT mesh shows V_{OC} of 0.738 V, J_{SC} of 17.2 mA cm^{-2} , FF of 59.3%, and PCE of 7.54%. This device shows lower V_{OC} and FF compared to device based on PEDOT:PSS, which is different from the P3HT/PCBM OSC where there is no change in V_{OC} . This result implies that the energy barrier for hole extraction may be formed at f-SWCNT mesh/low BG polymer interface.

The WF values of ITO substrates modified by different coverage f-SWCNT meshes were measured by kelvin probe (Figure S2b, Supporting Information). By increasing the coverage of f-SWCNT mesh, the WF value of ITO substrate is gradually improved from 4.70 to 4.94 eV, very close to the value (5.04 eV) of bulk f-SWCNT film. The energy level alignments of two types of solar cells are shown in Figure 2c,d. As can be observed, the increased WF of ITO electrode by modulating the f-SWCNT coverage easily enables energetic match with HOMO level (5.0 eV) of P3HT donor. Thereby, Ohmic contact is established at interface for barrier-free charge extraction and V_{OC} is dominated by the energy level alignment of active layer.^[53] Therefore, the optimized P3HT/PCBM solar cells with f-SWCNT mesh as HTL show similar V_{OC} with PEDOT:PSS based OSCs. On the contrary, the barrier-free contact is hardly

realized at ITO/low BG polymer system interface by merely changing f-SWCNT coverage because of the deep-lying HOMO level (5.3 eV) of low BG polymer. Consequently, the Schottky type contact is formed and V_{OC} loss is obtained in low BG OSCs when f-SWCNT mesh is applied as HTL. Thus, it is of significance to solve the energetic mismatch and awake the effectiveness of f-SWCNT mesh in low BG PBDT-TS1/PC₇₀BM OSCs with low-lying HOMO levels.

2.3. The Role of SAM Layer in Device Performance

In order to fully exploit the potential of f-SWCNT mesh in low BG system, commercial pentafluorobenzylphosphonic acid (F_5BnPA) was used as SAM to further modify the WF of ITO electrode coated with f-SWCNT mesh. The chemical structure of F_5BnPA is demonstrated in Figure S2 (Supporting Information). The effects of SAM modification on the surface WF of f-SWCNT mesh is investigated by ultraviolet photoelectron spectroscopy (UPS) (Figure S3, Supporting Information). The shift of secondary electron cutoff toward low binding energy is observed after SAM treatment, corresponding to the increase of WF from 4.89 to 5.26 eV. The illuminated J - V characteristics of P3HT/PCBM and low BG PBDT-TS1/PC₇₀BM based OSCs using PEDOT:PSS, SAM-only, and f-SWCNT/SAM hybrid HTLs under 100 mW cm^{-2} AM 1.5G irradiation are shown in

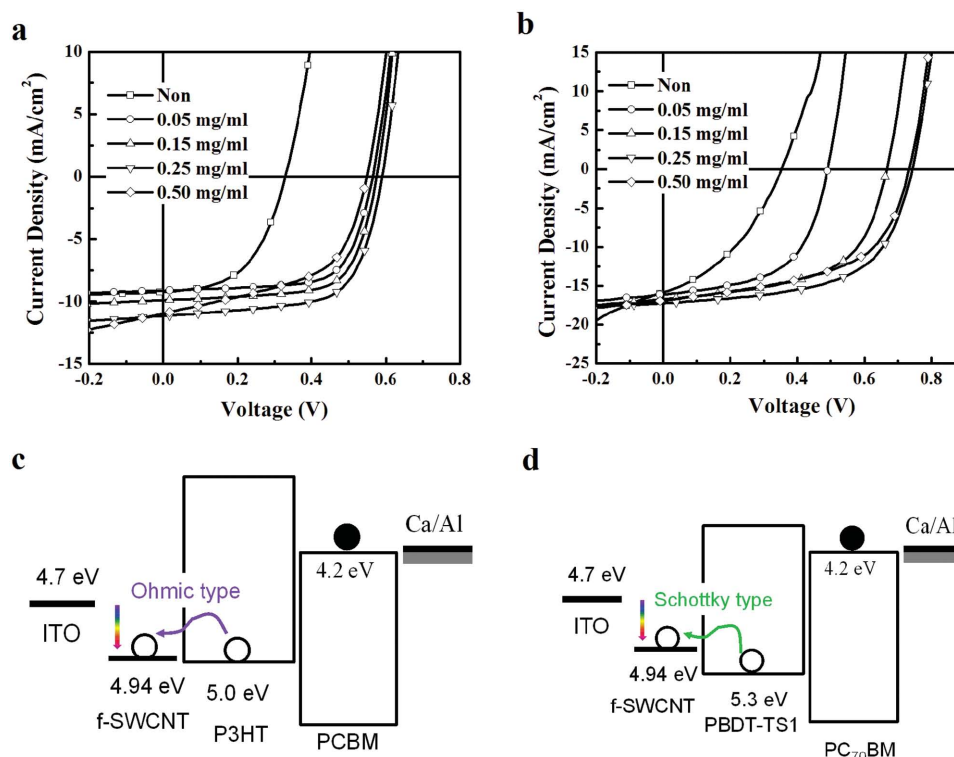


Figure 2. *J*-*V* characteristics of a) P3HT:PCBM based solar cells and b) PBDDT-TS1:PC₇₀BM based solar cells using f-SWCNT meshes of different coverage as HTL, and corresponding energy level alignment of c) P3HT/PCBM, and d) PBDDT-TS1/PC₇₀BM solar cells.

Figure 3a,b, and corresponding results are listed in Table 1. Compared to the P3HT:PCBM OSC with f-SWCNT only, the device with f-SWCNT/SAM hybrid structure shows very similar performance. This is reasonable because the Ohmic contact has already realized by the use of f-SWCNT mesh, and

further increased WF could not improve interface contact. However, in low BG PBDDT-TS1/PC₇₀BM system the incorporation of SAM with f-SWCNT together can substantially improve the device performance, rendering an average *V*_{OC} of 0.79 V, *J*_{SC} of 18.7 mA cm⁻², FF of 64.2%, and overall PCE of 9.49%.

Table 1. The device performance parameter summary of P3HT/PCBM and PBDDT-TS1/PC₇₀BM blends based solar cells with different HTLs under AM 1.5G 100 mW cm⁻² irradiation.

Devices	HTLs	<i>V</i> _{OC} [mV]	<i>J</i> _{SC} [mA cm ⁻²]	FF [%]	PCE [%]
P3HT:PCBM	w/o	333 ± 2	9.06 ± 0.17	52.1 ± 0.8	1.57 ± 0.05
	0.05 mg mL ⁻¹	565 ± 3	9.12 ± 0.21	68.7 ± 1.3	3.54 ± 0.12
	0.15 mg mL ⁻¹	580 ± 3	9.75 ± 0.17	66.6 ± 1.2	3.77 ± 0.15
	0.25 mg mL ⁻¹	581 ± 4	11.0 ± 0.14	66.0 ± 0.9	4.22 ± 0.08
	0.5 mg mL ⁻¹	550 ± 2	10.8 ± 0.10	54.3 ± 3.1	3.24 ± 0.07
	SAM	578 ± 1	9.49 ± 0.16	63.9 ± 2.1	3.51 ± 0.12
	f-SWCNT/SAM	588 ± 1	10.9 ± 0.06	64.9 ± 0.5	4.18 ± 0.03
	PEDOT:PSS	580 ± 7	9.48 ± 0.08	66.5 ± 0.3	3.66 ± 0.02
PBDDT-TS1:PC ₇₀ BM	w/o	350 ± 10	15.9 ± 0.2	38.6 ± 4.1	2.14 ± 0.13
	0.05 mg mL ⁻¹	490 ± 20	16.1 ± 0.3	56.7 ± 3.2	4.47 ± 0.18
	0.15 mg mL ⁻¹	660 ± 20	16.7 ± 0.2	57.7 ± 2.4	6.40 ± 0.14
	0.25 mg mL ⁻¹	738 ± 20	17.2 ± 0.3	59.3 ± 3.4	7.54 ± 0.17
	0.5 mg mL ⁻¹	730 ± 30	16.9 ± 0.5	54.6 ± 3.7	6.72 ± 0.23
	SAM	790 ± 10	17.3 ± 0.2	58.2 ± 2.1	7.94 ± 0.12
	f-SWCNT/SAM	790 ± 5	18.7 ± 0.3	64.2 ± 1.4	9.49 ± 0.13
	PEDOT:PSS	794 ± 5	17.5 ± 0.2	65.1 ± 0.7	9.08 ± 0.13

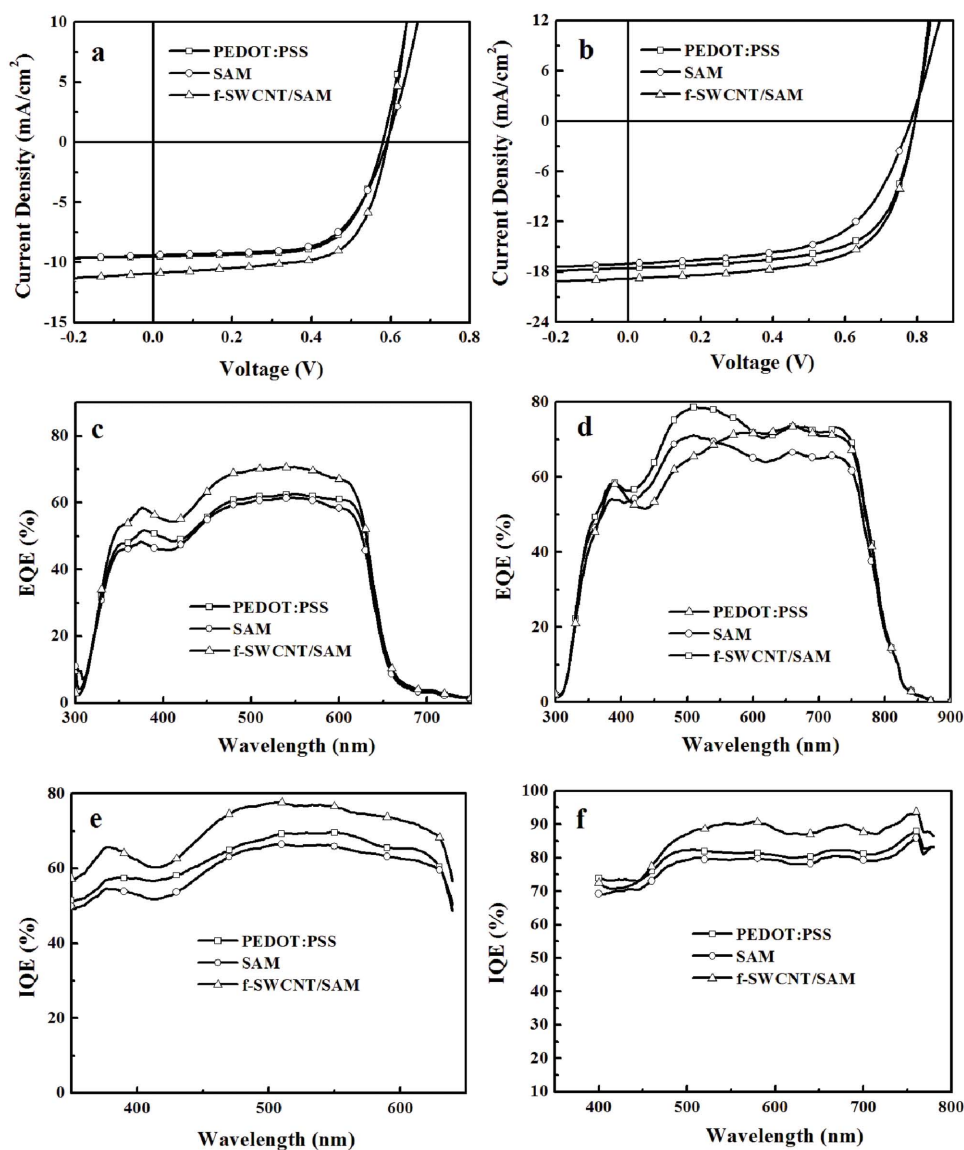


Figure 3. a) J–V characteristics, c) EQE spectra and e) IQE spectra of P3HT/PCBM based solar cells, and b) J–V characteristics, d) EQE spectra, and f) IQE spectra of PBDT-TS1/PC₇₀BM based solar cells, with PEDOT:PSS, SAM layer, and f-SWCNT/SAM hybrid HTLs.

The efficiency of PBDT-TS1/PC₇₀BM OSCs with f-SWCNT/SAM HTL even outperformed that of the control device with PEDOT:PSS HTL, indicating the effectiveness of f-SWCNT mesh in low BG OSCs.

The role of f-SWCNT mesh in hybrid HTL can be clarified by directly comparing the OSCs using SAM only with that using f-SWCNT/SAM hybrid structure. The OSCs based on both P3HT/PCBM and PBDT-TS1/PC₇₀BM using hybrid HTL both exhibit enhanced photocurrent and FF with respect to those OSCs with SAM only, contributing to efficiency enhancement up to 20%. The unprecedentedly high photocurrent of OSCs with hybrid HTL has also been validated by their external quantum efficiency (EQE) spectra. As shown in Figure 3c,d, the OSCs based on P3HT/PCBM and low BG OSCs using hybrid HTLs exhibit peak EQE values of 70% and 79%, respectively, which are higher than those of OSCs with PEDOT:PSS or SAM

only. The integrated photocurrents from EQE spectra of P3HT/PCBM and low BG OSCs with hybrid HTL are 10.7 mA cm⁻² and 18.8 mA cm⁻², respectively, agreeing well with the measured J_{SC} . The highest EQE value in hybrid HTL based OSCs indicated the improved photocurrent yield and contributed to the enhancement in device performance, accordingly. Figure S4 (Supporting Information) show the measured absorption spectra in a back reflective mode of two types of OSCs in the Supporting Information. To evaluate the effectiveness of three types of HTLs in parallel, the internal quantum efficiency (IQE) spectra are calculated via EQE/absorption and shown in Figure 3e,f. As can be seen, the OSCs with hybrid HTL exhibit highest IQE spectra with peak values of 78% and 90% for P3HT/PCBM OSCs and PBDT-TS1/PC₇₀BM OSCs, respectively. It can be concluded that the increased photocurrents in OSCs with hybrid HTL result from the enhanced charge extraction.

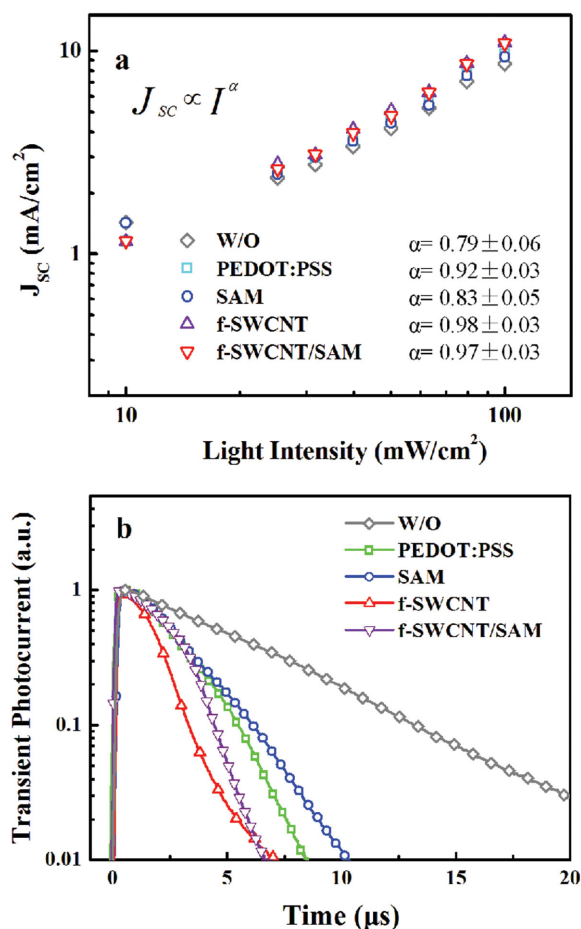


Figure 4. a) The measured J_{sc} plotted against light intensity on a logarithmic scale and b) transient photocurrent decay curves in P3HT/PCBM based OSCs with different HTLs.

2.4. The Mechanism of Enhanced Charge Extraction

Under the short-circuit condition, there is a competition between photogenerated carrier sweep-out by internal field and the loss of carrier by bimolecular recombination in OSCs. To gain deep insight into the hole-extraction capabilities of different HTLs, we further studied the dependence of J_{sc} on the light intensity in different OSCs as shown in **Figure 4a**. A power law dependence of J_{sc} upon light intensity is generally observed in OSCs and can be expressed as^[56–58]

$$J_{sc} \propto I^\alpha \quad (1)$$

where I is the light intensity and α is the exponential factor. The ideal device should possess α value close to unity, which is the result of weak bimolecular recombination of free charge during sweep-out. By fitting the experimental data using equation 1, $\alpha = 0.79, 0.92, 0.83, 0.98$, and 0.97 are obtained for OSCs without HTL and with PEDOT:PSS, SAM only, f-SWCNT only, and hybrid f-SWCNT/SAM HTLs, respectively. The results indicate that the f-SWCNT mesh indeed offers fast photogenerated

carrier extraction at short circuit and thus results in reduced bimolecular recombination with respect to other HTLs.

The fast extraction of photogenerated charge carriers by f-SWCNT can be further confirmed by the transient photocurrent (TPC) decay measurement as shown in **Figure 4b**. In principle, the decay rate of the TPC signal should be proportional to the rate of charge carriers being swept out of active layer.^[59] The photogenerated carriers in P3HT/PCBM based OSCs without HTL exhibit slowest decay. This is expectable because the formation of Schottky barrier at ITO/active layer interface would result in small selectivity of charge collection. After modification with PEDOT:PSS or SAM only, the WFs of ITO anodes are sufficiently increased, leading to the formation of energy barrier-free contact. Thereby the rates of charge carriers being swept out of the active layer are greatly enhanced. Using f-SWCNT mesh only as HTL, the photogenerated charge carriers show fastest decay, indicating the most efficient charge carrier extraction. After being further treated with SAM layer, the slightly reduced decay rate is observed in hybrid HTL based OSCs. This might result from weakened interaction between f-SWCNT mesh and active layer due to the SAM intercalation. However, this change only causes slightly reduction of FF values, while the photocurrent has no clear change. The TPC results are consistent well with the corresponding OSCs performances, further confirming the enhanced charge extraction delivered by f-SWCNT mesh. The previous study on morphology indicated the f-SWCNT mesh is relatively rough and would penetrate into active layer. The rough f-SWCNT mesh is supposed to not only change local electrical field distribution, but also provide fast charge transport pathways, resulting in enhanced charge extraction. In addition, the f-SWCNT mesh is able to facilitate the exciton dissociation (**Figure S5**, Supporting Information), which might also contribute to the charge extraction at interface.

2.5. Light Management by Using Optical Spacer

As the ultrathin f-SWCNT/SAM hybrid structure is used as HTL in PBDT-TS1/PC₇₀BM OSCs, the absorption in long-wavelength range is reduced compared to that of PEDOT:PSS based solar cells (**Figure S4b**, Supporting Information). Here, ZnO nanocrystal layer as optical spacer is used to tune the electromagnetic field spatial distribution in f-SWCNT/SAM-based low BG OSCs and corresponding optical simulation has been carried out to prove its effectiveness (see **Figure S6**, Supporting Information). **Figure 5a** displays the illuminated J - V characteristics of low BG OSCs with f-SWCNT/SAM HTL and different thickness ZnO films as optical spacer. The corresponding device parameters are listed in **Table 2**. When the thickness of ZnO layer is 20 nm, the devices exhibit an average J_{sc} of 20.5 mA cm^{-2} with an average (highest) PCE of 10.3% (10.5%), which is among one of best results for single-junction OSCs. The corresponding EQE spectra are shown in **Figure 5b**. The integral current from EQE spectrum of the best device with a value of 20 mA cm^{-2} agrees well with the measured J_{sc} value within 3% error, indicating the small spectrum mismatch.

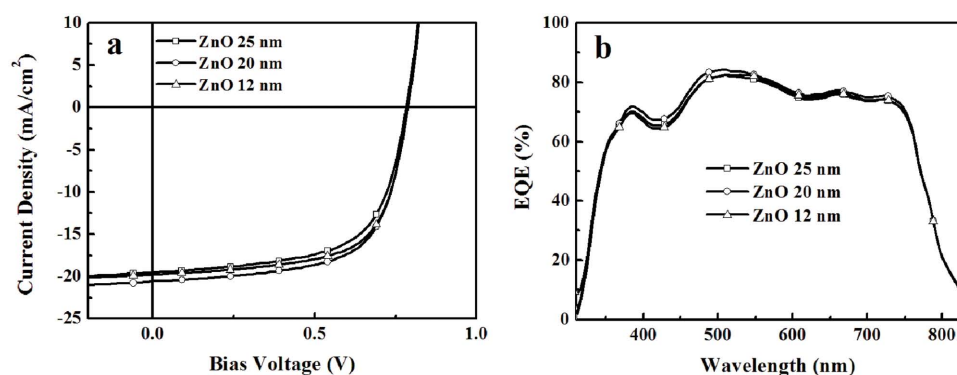


Figure 5. The illuminated a) J - V characteristics and corresponding b) IPCE spectra of PBDT-TS1/PC₇₀BM solar cells with f-SWCNT/SAM hole transport layer and ZnO optical spacer.

3. Conclusion

In summary, we demonstrated a facile solution-processed f-SWCNT mesh/SAM hybrid structure as hole-extraction layer in low bandgap OSCs with deep-lying HOMO levels. The enhancements in photocurrents and device efficiencies were obtained by using this hybrid structure as HTL. The enhancement of photocurrent has been identified as synergic effects of f-SWCNT mesh possessing ultrafast charge extraction and self-assembled molecule layer offering high WF modification. After optimizing the electromagnetic field spatial distribution by employing ZnO optical spacer, the device performance was further increased with the highest efficiency of 10.5%, which is among one of the best results for a single-junction OSCs. This facile hybrid HTL could be adaptive to various polymer systems with diverse energy levels because of the separate control of the anode work function by SAM layer and charge-extraction ability delivered by f-SWCNT mesh. Our work paved the way of fabricating low-cost, stable, and high-efficiency OSCs.

4. Experimental Section

Materials: P3HT, PCBM, and PC₇₀BM were purchased from Luminate Technology Corp., Solarmer Materials Inc. and Nano-C, respectively. PBDT-TS1 was provided from Prof. Jianhui Hou's group. SWCNT (purity: >90% and length: 5–30 μ m) was purchased from Chengdu Organic Chemicals Co., Ltd. The used SAM material is pentafluorobenzylphosphonic acid (F₅BnPA), which was purchased from Sigma Aldrich. Zinc oxide (ZnO) nanoparticles were synthesized according to previously reported procedure.^[60]

Table 2. The device performance parameter summary of PBDT-TS1/PC₇₀BM solar cells using f-SWCNT/SAM hybrid HTL and different thickness ZnO films as optical spacer under AM 1.5 G 100 mW cm⁻² irradiation.

Thickness of ZnO [nm]	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
12	0.783 ± 0.005	19.9 ± 0.3	64.9 ± 0.7	10.1 ± 0.05 (10.2)
20	0.783 ± 0.005	20.5 ± 0.1	64.6 ± 0.5	10.3 ± 0.16 (10.5)
25	0.783 ± 0.006	19.6 ± 0.3	62.9 ± 0.3	9.68 ± 0.20 (9.92)

Functionalization of SWCNT: 100 mg purchased SWCNTs powder was dispersed in 60 mL concentrated nitric acid (78%) and sonicated at room temperature for 1 h. The mixed solution was refluxed at 120 °C for 12 h. Then, the dispersion was filtered through a PTFE filter membrane after cooling down to room temperature and diluting with deionized (DI) water. The residues left on membrane were washed with DI water and dried in an oven (73 mg).

Device Performance and Characterization: ITO-coated glass substrates with sheet resistance of 15 Ω^{-1} were cleaned and subjected to UV-zone treatment for 25 min before hole transport layer deposition. Functionalized SWCNT were first dissolved in DMF solvent assisted by water-bath sonication with concentration of 0.5 mg mL⁻¹. The obtained f-SWCNT solution was centrifuged at 6000 rpm for 10 min to remove some bundles. The weight loss during centrifugation process was negligible in this study. The f-SWCNT solutions of 0.25, 0.15, and 0.05 mg mL⁻¹, were obtained by diluting with DMF solvent. The f-SWCNT solutions with different concentrations were spin-coated at 3000 rpm on clean ITO substrates to form different-coverage f-SWCNT meshes. Commercially obtained F₅BnPA powders were dissolved in 1-butanol with a concentration of 4 mg mL⁻¹. In order to modify the surface of f-SWCNT mesh, the F₅BnPA solution was spin-coated on f-SWCNT mesh followed by ethanol washing for producing a SAM layer with thickness of less than 5 nm. For reference, ITO-coated substrates modified with PEDOT:PSS (Baytron Al 4083) layer with thickness of 30 nm and pristine SAM layer were also prepared. P3HT:PCBM blend solution (1:1, 40 mg mL⁻¹ in 1,2-dichlorobenzene o-DCB) was spin-coated on ITO substrates with different hole transport layer to form 220-nm-thick active layer based on slow-growth method and followed by 130 °C thermal-annealing for 10 min. For low BG system, PBDT-TS1:PC₇₀BM solution (1:1.5, 25 mg mL⁻¹ in chlorobenzene (CB), with 3% v/v 1,8-diiodooctane (DIO) additive) was spin-coated to form 90 nm thick active layers. Ca (20 nm)/Al (100 nm) were sequentially thermal-evaporated as the cathode with defined area of 0.06 cm² by shadow mask.

Film Characterization: The Raman spectroscopic characterization was performed by using a laser confocal micro-Raman spectrometer (Renishaw in Via-Renishaw) at an excitation wavelength of 514 nm. The morphology of f-SWCNT meshes on ITO substrates was characterized by scanning electron microscopy (SEM, Hitachi S-4800).

The TEM images were recorded with FEI Tecnai G2 20 S-TWIN Scanning Transmission Electron Microscope. AFM measurements were conducted by using NanoScope III (Digital Instrument) in the tape mode. UPS spectra were obtained using a He discharged lamp (He 1 21.22 eV, Kratos Analytical) with an experimental resolution of 0.025 eV. During the testing, -10 V was biased on samples to favor observation of clear secondary-electron cutoff in the UPS spectra. J - V characteristics were obtained by using a Keithley 2635 source meter and Newport AM 1.5G solar simulator with irradiation intensity of 100 mW cm⁻². The thicknesses of layers were measured by a Dekak Stylus Profiler.

Supporting Information

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

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