Hybrid Carbon Nanotube Networks as Efficient Hole Extraction Layers for Organic Photovoltaics

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ABSTRACT

Transparent, highly percolated networks of regio-regular poly(3-hexylthiophene) (rr-P3HT) wrapped semiconducting single walled carbon nanotubes (s-SWNT) are deposited and the charge transfer processes of these nanohybrids are studied using spectroscopic and electrical measurements. The data discloses hole doping of s-SWNTs by the polymer, challenging the prevalent electron doping hypothesis. Through controlled fabrication, high to low-density

nanohybrid networks are achieved, with low dense hybrid carbon nanotube networks tested as hole transport layers (HTLs) for bulk heterojunction (BHJ) organic photovoltaics (OPV). OPVs incorporating these rr-P3HT/s-SWNT networks as the HTL demonstrate the best large area (70 mm²) carbon nanotube incorporated organic solar cell to date with a power conversion efficiency (PCE) of 7.6%. This signifies the strong capability of nanohybrids as an efficient hole extraction layer and we believe that dense nanohybrid networks have the potential to replace expensive and material scarce inorganic transparent electrodes in large area electronics towards the realization of low-cost flexible electronics.

Single walled carbon nanotubes (SWNT) with its unique electronic transport properties, continues to contribute to rapid advances in the fields of flexible electronics¹, photovoltaics², thin film transistors (TFT)³ and biosensors.⁴ Traditionally, as produced carbon nanotubes are known to form bundles which prevents the unique properties of individual carbon nanotubes being realized. As a result, techniques such as covalent⁵ and non-covalent functionalization⁶ have been utilized for isolating individual nanotubes. Recently, self-assembly of polymers into a supramolecular shell wrapping s-SWNTs has been gaining popularity as a route towards incorporation of nanotubes into organic optoelectronic devices^{7, 8} as well as for the fabrication of wafer scale thin film transistors (TFTs)³.

Despite the widespread use of polymer wrapped nanotubes, the nature of the charge transport within the nanotube, *i.e.* its electron or hole conduction has remained a matter of debate. While spectroscopic evidence has indicated an electron transfer to s-SWNTs from rr-P3HT^{7, 9, 10}, charge transport analysis has hinted of a hole transfer process¹¹.

In the field of organic photovoltaics (OPV), carbon nanotubes (CNTs) have been identified as promising candidates for excitonic antennas and concentrators¹², broadband energy harvesters¹³,

additional exciton dissociation sites in triple heterojunctions¹⁴ and as high mobility charge extraction paths.¹⁵ Over the past few years, much effort has been expended on producing a material system that can act as an efficient hole extraction layer for OPVs as a substitute for Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), the most common hole extraction material used.¹⁵⁻¹⁷ The hygroscopicity and acidity of PEDOT:PSS causes degradation of the active layer and the indium tin oxide (ITO) electrode resulting in a decreased life time of the solar cell.¹⁶ Among the potential solution processable candidates, CNTs have attracted much attention with recent reports indicating a PCE of 4.9% under AM1.5 G 1.3 sun illumination for OPVs incorporating CNTs as the hole extraction layer.¹⁸

In this study, strong evidence for preferential hole transport in solution processable large area networks of polymer wrapped s-SWNT networks is presented, indicating the role of such nanohybrids as hole extraction layers. In order to investigate the nanohybrids to perform in the capacity of hole transport layers (HTL) in OPVs, devices were fabricated with rr-P3HT/s-SWNTs as the HTL with rr-P3HT/PC₇₀BM ([6,6]-Phenyl-C71-butyric acid methyl ester) as the active photoabsorption layer. These investigations were further expanded for active layers based on the low bandgap donor polymer PTB7 (Poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]])/PC₇₀BM system.

Under an AM 1.5G 1 sun illumination, the PTB7/PC₇₀BM fabricated devices displayed a PCE of 7.6%, which is not only the best achieved for OPVs without a traditional hole transport layer, but also the best reported for organic solar cells utilizing carbon nanotubes as an active element to date.^{7, 18}

RESULTS AND DISCUSSION

Nanoscale ordering of the polymer on the nanotubes. To obtain a good dispersion, s-SWNTs were supramolecularly functionalized using rr-P3HT. Preparation of the rr-P3HT/s-SWNT nanohybrids were achieved through sonication of high purity (90%) s-SWNTs (0.50 mg) with rr-P3HT (0.60 mg) in 1.00 ml of chlorobenzene. The removal of excess rr-P3HT was achieved through a solvent extraction technique reported by Nish *et al.*¹⁹ using toluene as the extraction solvent with the prepared nanohybrids dispersed in 2.00 ml of 1,2-dichlorobenzene. The final weight ratio between rr-P3HT and s-SWNTs was ~1:3. Semiconducting nanotube enriched material in this study helped optimize device performance, which is known to be compromised due to the presence of metallic nanotubes.²⁰

Spin coating these nanohybrid solutions onto ITO coated glass substrates at 500 rpm and 1500 rpm is observed to lead to a network of nanohybrids as imaged using atomic force micrographs (AFM) (Fig.1B,C) over an area of $5\ \mu\text{m} \times 5\ \mu\text{m}$. In terms of the geometry of rr-P3HT in the presence of SWNTs, previous reports on nanohybrids prepared using techniques similar to that described in this work have indicated experimentally (through scanning probe microscopic techniques) as well as computationally, a natural tendency for the rr-P3HT to wrap around SWNTs due to π - π type super-molecular interactions.^{10, 21-24} To ascertain this fact further and to obtain a better understanding of the non-covalent functionalization process, optical absorption, valence and core level X-ray spectroscopy (XPS) measurements were carried out on the rr-P3HT/s-SWNT nanohybrid system.

Figure 1. AFM images of rr-P3HT/s-SWNTs spin coated on ITO/glass, absorption spectra and XPS analysis of nanohybrids. (A) A schematic representation of the spin casting process of nanohybrids from solution followed by thermal annealing giving rise to a network of nanohybrids. (B) A highly dense percolative network of nanohybrids (5 $\mu\text{m} \times 5\mu\text{m}$) spin coated from a $\sim 0.5 \text{ mg ml}^{-1}$ solution at a spin speed of 500 rpm on ITO/Glass and (C) is an image of a nanohybrid film spin coated at 1500 rpm from the same solution. The ITO surface is visible at this stage. (D) UV-Vis-NIR absorption spectra of rr-P3HT/s-SWNT (o) and pristine rr-P3HT (Δ) dispersions in 1,2-dichlorobenzene with a red shift in the 460 nm peak of rr-P3HT to 590 nm in the rr-P3HT/s-SWNTs indicating the increased crystallinity of rr-P3HT in nanohybrids. The

inset shows an expansion of the rr-P3HT/s-SWNT absorption spectrum in the range 475-700 nm.

The fitted peaks are assigned to the 0-0, 0-1, 0-2 and 0-3 transitions revealing the better ordered

nature of rr-P3HT due to π - π stacking with s-SWNTs. (E) Low energy XPS valence band spectra of rr-P3HT/s-SWNTs (---) and s-SWNTs (---) obtained at a photon energy of 125 eV.

A representative UV-Vis absorbance spectrum for rr-P3HT/s-SWNT nanohybrids in 1,2-dichlorobenzene is shown in Fig. 1D. The analysis of the spectroscopic evidence for the nanohybrids in comparison to free rr-P3HT indicates a large red shift of the absorption edge of rr-P3HT (from ~460 nm to ~590 nm) due to π - π^* transitions^{19, 25} upon the formation of the nanohybrids. The red shift coupled with the disappearance of the 460 nm absorption edge is due to the increased long range order of rr-P3HT chains as a result of π - π stacking with s-SWNTs in the polymer wrapping of carbon nanotubes.¹⁹ Furthermore, the absorbance spectrum of rr-P3HT/s-SWNTs indicates a structure within the wavelength region of 470 – 630 nm corresponding to vibronic progressions described by the Franck-Condon principle (Fig. 1D-inset).²⁶ The near unity value for the 0-0 to 0-1 intensity ratio combined with the low intensity for the 0-2 and 0-3 (relative to 0-1 peak)¹⁹ supports the ordering of rr-P3HT radial to the nanotubes indicating nanoscale ordering of rr-P3HT in an individual nanohybrid.

The nature of rr-P3HT surrounding the s-SWNTs was further examined using valence level X-Ray Photoelectron Spectroscopy (XPS). The valence band spectra of s-SWNT and rr-P3HT/s-SWNT shown in Fig. 1E displays an increase in the delocalized C 2p π signal (~4 – 7 eV)²⁷ in rr-P3HT/s-SWNTs than in the pristine s-SWNTs. The result should be an enhanced charge transport in the nanohybrids compared to pristine s-SWNTs. Furthermore, the lack of any discernible features in the range of 8.2-13.5 eV in the valence band spectrum of the nanohybrid results from a loss/weakening of π - π interactions between the P3HT chains due to tilting of adjacent polymer chains²⁸ and can be taken as indirect evidence for the polymer wrapping of nanotubes.

Further evidence to the nature of the interaction between rr-P3HT with the nanotubes is observed through the S 2p peak (due to carbon-sulphur bonding in rr-P3HT) at a binding energy (BE) of 164.5 eV²⁹ of the core level X-ray photoelectron spectrum (Fig.2A). The spin-orbit splitting corresponding to the S 2p^{3/2} and S 2p^{1/2} states expected for free rr-P3HT with an intensity ratio of 2:1 is not observed which is attributed to the high crystallinity of rr-P3HT in the nanohybrids³⁰ and/or interactions between S atoms in rr-P3HT with the s-SWNTs.²⁹ The possibility for higher crystallinity is further supported by the absence of satellite peaks on the high BE side at ~290 eV in the C 1s spectrum (Fig. 2B) which indicates a lack of fragments with a smaller conjugation length.^{29, 31}

Figure 2. XPS and Raman G-band spectra of s-SWNTs and rr-P3HT/s-SWNTs. (A) Core level XPS S 2p spectrum of rr-P3HT/s-SWNTs (---) obtained at a photon energy of 1250 eV. (B) Core level XPS C 1s spectra of rr-P3HT/s-SWNTs (---) and s-SWNTs (---) obtained at a photon energy of 400 eV. (C) Raman G-band spectra indicating an up-shift of 3 cm^{-1} in nanohybrids compared to pristine s-SWNTs. (D) Schematic diagram of a P3HT wrapped s-SWNT and the charge transfer process from the s-SWNT to P3HT creating hole doped carbon nanotubes.

Charge transfer between the polymer and nanotubes. Although the role of nanotubes in OPVs has been actively investigated, there still appears to be no clear consensus as to the nature of the charge transfer interaction between rr-P3HT and SWNTs. While the commonly held view has been an electron transfer from rr-P3HT^{9, 10}, Dissanayake and Zhong¹¹ reported a hole transfer to individual or few nanotubes in the presence of rr-P3HT. Therefore, the charge transfer process between wrapped rr-P3HT and s-SWNTs were examined using core level XPS and Raman Spectroscopy.

Analysis of the S 2p and C 1s of the core level XPS spectra of the nanohybrids (Fig. 2A,B) indicates a downshift of the BE for the former (~164.5 eV in the nanohybrid compared to 164.75 eV²⁹ in rr-P3HT) and an up shift for the latter (~284.5 eV in the nanohybrid compared to 284.3 eV in s-SWNT). An up (down) shift is attributed to a hole (electron) transfer to the s-SWNT (rr-P3HT).³² This cannot be due to any form of disordering effect caused by blending of rr-P3HT with s-SWNTs as a highly crystalline structure is imparted on the rr-P3HT by s-SWNTs as observed in the absorption and valence level XPS spectra discussed above (and given in Fig. 1E). The charge transfer process between the s-SWNTs and the surrounding rr-P3HT was further analysed by Raman spectroscopy. A small red shift (by 3 cm^{-1}) of the Raman G-band in nanohybrids compared to pure s-SWNTs (Fig.2C) is observed which could occur as a result of

hole doping of nanotubes.³³ It is important to note that the hole doping effect due to exposure to oxygen in the atmosphere can be ruled out as both s-SWNTs and nanohybrid films were prepared and stored under identical conditions. However, as the observed Raman shift is insufficiently robust, field effect transistor (FET) measurements were carried out on the thin films of nanohybrids, where deposition of the film on electrodes and device measurements were all carried out in a N₂ glove box. The use of a N₂ atmosphere mitigates against any unintended hole doping of the nanotubes due to O₂ exposure. Therefore, the observed characteristics are considered to be due to charge transfer processes occurring as a result of the polymer wrapping of the nanotubes.

Figure 3. Transfer characteristics and J-V curves of “hole only” devices of nanohybrids. (A) Transfer characteristics of the self-ordered nanohybrids for channel lengths of 10 μm under a VDS range of 0.5 V to 2.5 V. A prominent hole transportation is observed under negative gate biasing with a significantly weaker electron transportation under positive biasing indicating the preferential hole transport behaviour of the nanohybrids. Measurements were carried out under a N₂ atmosphere using a 230 nm SiO₂ gate dielectric with a global bottom gate and Au bottom contacts (inset). (B) Schematic of the device architecture used for the nanohybrids incorporated device. (C) The response of the reference P3HT only and nanohybrid incorporated rr-P3HT “hole only” devices under illumination with AM 1.5G simulated light. (D) The flat band diagram for the nanohybrid incorporated device used and the down shift of the ionization potential of s-SWNT due to hole doping by rr-P3HT is indicated by the red arrow. The band alignment favours the transportation of holes to ITO leading to the observation of 4th quadrant characteristics for the nanohybrid incorporated devices in (D).

The transfer characteristics of the nanotubes at a channel length of 10 μm is shown in Fig. 3A. Non-linear I-V characteristics have been observed under $V_g = 0$ V indicating the formation of a Schottky contact to the nanohybrids. Traditionally, due to its high HOMO level of -5.2 eV, rr-P3HT has been reported to form an Ohmic contact when spin coated onto Au (work function = -5.1 eV) electrodes³⁴, while Au is known to form a Schottky contact to carbon nanotubes.³⁵ The observation of non-linear characteristics therefore indicates that the polymer sheath wrapping the s-SWNT is sufficiently thin to act as a tunnel barrier allowing for charge transport through the nanotubes. However, the formation of a Schottky contact to nanotubes is considered to be detrimental to device performance by affecting the charge injection and hence the ballistic transport properties³⁶, as well as leading to ambipolar transport characteristics. This is due to the

tunnelling of electrons from the contacts to the nanotubes under positive gate voltages³⁵, especially when measured in vacuum.³⁷

As expected for Schottky barrier s-SWNT transistors, the transfer characteristics indicates a suppressed ambipolar charge transport with an electron transport that is 2-3 orders of magnitude lower in comparison to that of hole transport in the device. Despite this, the weak ambipolar nature leads to relatively low I_{on}/I_{off} ratios of $\sim 10^3$ for negative gate voltages. It is noted that similar observations for preferential hole transport has been made for carbon nanotube FETs measured in air, where hole doping due to exposure to O₂ suppresses the *n*-type behaviour (and hence the ambipolar nature) of the device.³⁷ As the transport measurements have been carried out in N₂ environment, the observed preferential hole transport in the nanohybrids is attributed to the hole doping of the s-SWNTs due to charge transfer interactions between rr-P3HT and the nanotubes. The measured lateral in-plane transport values for the nanohybrid structures are observed to be comparable to those reported in the self-organized nanotube networks in SiO₂ by Bao *et al.*³⁸

Nanohybrids as a hole extraction layer in OPVs. The potential of these hole doped s-SWNTs as hole extraction centres as well as its effect on the dissociation of excitons photogenerated in rr-P3HT was studied using the device architecture depicted in Fig. 3B. “Bilayer” heterojunction photovoltaic cells were fabricated by spin coating the nanohybrids onto an ITO coated glass followed by spin coating a layer of rr-P3HT with the photo characteristics being investigated under exposure to 100 mW cm⁻² AM 1.5G stimulated light. The hole collection was carried out on the ITO electrode, while the devices behave as “hole only” structures due to the low exciton diffusion length (of ~ 10 nm¹¹) and a low electron mobility of ($\sim 10^{-4}$ cm²V⁻¹s⁻¹) of rr-P3HT.³⁹ Under dark conditions, a forward rectifying behaviour is

observed while a 4th quadrant operation is noted upon exposure to light of 100 mW cm⁻² (Fig. 3C) with an open circuit voltage of ~0.2 V. Furthermore, the observed merging of light and dark characteristics at ~ 0.5 V (see supporting information) (which indicates the lack of photocurrent generation) indicates the built in potential of the system to be at this value.¹¹ On the otherhand, rr-P3HT based devices prepared without the nanohybrid hole transport layer indicates only a weak 4th quadrant behaviour and a higher open circuit voltage of ~0.4 V under photo illumination.

According to the metal-insulator-metal model which is traditionally used for describing the behaviour of organic semiconductors sandwiched between two metal contacts, the open circuit voltage is governed by the difference in the work function of the contacts used.⁴⁰ However, in the case of organic heterojunctions formed between two Ohmic contacts, the open circuit voltage is known to be better described by the alignment of the quasi Fermi level of the components.⁴¹ Therefore, the observation of a lower open circuit voltage for the nanotube (whose quasi Fermi level is closer to that of rr-P3HT) incorporated devices, in comparison to the P3HT only devices (open circuit voltage of ~0.4 eV due to work functions of ITO and Al which are 4.7 eV and 4.3 eV respectively) indicates a heterojunction is formed between the nanotubes and the rr-P3HT. Furthermore, this is confirmed by the enhancement in the short circuit current density for the nanotubes incorporated devices when compared to the P3HT only devices. This illustrates that the inclusion of the nanotubes lead to an enhancement in the exciton dissociation and photocurrent generation.¹⁴

Although the hole transporting and exciton dissociation capability of these nanohybrids is in contradiction to the conclusions made in the literature⁴², we note that these results are in agreement with those reported by Dissanayake and Zhong for few nanotubes (1-6 tubes)¹¹

coated with rr-P3HT. This is the first report on the hole doping effect by rr-p3HT for large area carbon nanotube networks and confirms the use of these nanohybrid networks as hole transport layers for organic optoelectronic devices.

Having confirmed the hole transporting nature of the nanohybrids, we proceed to understand the observed photovoltaic device performance given in Fig. 3C through energy level alignments in the device architecture employed (Fig. 3D). The built-in potential due to the work function difference of rr-P3HT and rr-P3HT/s-SWNT is ~ 0.5 V. Taking the work function of rr-P3HT to be -4.4 eV, the hole transporting nature of the nanohybrids requires a lower ionization potential at -4.9 eV.^{11, 43} However, the inferred value of the ionization potential of nanohybrids is lower than the ionization potential of pristine SWNTs (-4.7 eV)¹¹ and further confirms the hole doping of carbon nanotubes by rr-P3HT.

For application of these nanohybrid films for OPVs, 1-3 nm thin films of low nanotube density (0.02 mg ml^{-1}) were prepared by spin coating nanohybrids at a speed of 1500 rpm on ITO/glass and an AFM image of such a film is given in Fig. 4B. A low density of nanotubes prevents the short circuiting of carbon nanotube incorporated OPVs which can occur even in the presence of minute quantities of metallic nanotubes.¹⁰ The nanohybrids on ITO/glass have a transmission of $\sim 89\%$ at a wavelength of 550 nm (Fig. 4A), where a 40 nm thick PEDOT:PSS layer used for the reference device fabrication has a transmission of 85% at the same wavelength.

OPV devices were fabricated by employing nanohybrids as the hole transport layer (HTL) and a reference device was also fabricated without a hole transport layer. The active layer of the devices comprised of Poly(3-hexylthiophene) (P3HT) as the donor and [6,6]-Phenyl-C71-butyric acid methyl ester (PC₇₀BM) as the electron acceptor. The complete device architecture representing different cross sections of the device is depicted in Fig. 4C. Evaluation of the

effectiveness of the nanohybrid HTL was performed by comparing the device performance of the nanohybrid HTL incorporated device (Device Type A) with a device without a HTL (Device Type B). The current density-voltage (J-V) characteristics of a typical device of Type A and B under AM 1.5G illumination with an irradiation intensity of 100 mW cm^{-2} are depicted in Fig.4D and the device performance characteristics are given in Table 1.

Figure 4. Transmission of nanohybrids, OPV device architecture and the charge transfer at the interface of the active layer and the hole transport layer along with the corresponding energy level diagram and J-V characteristics of the devices. (A) Transmission spectrum of a typical

nanohybrid layer used as the HTL in devices, on ITO/Glass and (B) is an AFM image of the film displaying the thin but still percolated network of nanohybrids. (C) A schematic representation of the device architecture used to fabricate solution processed OPV structures employing rr-P3HT/s-SWNT HTLs. The active layer consists of rr-P3HT/PC₇₀BM which is sandwiched in-between rr-P3HT/s-SWNT hole transport and BCP electron transporter layers. ITO acts as the anode whereas the Al represents the cathode. (D) J-V characteristics of devices A (---) and B (---) under AM 1.5G illumination with an irradiation intensity of 100 mW cm⁻². (E) Suggested band diagram of a device (ITO/rr-P3HT/s-SWNT/P3HT-PC₇₀BM/BCP/Al) employing rr-P3HT/s-SWNT nanohybrids as an electron blocking layer. The energy values are in eV.

Table 1. Device performance parameters for devices A and B where, A = ITO/rr-P3HT-PC₇₀BM/BCP/Al and B = ITO/rr-P3HT/s-SWNT/rr-P3HT-PC₇₀BM/BCP/Al under AM 1.5G illumination.

Device	Thickness of the active layer(nm)	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	PCE (%)
A=ITO/rr-P3HT-PC ₇₀ BM/BCP/Al	210	0.57	8.66	57.03	2.81
B=ITO/rr-P3HT:s-SWNT/rr-P3HT-PC ₇₀ BM/BCP/Al	280	0.58	8.36	69.35	3.36

The importance of the nanohybrid HTL is evident by the increase in PCE from 2.8% to 3.4%, through the inclusion of the HTL. The drastic improvement of PCE of device A compared to device B is mainly governed by the increased fill factor (FF) of device A by 12% compared to device B. This indicates efficient hole extraction as a result of enhanced interfacial contact between the adjacent layers due to the chemical match between rr-P3HT in the active layer and the HTL, the high mobility of the extracted charges in the HTL and better Ohmic contact

between the ITO and HTL.^{40, 44} The most important phenomenon for the nanohybrids to act as an efficient HTL is the hole doping of s-SWNTs by rr-P3HT which increase the ionization potential of the nanotubes to 4.9 eV, which favorably aligns with HOMO level of the rr-P3HT (5.2 eV) (Fig.4E) in the active layer. Furthermore, analysis of the UV-Vis spectra given in Fig.1D clearly indicates the disappearance of the absorption edge at 460 nm in the nanohybrid spectrum corresponding to free rr-P3HT present in the medium. Therefore, considering the absence of free rr-P3HT within the nanohybrids, it is important to note that the enhancement of the PCE is solely due to the efficient hole carrier ability of the nanohybrids and not due to any form of free rr-P3HT present in the nanohybrid solution used to prepare the film.

Considering the high efficiency of the prepared nanohybrids as a hole extraction layer, a series of OPV devices were fabricated using the low bandgap PTB7 (HOMO~5.1, LUMO~3.3) polymer as the donor material in the active layer. An optimized reference device without any HTL for comparison and an optimized device employing PEDOT:PSS was fabricated to study the potential of nanohybrids as compared to the widely used HTL standard.

Evaluation of the performance of self-ordered nanohybrid grids as a HTL was carried out based on three different multilayer Device types: A, B and C (Table 2) with an active layer comprising of Poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7) and [6,6]-Phenyl-C71-butyric acid methyl ester (PC₇₀BM). While Device A did not incorporate a HTL, Device B consisted of a 40 nm thick PEDOT:PSS layer and Device C contained a 1-3 nm thin network of nanohybrids as the HTL (Fig. 4A).

Table 2. Device performance parameters for best performing device types A, B and C where, A=ITO/PTB7-PC₇₀BM/BCP/Al, B=ITO/PEDOT:PSS/PTB7-PC₇₀BM/BCP/Al and C=ITO/rr-P3HT/s-SWNT/PTB7-PC₇₀BM/BCP/Al under AM 1.5G, 1 sun illumination.

Device type	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	PCE (%)
A=ITO/PTB7-PC ₇₀ BM/BCP/Al	0.66	15.50	55.04	5.63
B=ITO/PEDOT:PSS/PTB7-PC ₇₀ BM/BCP/Al	0.68	15.41	69.96	7.33
C=ITO/rr-P3HT/s-SWNT/PTB7-PC ₇₀ BM/BCP/Al	0.68	15.46	72.58	7.63

The current density-voltage (J-V) characteristics of best performing devices A, B and C under AM 1.5G illumination with an irradiation intensity of 100 mW cm⁻² are depicted in Fig.5A. Devices of Type C, incorporating nanohybrid hole transport layers were fabricated in the range of 100-180 nm active layer thicknesses, whereas the maximum efficiency of 7.6% was recorded at an active layer thickness of ~170 nm. Four devices of the same type were fabricated with an identical active layer thickness and the PCE was in the range of 7.2% - 7.6%.

The potential of the nanohybrids to act as a HTL is proven by the significant improvement of 36% in the PCE of device type C compared to device type A, leading to a PCE of 7.6% which is the highest reported for a carbon nanotube incorporated OPV to date. It is clearly noted that the enhanced PCE of device type C is governed by the enhanced FF of 73% compared to 55% of device type A.

It is evident that the nanohybrids are a potential candidate for replacing most HTLs including the widely used PEDOT:PSS considering the solar cell performances of the two devices B (PCE~7.3%) and C (PCE ~7.6%). Four of the best performing Type B devices was also

fabricated and the PCE was in the range of 7.1%-7.3%. These were examined over different dates with all data showing consistent improvements to performance with the nanohybrid HTL.

For completion the hole mobility (μ) of the fabricated devices were measured using nanohybrids and PEDOT:PSS as the HTL using space charge limited current (SCLC) analysis method (see supporting information). Both devices were identical in terms of materials employed and the layer thicknesses, the only difference being the HTL. The calculated μ of such nanohybrid HTL incorporated devices was $1.21 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ whereas the μ of PEDOT:PSS incorporated devices was $1.11 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Since, under identical conditions the hole mobilities of both devices are comparable it is reasonable to conclude that the hole mobility of nanohybrids is almost similar to the hole mobility of PEDOT:PSS. The better solar cell performance, higher light transmission through the HTL and the lack of degradation of ITO due to the inert nature of nanohybrids makes the novel nanohybrid material a desirable candidate for hole extraction in OPVs and hole injection in OLEDs.

Figure 5. J-V characteristics of Devices A, B, C and a comparison of CNT incorporated OPVs. J-V characteristics of Devices A (---), B (---) and C (---) under AM 1.5G illumination with an irradiation intensity of 100 mW cm^{-2} . The same device architecture as in Fig.4 has been used

here and PTB7 is used in the active layer as the donor material. The plot displays the significant enhancement in the FF when a HTL layer is incorporated to the device architecture.

CONCLUSIONS

Preferential hole transport has been observed for the first time in conjugated polymer wrapped carbon nanotubes network through spectroscopic analysis (XPS and Raman spectroscopy) and electrical measurements (photo response of a hole only photovoltaic device and field effect transistor measurements). The hole transportation is facilitated by the downshifting of the nanotube ionization potential due to its hole doping by the surrounding polymer sheath.

The PCE of 7.6 % for the nanohybrid-photovoltaic device is the highest efficiency reported for BHJ OPV devices employing any type of carbon nanotubes to date. Our device is one of the most efficient organic solar cells over 50 mm² active area, where the majority of the reported best in class OPVs consist of device areas < 20 mm².^{45,46} These results will inform the design of future large area CNT hybrid OPVs and opto-electronic devices, considering the efficient charge extraction, low cost, low material consumption, high transparency and the chemical inertness of the nanohybrid networks proposed.

METHODS

rr-P3HT wrapping of s-SWNTs.

A mass of 0.6 mg of rr-P3HT (Rieke Metals Inc, weight average molecular weight, $M_w = 50000 \text{ g mol}^{-1}$ and regioregularity = 95%) was added to 1.00 ml of chlorobenzene such that the concentration of rr-P3HT was 0.60 mg ml^{-1} and sonicated for 60 minutes. A mass of 0.50 mg of s-SWNTs (NanointegrisIsoNanotubes-s (90% semiconducting)) was added to the solution (0.5 mg ml^{-1}) and was ultrasonically treated at a frequency of 32 – 38 kHz for further 60 minutes. A

volume of 1.00 ml of toluene was added to the solution mixture, sonicated for 15 min and centrifuged for 8 minutes at 16000g in order to remove the excess rr-P3HT in the medium. The precipitate was collected while the supernatant (dark yellow) was discarded. The above sonication and centrifugation procedure was performed twice more and the precipitate was collected while the supernatant (pale yellow) was discarded. The precipitate obtained was dissolved in 1.0 ml of 1,2-dichlorobenzene by ultra-sonication for 60 minutes (rr-P3HT/s-SWNT) such that the final concentration of s-SWNTs in rr-P3HT/s-SWNTs is $\sim 0.5 \text{ mg ml}^{-1}$.

Fabrication and performance measurement of OPV devices.

rr-P3HT/PC₇₀BM devices: A mass of 20.00 mg each of rr-P3HT and PC₇₀BM (99% pure; Solenne) were added to 1.0 ml of 1,2-dichlorobenzene and the solution was stirred overnight after which filtering of the solution was carried out using a 0.2 μm filter.

Device A: ITO coated glass which had been cleaned in an ultrasonic bath using acetone and methanol and subjected to an oxygen plasma treatment for five minutes was used to spin coat the filtered rr-P3HT/PC₇₀BM active layer. A two-step spin coating process was utilised for the spin coating of the active layer; first step at 750 rpm for 40 seconds and second step at 1500 rpm for 1 second, which was found to yield optimal active layer thickness. *Device B:* A diluted solution ($\sim 0.02 \text{ mg ml}^{-1}$) of the original rr-P3HT/s-SWNT solution (0.5 mg ml^{-1}) was spin coated on cleaned ITO coated glass (same cleaning procedure as above) at a speed of 1500 rpm for 1 minute and was annealed at a temperature of 120°C for 10 minutes allowing the solvent to evaporate. The active layer consisting of rr-P3HT/PC₇₀BM was spin coated on top of the rr-P3HT/s-SWNT film in a two-step process; first step at 500 rpm for 40 seconds and second step at 1500 rpm for 1 second.

The spin coated devices were allowed to dry slowly in closed Petri dishes (60 mm diameter, 15 mm height) at room temperature and the films were then annealed at 120°C for 10 minutes. The hole blocking layer, Bathocuproine (BCP) (2 nm) and Al (70 nm) electrode (cathode) were then thermally evaporated under vacuum of $<3 \times 10^{-6}$ mbar yielding a device with area $\sim 0.7 \text{ cm}^2$. All the steps involved in device fabrication were carried out in a nitrogen filled MBRAUN glove box. Current density – Voltage (J-V) measurements were performed using a Keithley 2400 exposing the devices to stimulated AM 1.5G light (obtained from 300 W Xe Arc lamp ORIEL simulator calibrated to an intensity of 1000 Wm^{-2} with a Newport reference solar cell) at room temperature.

PTB7/PC₇₀BM devices: A mass of 10.00 mg of PTB7 (1-material Chemsitech Inc.) and 15.00 mg of PC₇₀BM (99% pure; Solenne) were added to 1.0 ml of chlorobenzene/1,8-diiodooctane (97:3 vol%) and the solution was stirred overnight at 70°C after which filtering of the solution was carried out using a 0.2 μm filter.

Device Type A: ITO coated glass which had been pre-cleaned as described above. Spin coating of PTB7/PC₇₀BM active layer was carried out at 800 rpm for 2 mins.

Device Type B: A solution of PEDOT:PSS was spin coated on cleaned ITO coated glass (same cleaning procedure as above) at a speed of 5000 rpm for 40 seconds to obtain a thickness of 40 nm and was annealed at a temperature of 155°C for 10 minutes. The active layer consisting of PTB7/PC₇₀BM was spin coated at 1000 rpm for 2 mins on top of the PEDOT:PSS film.

Device Type C: A diluted solution ($\sim 0.02 \text{ mg ml}^{-1}$) of the original rr-P3HT/s-SWNT solution (0.5 mg ml^{-1}) was spin coated on cleaned ITO coated glass (as given above) at a speed of 1500 rpm for 1 minute and was annealed at a temperature of 120°C for 10 minutes allowing the

solvent to evaporate. The active layer consisting of PTB7/PC₇₀BM was spin coated at 600 rpm for 2 mins on top of the rr-P3HT/s-SWNT film where the active layer thickness is 170 nm.

All devices were slow dried at room temperature. The hole blocking layer, Bathocuproine (BCP) (4 nm) and Al (80 nm) electrode (cathode) were then thermally evaporated under vacuum of $< 3 \times 10^{-6}$ mbar yielding a device with area 70 mm². All the steps involved in device fabrication were carried out in a nitrogen filled MBRAUN glove box. Current density – Voltage (J-V) measurements were performed using a Keithley 2400 exposing the devices to stimulated AM 1.5G light (obtained from Abet Technologies-10500 solar simulator calibrated to an intensity of 1000 W m⁻² with a Newport reference solar cell) at room temperature.

“Hole only” device fabrication and measurement.

Fabrication of devices was carried out on pre-cleaned ITO coated glass substrates as described above. The nanohybrid layers in 1,2-dichlorobenzene (0.01 mg ml⁻¹) were spin coated onto the cleaned substrates inside an MBRAUN glove box. Upon drying the substrate at ~110°C for 10 min inside the glove box, the active layer consisting of rr-P3HT (50 nm) was spin coated onto the substrate at 750 rpm. Subsequently, 2 nm bathocuproine (electron blocking layer) and 70 nm Al were thermally evaporated. Photovoltaic device measurements were carried out in air using an AM1.5 G solar simulator calibrated using a Si reference cell.

Field effect device fabrication.

Field effect devices with interdigitated electrode architectures (Channel width of 2000 μm and channel length of 10 μm) were fabricated on 230 nm SiO₂ on n-type Si using standard photolithographic techniques. Spin coating of the 0.02 mg ml⁻¹ nanohybrids was carried out inside an MBRAUN glove box. Upon spin coating all devices were annealed at 110 °C for 10

min. Electrical characterization was carried out inside the glove box using a Keithley 4200 SCS system using the Si substrate as a global back gate.

Film thickness measurements.

The thickness measurements of the devices were carried out using an Alpha-step 200 profilometer.

UV-Vis-NIR absorption spectra.

1,2-dichlorobenzene was used as the solvent to obtain solution phase absorption spectra of pristine rr-P3HT and nanohybrids. Pristine s-SWNTs were dispersed in deionized water using Triton X-100 as the surfactant. All measurements were carried out using a Varian Cary 5000 UV-Vis spectrophotometer.

Optical transmission spectra.

Films of rr-P3HT/s-SWNTs spin coated on ITO substrates at 1500 rpm for 1 minute and annealed at a temperature of 120°C for 10 minutes was used to obtain the optical transmission through the nanohybrids. Measurements were carried out using a Varian Cary 5000 UV-Vis spectrophotometer.

Raman spectroscopic analysis.

Films of rr-P3HT/s-SWNTs spin coated on ITO substrates and a bucky paper of s-SWNTs (as received) were used to obtain Raman spectra. The measurements were carried out using a Renishaw micro-Raman system with an Ar⁺ laser operating at a wavelength of 514.5 nm.

AFM imaging of nanohybrids.

rr-P3HT/s-SWNT nanohybrids were spin coated on ITO substrates to obtain AFM images and the images were taken using a Veeco dimension 3000 instrument.

XPS measurements.

X-ray photoelectron measurements were conducted at the synchrotron beam line UE 52 PGM, Bessy II, *Universität Würzburg*, using a hemispherical SCIENTA SES 200 photoelectron energy analyzer. The base pressure in the setup was maintained below 10^{-10} mbar. Core level spectra of s-SWNTs and rr-P3HT/s-SWNTs was obtained using photon energies of 1250 eV and 400 eV and valence level spectra was taken using a photon energy of 125 eV.

Supporting Information Available: A magnified AFM image of the nanohybrids, the response of the “hole only” nanohybrid incorporated device under dark and illuminated conditions, method of fabrication of hole only devices and hole mobility calculations. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

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G.M.R.D, K.D.G.I.J, A.A.D.T.A and S.R.P.S have filed a patent application on this work.

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