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Review Article

Solar Cells with SWCNTs and MWCNTs

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Abstract

The use of semiconductors in photovoltaics, or solar cells, allows them to transform light into energy. Because of its potential as eco-friendly and effective light-harvesting technologies, solar cells have been in the spotlight recently. Extensive and ongoing research has focused on the potential critical role of single-walled carbon nanotubes (SWNTs) in these devices. The most essential metric in comparing single-walled carbon nanotubes (SWNTs) with multi-walled carbon nanotubes (MWNTs) is their optical transmittance, which is different at low densities. As a result, SWNTs are known to perform better than MWNTs. The semiconducting properties of SWNT films allow them to serve as active or charge-transporting materials.

Keywords: SWNTs, MWNTs, Optical, Transmittance, Densities.

1. INTRODUCTION

SWNTs are an optimal light-harvesting medium that exhibits a high carrier mobility, a wide range of direct band gaps, robust absorptions within the solar spectrum, and exceptional chemical stability. Organic compounds possess intrinsically low carrier mobility and stability when contrasted with carbon nanotubes (CNTs). The carrier mobility of organic semiconductors is one hundredth that of inorganic materials. This results in a performance limitation for organic solar cells (OSCs) [1]. Consequently, the efficacy of devices can be significantly enhanced by the integration of CNTs into OSCs. This section examines the utilization of SWNTs in the photoactive layer of photovoltaics and provides a review of the literature's demonstrations of this technology [2].

A single SWNT has the capability to establish a p-n junction diode, which results in the photovoltaic effect. 12, 13 Consequently, single-walled carbon nanotubes demonstrate elevated power conversion efficiency when subjected to illumination. Single-walled carbon nanotubes (SWNTs) consist of both semiconducting and metallic varieties, typically observed in a ratio of approximately 2 to 1. Semiconducting single-walled carbon nanotubes (SWNTs) establish Schottky contacts with metallic entities, which contribute to the observed ideal diode characteristics. In contrast, metallic SWNTs exhibit a propensity for the recombination of electrons and holes [3]. Consequently, the purification of SWNTs should be tailored to their specific applications [4]. The distinction in electronic structure between semiconducting and metallic single-walled carbon nanotubes (SWNTs) arises from their chirality [5]. These nanotubes can be synthesized in a chiral-specific manner or sorted through various techniques that take into account their diameters and electronic characteristics (Fig. 1). Prominent sorting techniques include density gradient ultracentrifugation, gel chromatography, and aqueous two-phase separation. The methodologies employed leverage variations in diameter, chirality, and electronic characteristics of carbon nanotubes to accurately isolate multiple chirality's of semiconducting single-walled carbon nanotubes [6]. The distinct absorption of specific light wavelengths by each chirality indicates that the semiconducting single-walled carbon nanotubes (SWNTs) produced through this method possess potential utility as a photoactive material [6]. Due to their elevated conductivity along the tube axis, single-walled carbon nanotubes (SWNTs) serve a dual purpose, functioning effectively as both light harvesters and charge transporters within the photoactive layer [7]. SWNTs exhibit a dual functionality, serving as both a light absorber and a charge-selective material [8].

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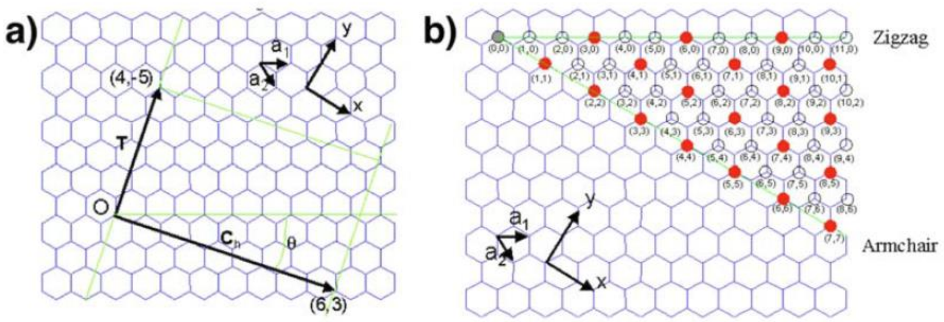

Figure 1. a) Definition of chiral vectors in a hexagonal lattice. b) For a SWNT chirality of (n,m), if the value of (n-m)/3 is an integer, the SWNT is metallic. The red dots represent metallic SWNTs.

Solar cell devices typically consist of an active layer, a charge-selective layer, and a charge-conductive layer. The active layer captures light and produces excitons. The charge-selective layers are positioned above and below the active layer to exclude any extraneous charges, hence preventing recombination following excitation [9]. The conductive layers then extract the filtered charges. A polymer matrix consisting of conductive polymer and SWNTs facilitates exciton dissociation in a high electric field, with the CNTs serving as the electron transporters [10]. Twenty-one A donor-acceptor heterojunction facilitates effective charge separation and collection, enabling electrons and holes to migrate towards their appropriate contacts via the polymer donors and carbon nanotube acceptors. Poly(3-hexylthiophene) (P3HT) and poly(3-octylthiophene) (P3OT) are the predominant polymer donors and are often combined with single-walled carbon nanotubes (SWNTs) in solutions [12].

1.1 CNT as Electron Acceptors / Transporters

The thermal post-treatment was identified at this stage, including the heating of devices beyond the glass transition temperature of the polymer donor. This treatment induced advantageous phase separation of the mix and enhanced the organization of the polymeric chains, hence facilitating charge transfer, transport, and collection. This treatment significantly enhanced the hole mobility of the polymer-CNT composites [13-18] Jousselme and colleagues documented the preparation of SWNT, P3HT, and 1-(3-methoxycarbonyl)-propyl-1-phenyl[6,6]C61 (PCBM) nanocomposites utilizing a technique involving high dissolution followed by concentration to regulate the ratio of CNTs to P3HT/PCBM in the mixture, ensuring homogeneous dispersion of the CNTs within the matrix (Table 1: Report D) [12]. Five A P3HT/PCBM (1:1) blend with 0.1 wt % MWNTs had the best power conversion efficiency of 2.0%. Ozkan and colleagues achieved the controlled deployment of a single-walled carbon nanotube (SWNT) monolayer network at four distinct locations within polymer-fullerene solar cells, discovering that SWNTs positioned on the hole-collecting side of the active layer resulted in a high power conversion efficiency (PCE) of 4.9% (Table 1: Report E) (Figure 2).

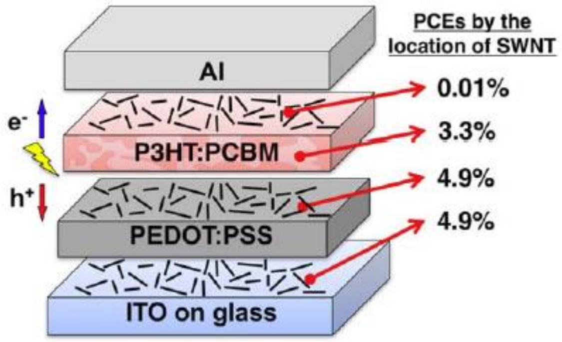

Figure 2. Illustration of a work reported in reference 6. SWNTs located either above or below the hole-transporting layer of OSCs perform the best (the numbers indicate PCEs obtained with different position of the SWNT layer).

They also showed that SWNTs positioned atop the active layer resulted in an extended fluorescence lifespan of P3HT. This experiment employed dip coating from a hydrophilic solution. The investigation of SWNTs as an electron acceptor, conducted by Gradecak and colleagues, showcased SWNT/P3HT bulk heterojunction solar cells achieving a power conversion efficiency (PCE) of 0.72% (Table 1: Report F) [19]. A major aspect of this study was employing only semiconducting SWNTs coated with meticulously organized P3HT through π–π interactions to improve charge separation and transport [20].

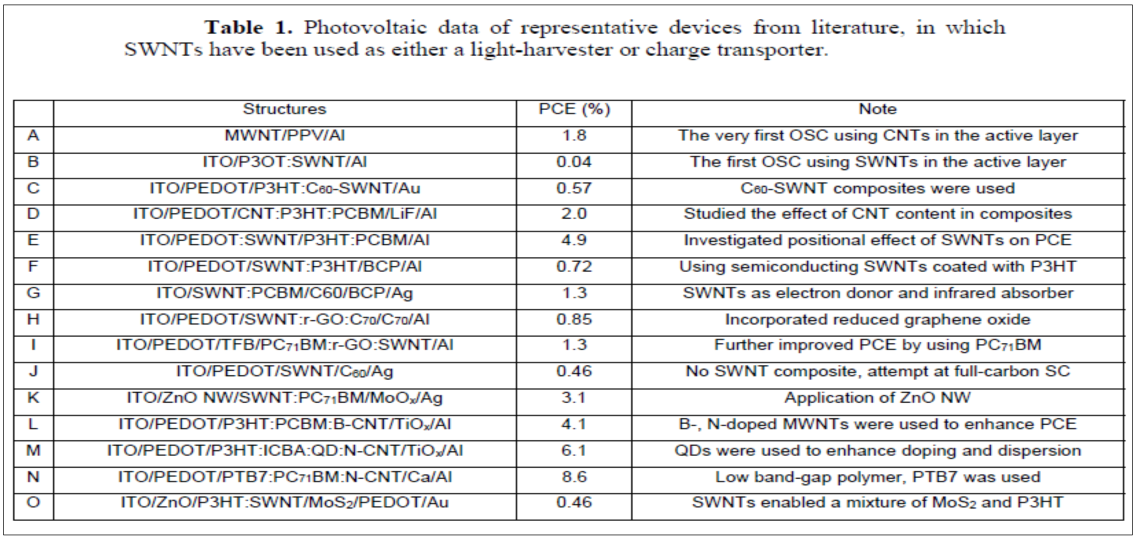
Table 1. Photovoltaic data of representative devices from literature, in which SWNTs have been used as either a light-harvester or charge transporter.

	Structures	PCE (%)	Note
A	MWNT/PPV/Al	1.8	The very first OSC using CNTs in the active layer
B	ITO/P3OT:SWNT/Al	0.04	The first OSC using SWNTs in the active layer
C	ITO/PEDOT/P3HT:C_{60}-SWNT/Au	0.57	C_{60}-SWNT composites were used
D	ITO/PEDOT/CNT:P3HT:PCBM/LiF/Al	2.0	Studied the effect of CNT content in composites
E	ITO/PEDOT:SWNT/P3HT:PCBM/Al	4.9	Investigated positional effect of SWNTs on PCE
F	ITO/PEDOT/SWNT:P3HT/BCP/Al	0.72	Using semiconducting SWNTs coated with P3HT
G	ITO/SWNT:PCBM/C60/BCP/Ag	1.3	SWNTs as electron donor and infrared absorber
H	ITO/PEDOT/SWNT:r-GO:C_{70}/C_{70}/Al	0.85	Incorporated reduced graphene oxide
I	ITO/PEDOT/TFB/$PC_{71}BM$:r-GO:SWNT/Al	1.3	Further improved PCE by using $PC_{71}BM$
J	ITO/PEDOT/SWNT/C_{60}/Ag	0.46	No SWNT composite, attempt at full-carbon SC
K	ITO/ZnO NW/SWNT:$PC_{71}BM$/MoO_x/Ag	3.1	Application of ZnO NW
L	ITO/PEDOT/P3HT:PCBM:B-CNT/TiO_x/Al	4.1	B-, N-doped MWNTs were used to enhance PCE
M	ITO/PEDOT/P3HT:ICBA:QD:N-CNT/TiO_x/Al	6.1	QDs were used to enhance doping and dispersion
N	ITO/PEDOT/PTB7:$PC_{71}BM$:N-CNT/Ca/Al	8.6	Low band-gap polymer, PTB7 was used
O	ITO/ZnO/P3HT:SWNT/MoS_2/PEDOT/Au	0.46	SWNTs enabled a mixture of MoS_2 and P3HT

The electrical properties of the devices were significantly influenced by the SWNT loading. The modeling of the VOC indicated that, despite the high carrier mobility in SWNTs, the power conversion efficiency was constrained by carrier recombination [21].

1.2 CNT as a Light Absorber and Electron Donor

Arnold and colleagues demonstrated that semiconducting SWNTs function as both electron acceptors and light-harvesting electron donors. 30 to 32 a semiconducting SWNT/PCBM bulk heterojunction was formed with a layer of bathocuproine (BCP), addressing the limited diffusion of semiconducting SWNTs, resulting in a near-infrared efficiency of 1.3% (Table 1: Report G). 33 A subsequent study provided mechanistic insights; however, it did not achieve higher efficiency, especially in the visible region of the solar spectrum. The introduction of reduced graphene oxide (r-GO) as a cascade material linking SWNTs and fullerene acceptors enabled the realization of higher efficiency. Pristine carbon nanotubes and graphene exhibit low surface energy due to the presence of neutral carbon-carbon bonding [22]. In contrast, chemically modified graphene, including reduced graphene oxide (r-GO) and nitrogen-doped graphene oxide (GO), exhibits higher surface energy attributed to the presence of surface functional groups and doped heteroatoms with varying electronegativity. 37 to 39 Chemically modified graphene, characterized by atomic-scale flatness and elevated surface energy, provides a strong foundational layer for subsequent nanoscale processing [23]. The enhanced thermal and chemical stability of chemically modified graphene facilitates direct nanoscale processing. Huang *et al*.. reported power conversion efficiencies (PCEs) of 0.21% and 0.85% utilizing C60 and C70, respectively, in a system comprising semiconducting single-walled carbon nanotubes (SWNTs) as the donor, fullerenes as the acceptor, and reduced graphene oxide (r-GO) as an energetically mediating component (Table 1: Report H). 40, 41 Ren and colleagues replicated the approach, utilizing r-GO and SWNTs in conjunction with [6,6]-phenyl C71-butyric acid methyl ester (PC71BM). Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,40-(N-(4-sec-butylphenyl)) diphenylamine)] (TFB) was employed as a hole-blocking layer, a choice that is relatively uncommon. A power conversion efficiency of 1.3% was attained with a composition of PC71BM (88-97%), semiconducting-SWNT (1-10%), and r-GO (~2%). Table 1: Report I. Bao and colleagues documented an effort to create all-carbon organic solar cells (OSCs), wherein the anode, active layer, and cathode were composed entirely of carbon materials. Initially, they optimized the active layer, which consisted of a bilayer film of solution-sorted semiconducting single-walled carbon nanotubes (SWNTs) serving as the light absorber and donor, with C60 functioning as the acceptor, positioned between indium tin oxide (ITO) and metal electrodes. Through the optimization of semiconducting SWNT dispersion and deposition conditions, as well as the C60 layer thickness, a power conversion efficiency (PCE) of 0.46% was achieved (Table 1: Report J) [24]. Subsequently, the ITO anode was substituted with r-GO layers, and the metallic cathode was replaced with an n-type SWNT film to realize an all-carbon organic solar cell (OSC). Nonetheless, PCEs were approximately 0.1%. In 2014, Hersam and colleagues reported a National Renewable Energy Laboratory-certified power conversion efficiency (PCE) of 2.5% and a maximum

PCE of 3.1% utilizing semiconducting single-walled carbon nanotubes (SWNTs) of various chirality as hole-transporting and light-harvesting materials (Table 1: Report K) [25]. In contrast to single-chirality semiconducting SWNTs, multi-chirality semiconducting SWNTs facilitate a broader absorption spectrum extending from the visible to the near-infrared region. Normal and inverted architectures were fabricated and subsequently compared. Inverted architecture demonstrated increased efficiency due to the penetration of ZnO nanowires (NWs) into the active layer (Figure 3).

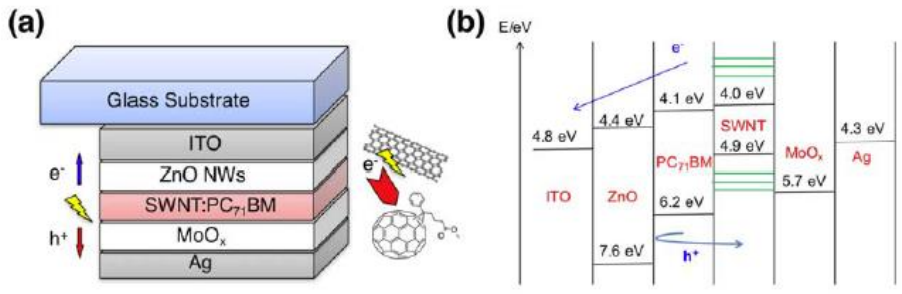

Figure 3. Illustration of a) an inverted solar cell where ZnO NW and SWNT:$PC_{71}BM$ were used and b) the energy level diagram.

1.3 CNT as a Charge Transporter and Additional Functions

Despite extensive research, the application of CNTs as charge transporters has not resulted in a significant improvement in power conversion efficiency without the incorporation of dopants and inorganic materials, such as quantum dots (QDs). Kim and colleagues tackled the inherent limitation caused by the recombination effect and enhanced power conversion efficiency (PCE) by over 30% via B- and N-doping (Table 1: Report L). 46 B and N doped CNTs served as efficient charge-selective transport materials, exhibiting no quenching effect. The low work function of nitrogen-doped carbon nanotubes (CNTs) corresponds effectively with the electron transport energy level, whereas the high work function of boron-doped CNTs aligns suitably with the hole transport level [26].

Kamat and colleagues investigated the interaction between single-walled carbon nanotubes (SWNTs) and light-harvesting cadmium sulfide (CdS). 47, 48 in 2005, Raffaelle and colleagues demonstrated the initial incorporation of quantum dots into single-walled carbon nanotube composites, and subsequently, colloidal quantum dot-decorated nitrogen-doped carbon nanotubes were developed to enhance synergistic charge separation and transport. Positively charged quantum dots can directly bind to nitrogen-doped sites of carbon nanotubes through electrostatic interactions [27].

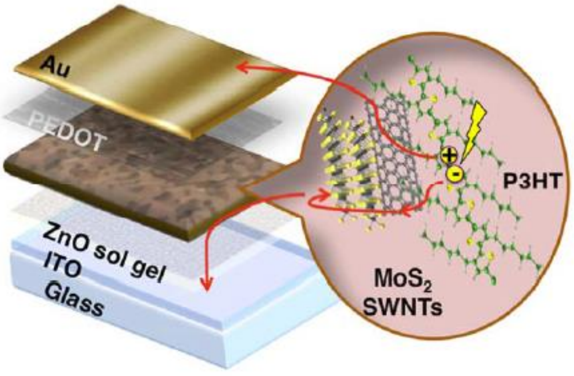

Figure 4. Illustration of MoS_2:SWNT:P3HT-based solar cells.

This optimal hybrid structure, devoid of an adhesive layer, exhibited a synergistic effect that facilitated effective separation of electrons and holes. Efficiency scores ranged from 4.7% to 6.11% (Table 1: Report M) when utilizing indene-C60 bisadduct (ICBA) as the electron acceptor, and increased to 7.5% to 8.6% with further advancements employing various organic photoactive materials (Table 1: Report N). This research indicates that using quantum dots (QDs) as acceptors and doped carbon nanotubes (CNTs) as effective charge transporters can enhance charge separation, transport, and recombination in single-walled carbon nanotube (SWNT)-based organic solar cells (OSCs). These OSCs typically experience issues related to charge carrier trapping and slow transport within their organic active layers, as well as energy-level mismatches at interfaces [28]. Alternative methods have been employed to utilize SWNTs in the active layer. The utilization of multilayered MoS2 as the electron acceptor in a bulk heterojunction with P3HT in inverted organic solar cells (OSCs) was reported, employing low-cost metallic/semiconducting single-walled carbon nanotubes (SWNTs) (Figure 4) [29]. MoS2 is an inorganic substance that is inherently immiscible with organic compounds. We successfully dispersed it in an organic matrix by utilizing the propensity of SWNTs to intercalate with P3HT via π–π interactions. The effective binding of MoS2 to SWNT bundles and its photovoltaic effect is evidenced by a power conversion efficiency of 0.46% (Table 1).

This study provides a concise review of the application of SWNTs as light harvesters or charge transporters within the photoactive layer of solar cells. Chirality, chemical doping, and solution dispersibility were essential factors in attaining high performance. Multiple strategies have been developed to enhance the applications of SWNTs, thereby broadening the potential of CNT technology in solar cell systems. This represents only a preliminary observation [30]. The uniform blending of the electron-donating conjugated polymer with the electron-accepting carbon nanotubes (CNT) presents significant challenges and is essential for optimizing photocurrent collection in CNT-based organic solar cell (OSC) devices. Research on the application of carbon nanotubes (CNTs) in the photoactive layer of organic solar cell (OSC) devices is still in its nascent phase, indicating potential for innovative approaches to optimize the beneficial properties of CNTs [31].

2.1 Single-Walled Carbon Nanotubes as a Transparent Electrode in Silicon Photovoltaic Cells

The elevated expense of silicon prompted researchers to seek alternate semiconductors that were feasible substitutes. Carbon nanotubes (CNTs) can function as both sites for photogeneration and as the charge transport layer. A semi-transparent CNT layer next to an n-type crystalline silicon substrate forms high-density p-n heterojunctions that facilitate charge separation, with electrons being removed via n-Si and holes through CNTs. The mechanism remains incompletely elucidated, however two predominant explanations exist. In the initial hypothesis, the CNT sheet functions as the p-type semiconductor material, whereas silicon mostly absorbs photons, akin to conventional silicon solar cells. Seventy-five While CNT films can absorb photons, this capability is constrained when the film is transparent to the incident light. Photons produce excitons, which are then dissociated into free charge carriers by the inherent potential between the p-type CNT and n-type Si. The second hypothesis posits that a Schottky junction is established when metallic carbon nanotubes (CNT) meet semiconductor silicon (Si), with the prevailing belief that a thin insulator, silicon dioxide (SiO2), is present, analogous to conventional silicon solar cells [31]. Excitons are generated when silicon absorbs photons and then diffuse into SiO2, which is established by the built-in potential of the Fermi level disparity, while minority carriers are conveyed by tunneling through the thin SiO2 layer [32]. Considering the chirality of carbon nanotubes may further complicate the process. A multitude of individual nanotubes exists within a device, each establishing a heterojunction with the n-type silicon. Due to their chirality, carbon nanotubes (CNTs) display either semiconducting or metallic properties, resulting in the formation of a p-n junction for the former and a Schottky junction for the latter.

The inaugural CNT-based silicon solar cell was documented by Jia *et al.*, utilizing double-walled CNTs. The CNTs executed many duties, including charge separation, charge transmission, and charge collecting eighty in the same year, Biris and colleagues demonstrated a power conversion efficiency (PCE) of 1.3% with single-walled carbon nanotubes (SWNT). The SWNT film was created using spray coating from a dimethylformamide solution. They conducted post-treatment tests with SOCl2 for the first time, resulting in an increase in mobility and carrier density above 60%, as indicated by Hall effect measurements. Subsequently, in the following year, Biris and colleagues documented a PCE of 4.5% eighty-two Once more, they employed the identical SOCl2 procedure, but put the as-synthesized SWNT onto silicon. Eighty-three Subsequent investigations of acid doping were undertaken in greater depth. They recognized SOCl2 as a p-type dopant that displaces the Fermi level of SWNTs beneath v1, hence enhancing mobility and carrier density. Eighty-four This leads to the suppression of the S11 transition in semiconducting SWNTs, whereas increased doping would also suppress the S22 transition, as seen by near-infrared absorption spectroscopy. Some researchers contend that following acid treatment, CNTs and silicon transitioned from functioning as a p-n junction to a Schottky junction, hence enhancing the metallic characteristics of the CNTs. The mechanism operating within the interface network transitioned from variable range hopping to tunneling. Levitsky and colleagues conducted a detailed analysis of the association between the suppression of transitions and CNT chirality. 85 The photocurrent, together with a high-resolution absorption spectra, was utilized to discover the S11 band at around 1100 nm, which corresponds to the (7,6) and (8,6) chiralities of SWNTs. They also found that metallic SWNTs serve as light absorbers in a Schottky junction, but their device exhibited a PCE of just 1.7%. In the same year, Rinzler and associates reported an impressive 10.9%. eighty-six the devices initially exhibited a power conversion efficiency (PCE) of 8.5%. However, by employing electrolyte junction control of gate potential, they regulated the Fermi level to enhance the interface dipole at the electronic junction. Jia *et al.,* enhanced the power conversion efficiency by treating single-walled carbon nanotubes with dilute nitric acid. Eighty-seven The HNO3 treatment significantly enhanced FF by reducing series resistance (RS) due to p-doping, which lowered the Fermi level of the MWNTs.

The carbon nanotubes facilitated various functions, including charge separation, charge transport, and charge collection. 80 In the same year, Biris and colleagues demonstrated a power conversion efficiency (PCE) of 1.3% utilizing single-walled carbon nanotubes (SWNT). 81 The SWNT film was formed through spray coating from a dimethylformamide suspension. The study introduced post-treatment with SOCl2 for the first time, resulting in an increase in mobility and carrier density exceeding 60%, as indicated by Hall effect measurements. In the subsequent year, Biris and colleagues reported a PCE of 4.5%. SOCl2 was identified as a p-type dopant that lowers the Fermi level of SWNTs below v1, thereby enhancing mobility and carrier density. 84 This leads to the suppression of the S11 transition in semiconducting SWNTs, and increased doping would also suppress the S22 transition, as observed through near-infrared absorption spectroscopy. Some researchers argue that following acid treatment, CNTs and silicon transition from functioning as a p-n junction to a Schottky junction, resulting in an increased metallic character of the CNTs. The mechanism operating in the interface network transitioned from variable range hopping to tunneling. Levitsky and colleagues conducted a detailed analysis of the correlation between the suppression of transitions and CNT chirality. 85 The photocurrent, in conjunction with a high-resolution absorption spectrum, facilitated the identification of the S11 band near 1100 nm, which corresponds to the (7,6) and (8,6) chiralities of SWNTs. It was also found that metallic SWNTs serve as light absorbers in a Schottky junction; however, the device exhibited a power conversion efficiency of merely 1.7%. In that year, Rinzler and colleagues reported a significant 10.9%. 86 the devices initially exhibited a power conversion efficiency (PCE) of 8.5%. However, through the implementation of electrolyte junction control of gate potential, the Fermi level was manipulated to enhance the interface dipole at the electronic junction. Jia *et al*., enhanced power conversion efficiency by treating single-walled carbon nanotubes with dilute nitric acid. 87 The treatment with HNO3 significantly enhanced the field factor (FF) by decreasing the series resistance (RS), attributed to p-doping that lowers the Fermi level of the single-walled carbon nanotubes (SWNTs).

CONCLUSION

The performance of photovoltaic devices is significantly influenced by the properties of carbon nanotubes (CNTs) in terms of conductivity and transparency. The sheet resistance and transparency of carbon nanotubes (CNTs) currently do not match those of indium tin oxide (ITO), which exhibits a sheet resistance of approximately 5 Ω sq-1 and a transparency exceeding 90%. It is essential to investigate more stable and effective dopants. The work will focus on The Fermi level is crucial for optimizing performance in organic solar cells (OSCs). Carbon nanotube (CNT) electrodes require an appropriate Fermi level to reduce energy barriers associated with charge transfer. Carbon materials typically exhibit a Fermi level ranging from 4.5 to 5 eV, which is comparable to the work function of an ITO film, measured at 4.6 to 4.8 eV. The Fermi level can be adjusted for different electrode applications. 128 to 131 Materials such as PEDOT are utilized to elevate the Fermi level for charge injection at the anode, while substances like Cs2CO3 serve to lower the Fermi level for electron collection at the cathode.

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