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Carbon Nanotube–Polymer Composites: Device Properties and Photovoltaic Applications

T. Hosseini and N. Kouklin

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Abstract

This chapter provides an in-depth coverage of recent advances in the areas of the development and characterization of electro-optically active, device-grade carbon nanotube (CNT)–polymer blends. These new organic–inorganic multifunctional nanocomposites share many advanced characteristics which make them ideally suited for industrial scale, high-throughput manufacturing of lightweight, flexible electronic, light switching and emitting as well as energy harvesting devices of extremely low cost. The fundamental aspects and the physical mechanisms controlling light–matter interaction, photo-conversion, and photo-generated charge-carrier transport in these nanotube–polymer composites as well as the influence of the processing conditions on the electronic properties and device-related performances are further reviewed and discussed.

Keywords: Carbon nanotube, Polymer, Composite, Exciton, Photovoltaic, Solar cell, Diode, Detector

1. Introduction

Blends of conjugated polymers and high performance carbon-based nanosemiconductors are an emerging class of easy-to-fabricate organic–inorganic nanocomposite materials with the potential to profoundly influence many electronic device market segments, including optoelectronics. Extraordinary characteristics of carbon nanotubes (CNTs) and prevalence of interfacial regions and the nanoscopic phase are a source of drastic change and gain in the optoelectrical response of the polymer matrix that typically falls outside of classical scaling behavior of conventional polymer composites. These novel nanocomposites and their based devices

can be fabricated using roll-to-roll techniques that makes them ideally suited to industrial scale, high-throughput manufacturing of lightweight, flexible electronic, light switching and emitting as well as energy harvesting devices at extremely low cost [1–6].

Conjugated polymers exhibit electronic and light emission properties that are similar to those of crystalline semiconductors and have been already implemented in organic optoelectronic devices such as organic light-emitting diodes (OLEDs), switches, and organic photovoltaic (OPV) cells [7]. Incorporating n-type dopants in the form of metallic CNTs into p-type polymer matrix has been shown to greatly enhance performance of such OPV cells by increasing the rates of non-radiative dissociation of excitons as well as charge-carrier collection efficiency. The formation of optimally loaded networks of electrically conductive nanotube network in turn entails detailed the consideration of the influence of the process parameters on the physical characteristics and interaction of the polymer with the nanotubes in a liquid phase. As the absorption coefficient of photosensitive polymers remains large, light is typically absorbed within a very thin layer, which drastically benefits the efficiency-to-cost ratio for these cells [8, 9]. The π -conjugation in polymers results in an energy separation of $\sim 1\text{--}3$ eV between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO). As a result, the light absorption–emission spectrum falls in the visible near-infrared (NIR) spectral range that complements that of single-walled carbon nanotubes (SWNTs), that is, the near IR–UV [2, 10–12]. An abrupt, type-II band alignment between polymer matrix and carbon phase is required and can be realized for many nanotube–polymer composites to achieve sufficiently fast interfacial charge separation and pronounced photovoltaic effect [13, 14].

Among different classes of nanomaterials including semiconductor quantum dots and fullerenes, SWNTs have been proven particularly suitable for uses in OPV, photodetector, and light-emitting diode applications based on conjugated polymers because of their large aspect ratio and remarkable optoelectronic properties including bandgap tunability, strong optical absorptivity, ballistic transport, solution-processability, and excellent chemical stability [15, 16]. Owing to their quasi-one-dimensional structure and improved transport characteristics, a class of SWNTs has been confirmed to exhibit many favorable device functionalities which make them attractive for application in a variety nano-electronic and mechanical devices and systems, among which are interconnects, rectifies, field-effect transistors, analyte, and light sensors. Compared with other nanostructures, SWNTs are also known to exhibit strong multi-range absorption in part associated with resonance-type interband electronic transitions (e.g., S_{11} , M_{11} , S_{22}) as well as free carrier and plasmonic excitations. Recent experiments further confirmed on the presence of a strong photoconduction response in the infrared (IR) which can in turn afford many new opportunities in engineering nanophotovoltaic and optoelectronic organic polymer–SWNT-based devices operating over multiple spectral ranges, including IR [17–19].

High conversion efficiencies of ~ 5 and 9% were extracted in case of polymer-based OPV cells featuring C_{60} molecules and CNTs, respectively. Yet, unlike to C_{60} , polymers incorporating aligned CNTs demonstrate much larger intrinsic charge mobility at lower percolation threshold/limit. At the same time, the increased photo-generated charge transport and in turn

collection efficiency facilitate the development of OPV cells featuring larger light absorption (thicker active device layer) and electrical power output, which translates into overall higher efficiency-to-cost ratio for these cells. Combining SWNTs with electrooptically active polymers thus provides an attractive route to creating a new generation of multifunctional device-grade organic–inorganic electronic materials for uses as sensors, OLEDs, PV cells, electromagnetic absorbers, and other electronic devices [20–22].

In this chapter, we review the progress while focusing on the fundamental aspects behind the light–matter interaction, photo-conversion, and photo-carrier generation as well charge-carrier transport in SWNT–polymer composites. The fabrication, structural–mechanical, and transport characteristics of various nanotubes–polymer-based composites are reviewed in Section 2. Key photo-physical processes that take place at the interface between SWNT and polymer molecules including energy transfer, exciton dissociation, charge transfer, and related effects are reviewed in Section 3. Section 4 discusses the electronic and optoelectronic devices built based on SWNT/polymer composites including OPV cells, light-emitting diodes, and IR sensors.

2. Carbon nanotubes/polymer composites: synthesis and properties

Recent studies involving fabrication and characterization of structural and underlying device characterizations have identified several processing-related challenges pertaining to producing polymer/nanotubes composites of high purity, structural anisotropy/alignment, and uniform dispersion [23, 24]. Because of the π -orbitals of the sp^2 -hybridized C atoms, CNTs show a tendency for strong intermolecular interaction and spontaneous aggregation (van der Waals interaction) into large diameter bundles that are not readily dispersible in organic solvents or polymer matrix. To address the dispersion-related and mixing challenges, the use of surfactants [25–31], performing shear mixing [32–34], sidewall chemical modification [35, 36], and in situ polymerization [37–41] were proposed. Among all these strategies, covalent chemical functionalization and introduction of defects into SWNT surfaces have been proven highly effective in achieving stable SWNT suspensions in polar solvents as discussed below.

2.1. Defect functionalization

In defect functionalization, nanotubes are treated by oxidative methods that also help remove metal particles and amorphous carbon deposits, that is, raise purity. The resultant SWNTs oftentimes gain in localized surface defect density most of which are in the form as carboxyl, that is, $-\text{COOH}$ attachments. Mawhinney et al. [42] studied surface defect site density of oxidatively treated SWNTs by probing the amounts of $\text{CO}_2(\text{g})$ and $\text{CO}(\text{g})$ released during heating to up to 1273 K. The results indicated that as much as $\sim 5\%$ of the carbon atoms in such SWNTs can be defect-associated. Acid–base titration method [43] yielded similar results, that is, 1–3% of acidic sites in purified SWNTs. The density of defective sites created at the surfaces by this method is viewed generally insufficient for good nanotubes dispersion in the polymer matrix. However, the strategy can be used for covalent attachment of organic groups by first

2.3. Covalent functionalization

Despite the fact that sp^2 -hybridized C atoms form a chemically stable backbone, a number of strategies were developed to covalently link chemical groups to CNTs [62–64]. In the case of covalent functionalization, the translational symmetry of nanotubes is disrupted by changing sp^2 carbon atoms to sp^3 carbon atoms that were reported to affect the electronic and transport properties of nanotubes [65, 66]. This route is highly effective in increasing solubility as well as dispersion of nanotubes in many organic solvents as well as polymers. Covalent functionalization can be accomplished either by the modification of surface-bound carboxyl groups on the nanotubes or by the direct elemental reaction with carbon atoms such as in the case of CH_x -modified nanotubes. Poly (ϵ -caprolactone) [67, 68], poly(L-lactide) [69, 70], poly(methyl methacrylate) [71–73], Polystyrene [74–76], poly(N-isopropyl acrylamide) [77–80], polyimide [81, 82], polyvinyl (acetate-co-vinyl alcohol) [83], have been used to covalently attach to CNTs.

From the standpoint of device application, non-covalent functionalization remains preferred over the covalent approach, as the latter has the propensity to induce strong structural damage [24, 84]. The dispersion of nanotubes in polymer matrices is one of the most critical bottlenecks in the preparation of CNTs/polymer composites. Additional strategies to enhance dispersion of nanotubes included melt mixing and in situ polymerization, whereas Ni et al. confirmed considerable improvement in the dispersion of multi-walled CNTs in poly(vinyl alcohol) (PVA) matrix through gum Arabic treatment [24].

3. Photo-physical properties of carbon nanotube–polymer composites

3.1. Energy transfer in carbon nanotube–polymer composites

Absorption of a photon by aromatic polymers leads to a formation of bound electron–hole pair known as exciton, which can dissociate radiatively by emitting a lower energy photon. The presence of semiconducting SWNTs has been shown to strongly affect the rate of radiative recombination by inducing the transfer of either holes or electrons to the nanotubes which depends on the electronic band alignment between SWNTs and polymer [85]. Alternatively, resonant energy transfer from polymers to SWNTs has been confirmed experimentally [86, 87]. In Umeyama et al. [86] study, a conjugated polymer, poly [(p-phenylene-1,2-vinylene)-co-(p-phenylene-1,1-vinylidene)] (coPPV), was synthesized and used to study the influence of SWNTs on the light emission characteristics of the former. UV–vis–NIR absorption and AFM measurements revealed that SWNTs were dispersed well in organic solvents likely via π – π interaction. The composite solution of coPPV–SWNTs exhibited a strong NIR emission originating from SWNT when the polymer was subject to a direct optical excitation with the light source operating at ~400–500 nm.

The efficiency and rate of the energy transfer from polymers to SWNTs have been shown to be strongly dependent on the polymer concentration/aggregation on SWNTs [22, 88]. Further studies point to the polymer π -conjugation chain that governs the energy transfer in the polymer–SWNT system to remain more extended compared with that of the pure polymer

system [85]. Massuyeau et al. [89] studied energy transfer between the polymer and nanotubes by examining steady state PL spectra of a series of composite films containing both metallic and semiconducting nanotubes. The results of these studies show that there is a substantial spectral overlap of PL and optical absorption of SWNTs, which favors the Förster energy transfer between polymer chains and CNTs.

3.2. Charge transfer in carbon nanotube–polymer composites

Combining CNTs with polymers offers an attractive route not only to mechanically reinforcing polymer films but also to enhancing polymers' charge transport properties and modifying electronic properties through a morphological modification or electronic coupling between the two [90]. The effect of nanotube doping has been systematically investigated by embedding nanotube powders in the emission, electron transport, and hole transport layers of OLEDs [91]. Such polymer/nanotube composites have been successfully exploited for various applications including OPV [92–95], OLEDs [96], and organic field-effect transistors [97, 98]. Among different transport models [99–104], percolation of the nanotube network within the polymer matrix has been suggested to play a primary role behind improved charge mobility of up to two orders of magnitude compared with that in the pristine polymer. This provides a technologically simple pathway to improving the performance of organic electronic and optoelectronic devices, while keeping their fabrication costs as low as possible [90].

The low dielectric constant of conjugated polymers results in large Coulomb interactions between charge carriers, increasing exciton binding energy and photo-response characteristics. The majority of OPV devices operate based on exciton dissociation at the interface formed by two dissimilar materials with a type-II band alignment that favors interfacial charge separation and formation of free polarons. If the rate of bound electron–hole pair separation is low, other, that is, radiative and non-radiative recombinations will prevail, which is a primary reason behind efficiency loss. Internal electric fields at the polymer–metal interfaces (interface dipoles) or dissociation centers, for instance, oxygen impurities that can act as electron traps (monopoles) promote fast exciton dissociation. As the electron affinity remains smaller for conjugated polymers [105], percolated CNTs act as high mobility electron extraction paths or excitonic antennas. Even at low doping levels, highly conductive pathways can be still established due to a large aspect ratio and propensity of SWNT to bundling. While photo-generated electrons will tend to transfer to SWNT, the photo-generated holes are to remain in the polymer matrix that helps to lower the rate of internal recombinations and to mitigate charge-carrier losses [13, 106].

The first solid evidence of the charge transfer between SWCNTs and conjugated polymers (MEH-PPV) was provided by Yang et al. [107] by performing photoinduced absorption spectroscopy. In their study, photoinduced charge transfer was deduced by observing a reduction of the emission from the polymer accompanied by an increase of the polaron peak in the MEH-PPV-SWCNT hybrids. Bindl et al. [108] examined exciton dissociation and charge transfer at s-SWCNT heterojunction formed with archetypical polymeric photovoltaic materials including fullerenes, poly(thiophene), and poly(phenylenevinylene) using an exciton dissociation-sensitive photo-capacitor measurement technique that is advantageously

insensitive to optically induced thermal photoconductive effects. It was found that fullerene and polythiophene derivatives induce exciton dissociation resulting in electron and hole transfer away from optically excited s-SWCNTs. Significantly weaker and almost no charge transfer was observed for large bandgap polymers largely due to insufficient energy band offsets.

In another study, Ham et al. [109] fabricated a planar nano-heterojunction comprising well-isolated millimeter-long SNWTs placed underneath a poly(3-hexylthiophene) (P3HT) layer. The resulting junctions displayed photovoltaic efficiencies per nanotube in the range of 3–4%, which exceeded those of polymer/nanotube bulk heterojunctions by almost two orders of magnitude. The increase was attributed to an absence of aggregates in case of the planar device geometry. It was shown that the polymer/nanotube interface itself can be responsible for the exciton dissociation with the best efficiency realized for ~60 nm thick P3HT layer.

Among different classes of nanomaterials, semiconducting CNTs remain the primary candidates to enhance the charge separation when interfaced with conjugated polymers. The difference in the behavior of semiconducting and metallic CNTs in polymer was studied theoretically by Kanai et al. [110] who employed a density functional theory. Case studies involving poly-3-hexylthiophene (P3HT) interfaced with semiconducting and metallic CNTs were carried out. In case of semiconducting nanotubes, the theory predicts a formation of type-II heterojunction, critical to photovoltaic applications. In contrast, in case of the metallic nanotubes, substantial charge redistribution occurred and the built-in-potential was quite small, whereas P3HT became electrostatically more attractive for electrons. These observations confirm that in case of mixed single-walled nanotubes, a majority of interfaces would be made by metallic components to compromise the device performance. Similar conclusions were drawn by Holt et al. [111] in his study of P3HT-polymer/SWNT blends containing varying ratios of metallic to semiconducting SWNTs.

4. Electronic and optoelectronic applications of carbon nanotube/polymer composites

4.1. Organic photovoltaic devices

OPV devices based on π -conjugated polymers have been suggested as low-cost alternatives to silicon-based solar cells [106, 112]. Unlike to energy conversion devices based on semiconductors, in organic solar cell devices, a donor/acceptor (D/A) interface is required to break free photo-generated excitons into free charges carries before they can be collected by the electrodes [113, 114]. The list of the requirements for the materials for application in bulk PV devices includes the following: (1) strong light absorption over the whole solar emission spectrum; (2) sufficient separation between HOMO and LUMO; (3) large electron and hole mobilities within the device active layer; and (4) low device fabrication cost [22, 115]. In addition to a detailed consideration of intrinsic electronic aspects of the constituent components, geometric aspects and chemical stability play equally important role. For example, the dimensions of active layer should not exceed the exciton diffusion length, reportedly on the order of ~10 nm [22, 113].

In CNTs/polymer photovoltaic devices, the dissociation of excitons can be accomplished through the formation of a staggered gap donor/acceptor, type-II heterojunction formed between the s-SWCNTs and the polymer in which the energy offsets at the hetero-interface exceed the exciton binding energy, E_B . Recent experimental and theoretical studies by Schuettfort [116] and Kanai [110], respectively, demonstrate that a type-II band alignment only exists for certain interfaces, such as between small diameter semiconducting SWNTs and P3HT. Even for such blends, energy transfer from the polymer to SWNTs remains one of the fastest de-excitation channels that compete with the charge transfer processes, with the former facilitated by larger surface area and electron affinity of the nanotubes vs. polymers [105, 117].

Kymakis et al. [118] examined both dark and photocurrent–voltage (J–V) characteristics of poly(3-octylthiophene) (P3OT)/SWNT composite photovoltaic cells as a function of SWNT concentration. An open-circuit voltage (V_{oc}) as high as 0.75 V was obtained for 1% doped SWNTs/ P3OT composite which served as a device active layer. An almost 500-fold increase in the photo-response was partly attributed to a 50-fold increase in the hole mobility due to a reduction in the density of the localized states in P3OT matrix, and in part due to enhanced exciton extraction at the polymer/nanotube junctions. Despite the improvement in the rate of the charge separation, the power conversion efficiency was only 0.04% under 100 mW/cm² illumination conditions. A poor dispersion of SWNT and the presence of a mixture of metallic and semiconducting tubes were believed the primary factors behind the low efficiency numbers. In 2011, the same group investigated the use of spin-coated SWNTs as a hole transport layer (HTL) in organic bulk heterojunction photovoltaic devices shown schematically in **Figure 2** to raise the conversion efficiency [119]. Varying thickness SWNT films were repetitively spin coated with dichloroethane and next evaluated as the HTL in P3HT and 1-(3-methoxy-carbonyl)-propyl-1-phenyl-(6,6)C61 (PCBM) photovoltaic devices. It was shown that insertion of ~12-nm-thick SWNT layer led to power conversion efficiencies as high as 3.0%, compared with 1.2 and 2.8% for the devices without and with the traditional PEDOT:PSS acting as the HTL. The improved efficiency was attributed to improved hole transport in the polymer matrix due to a higher degree of crystallinity provided with SWNT.

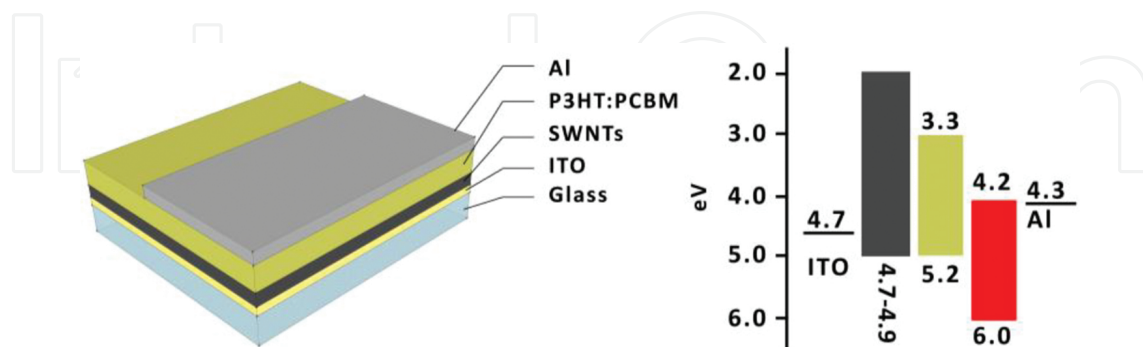


Figure 2. (a) Schematic drawings of the P3HT:PCBM photovoltaic cell with the SWNTs acting as the HTL. (b) Energy level diagrams of photovoltaic device components referenced to the vacuum level.

In another study, June et al. implemented homogeneously dispersed CNTs using alkyl-amide groups to chemically modify nanotubes to improve their dispersion in organic medium [16].

The resultant composites and their based OPV cells exhibited gain in their optical and electrical properties with the device efficiency approaching ~4.4%. The schematic of the fabricated solar cell is shown in **Figure 3**.

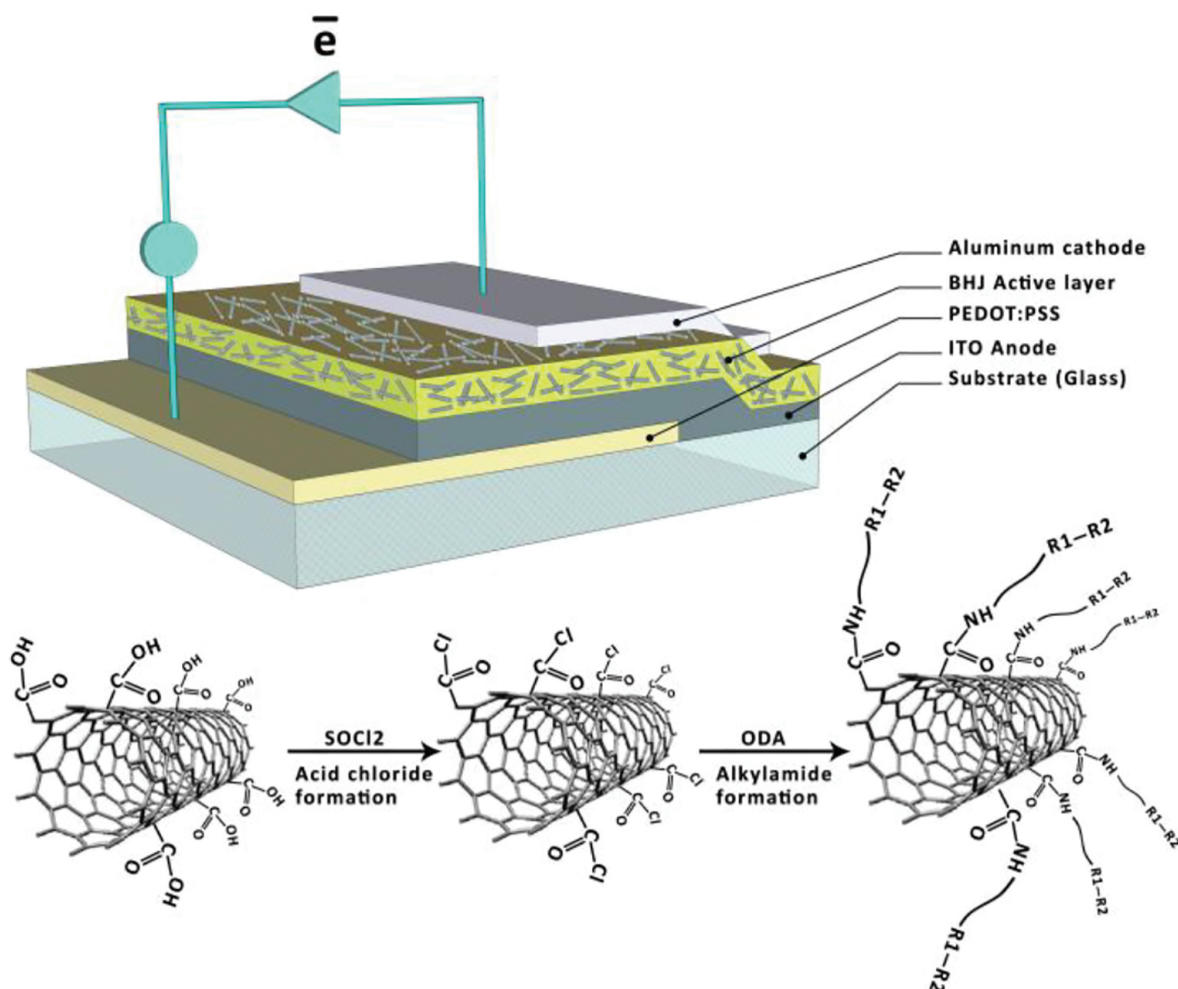


Figure 3. Schematics of the functionalization of nanotubes with the alkyl-amide group for a homogeneous dispersion in organic solvent and the PV devices fabricated in [16].

In most OPV cells that host nanotubes, the open-circuit voltage (V_{oc}) generally stayed below 1 V, another performance limiting factor. Rodolfo et al. [120] was able to raise V_{oc} by ~20% by inserting continuous polymer layer between the electrode and SWNTs, which helped address problems with electrical shorting and shunts by the metallic tubes.

Some prior studies pointed out that uncontrolled interactions at the CNT–polymer interface can not only reduce the ability of the tubes to transport charge but also interfere with the photo-physical processes, which act as a source of recombination centers for excitons (metallic tubes) and energy quenchers (polymer–s-SWCNT), or by electrically shorting the circuit (long tubes). From the standpoint of device engineering practices, a more rational design of the CNTs–polymer interface across different length scales, that is, nano to meso and careful consideration/control of intermolecular level interactions via dispersion will be required [107, 121, 122].

On this front, Arranz-Andres and Blau [122] investigated the influence of the nanotube dimensions (length and diameter) and concentration on the performance of a CNT-polymer device. They found that adding 5% of nanotubes by weight increased the power conversion efficiency (PCE) by three orders of magnitude compared with that of the native polymer. The incorporation of nanotubes into the P3HT matrix favorably affected the energy levels of the P3HT and the morphology of the active layer. They also found that the nanotubes can act as nucleation sites for P3HT chains, improving charge separation and electron transport.

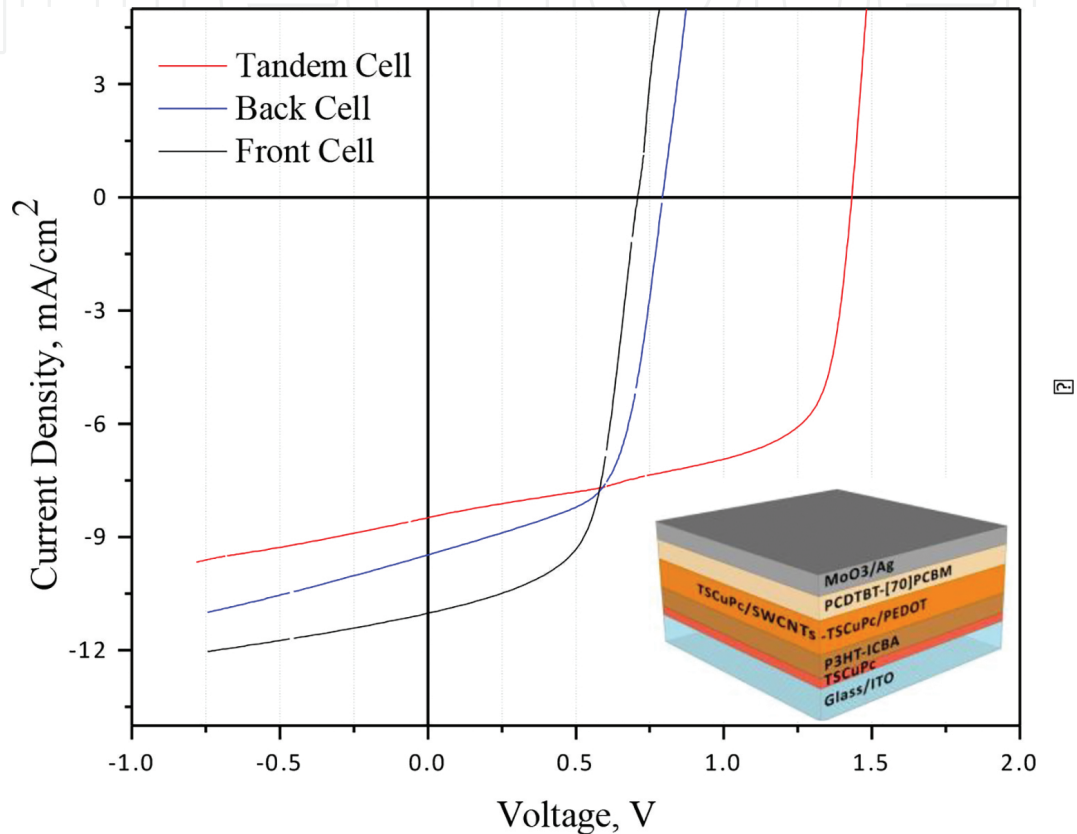


Figure 4. J-V characteristics of series-connected inverted tandem solar cell. Tandem cell curves (red), back cell (blue), front cell (black).

The three-component architectures based on nanotubes-fullerene-conjugated polymer composites were proposed to achieve better photovoltaic efficiencies. Li et al. [125] suggested using C_{60} as an electron acceptor and nanotubes for the photo-generated charge transport. Two types of chemically functionalized nanotubes were tested: carboxylated and octadecylamine functionalized multi-walled nanotubes, in short c-MWNT and o-MWNT. All three photovoltaic parameters, namely short-circuit current density, open-circuit voltage, and fill factor of the P3HT:c-MWNT/ C_{60} -based cells showed improvements over those of the P3HT:o-MWNT/ C_{60} cell as a result of a faster electron transfer from C_{60} to the nanotube backbone. Derbal-Habak et al. [94] reported organic PV cells with power conversion efficiency of 3.6% by incorporating functionalized SWNTs within P3HT:PCBM layer that helped improve both the current density J_{sc} and open-circuit voltage, V_{oc} attributed to a partial crystallization of the

RR-P3HT as revealed by XRD studies. Nismy [126] probed the optical and electronic response of the composite devices comprising donor polymer and localized MWNTs also featuring triple heterojunction architecture/scheme. A significant improvement in photoluminescence quenching was observed for the devices with nanotubes embedded into the polymer matrix, with the former facilitating the formation of the trap states. The triple scheme is generally confirmed to yield a lower dark current and hence a significantly improved photovoltaic performance with the PCE approaching ~3.8%.

Relatively high PCEs of ~7.4% were demonstrated by introducing copper-phthalocyanine derivative (TSCuPc)/SWNT layer into the series-connected inverted tandem devices featuring front P3HT–ICBA and back PCBM–PCDTBT active layers, **Figure 4**.

As summarized in **Table 1**, repeated results from studies on CNTs/polymer OPV devices reveal that the performance of nanotubes incorporated OPV cells is dependent on several factors such as the device architecture, treatment or functionalization method of nanotubes, type of CNTs, concentration of nanotubes as well as thickness of the nanotube-incorporated active layer.

Type of CNT	Type of polymer	Preparation method	PCE (%)	FF (%)	References
SWNT	P3HT:PCBM	Spin coating of surfactant-free CNTs as the hole transport layer	3.04	50.7	[119]
SWNT	P3HT:PCBM	Homogenous dispersion by alkyl-amide functionalization of CNT	3.2–4.4	38–52	[16]
SWNT 5 wt%	P3HT	Dispersion in chloroform	52.3	20.3	[122]
SWNT	RR-P3HT: PCBM	Solution mixing	3.66	52.2	[94]
DWNT (double-walled CNT)	P3HT	Dispersion in chloroform	47.2	20.3	[122]
c-MWNT/C ₆₀	P3HT	Dispersion of carboxylated nanotubes in o-dichlorobenzene (ODCB) solutions	0.8	44	[125]
MWCNT	P3HT	Dispersion in chloroform	26.8	22	[122]
O-MWCNTs	P3HT, PCBM	Solution mixing	3.8	70	[126]

Table 1. Summary of organic photovoltaic devices reviewed in this chapter

To overcome problems with poor performance of bi-layer devices that stem from short exciton diffusion length in polymers, poor exciton dissociation and absence of a percolated network required for improved photo-generated charge transport, the devices incorporating polymer-fullerene-based donor–acceptor (D–A) material have been reconsidered. Comparative studies

on bulk heterojunction devices vs. those with a nanotube-incorporated active layer formed by sequential deposition show that the latter architecture is prone to a higher recombination of carriers due to the introduction of trap states associated with the nanotubes. Photo-generated excitons are also quenched at the D/A material interface due to these additional energy levels and render lower J_{sc} values. On the other hand, the heterojunction scheme yields lower dark currents and better photovoltaic performance confirming a very critical role of the heterojunction in devices with organic/hybrid architectures. For the nanotube/polymer-based OPV cells, the nanotube type is also to influence the performance of such devices. While there is no clear link between the number of walls or the diameter of the nanotubes and the performance of the OPV device, the semiconducting nanotubes were concluded to form a needed, type-II heterojunction. In contrast, in case of metallic nanotubes, a substantial charge redistribution is to take place at the interface. As a result, the built-in-potential is quite small and unlikely to contribute significantly to the subsequent charge separation at this interface, leading to an inefficient PV device. The photovoltaic characteristics of the PV cells are also to depend on the concentration of nanotubes. In particular, the incorporation of low concentrations of nanotubes in the photoactive layer leads to an increase of the current density J_{sc} . The functional groups as well as the preparation methodology are among the other factors that were found to influence the performance of OPV cells.

4.2. Organic light-emitting diodes (OLED)

OLEDs are indispensable to flexible light displays because of their excellent properties: They are lightweight and feature low power consumption, wide angle of view, fast response, low operational voltage, and excellent mechanical flexibility [127, 128]. Light-emitting polymers demonstrate excellent quantum efficiencies and can be solution processed to build electroluminescent devices of very low cost. OLEDs are generally considered as “dual-injected” devices as holes and electrons are injected from the anode and cathode, respectively, into active molecular/macromolecular medium, where they form excitons that recombine radiatively [128, 129].

Recent progress in OLEDs stems not only from the advancement of the polymer science but also from achieving better control over the charge transport in the electroluminescent layers and doping of the emissive materials [22]. A proper layer sequence in OLEDs ensures that the injected charges are properly balanced within the emissive layer to achieve high external efficiency. SWNTs introduced into conducting polymers lower the charge injection barrier formed at the electrode–organic interface and hence favorably affect the device performance [130].

One of the first studies to combine SWNT with conjugated polymer-based OLEDs was attempted by Curran et al. [131]. The observed increase in the quantum yield was attributed to intermolecular π – π stacking interactions that take place between the polymer and nanotubes. A polymer stiffening is another factor that can lead to an increase in the luminescence output. Moreover, when SWNTs are added the strength of the polymer–polymer interaction becomes weaker, which is a source of self-quenching effects. The concentration of SWNTs of 1% (by weight) is considered optimal/sufficient for the polymer strands to experience inter-

action with the nanotubes. Excess concentrations of SWNTs lead to a drop in the luminescence. Woo et al. [132] prepared double-emitting OLEDs (DE-OLEDs) based on SWNTs-PmPV. A low bias I-Vs obtained on the devices made from the composites were quadratic, while in the devices with pure PmPV, the dependence was significantly more nonlinear: $I \sim V^5$; the result was explained by the presence of structural and chemical defects in the PmPV composite that favors continuous trap-limited charge transport.

In a recent study, Gwinner et al. [134] investigated the influence of small amounts of semi-conducting SWNTs on characteristics of ambipolar light-emitting field-effect transistors (LEFETs) comprising polyfluorenes such as poly(9,9-di-n-octylfluorene-alt-benzothiadiazole) (F8BT) and poly(9,9-dioctylfluorene) (F8)-conjugated polymers, **Figure 5**. Incorporating SWNTs within a semiconducting layer at the concentrations below the percolation limit significantly augments both hole and electron injections, even for a large bandgap semiconductor such as F8, without invoking a significant luminescence quenching. In general, owing to lower contact resistance and threshold voltage, larger ambipolar currents and in turn higher output/light emissions can be realized.

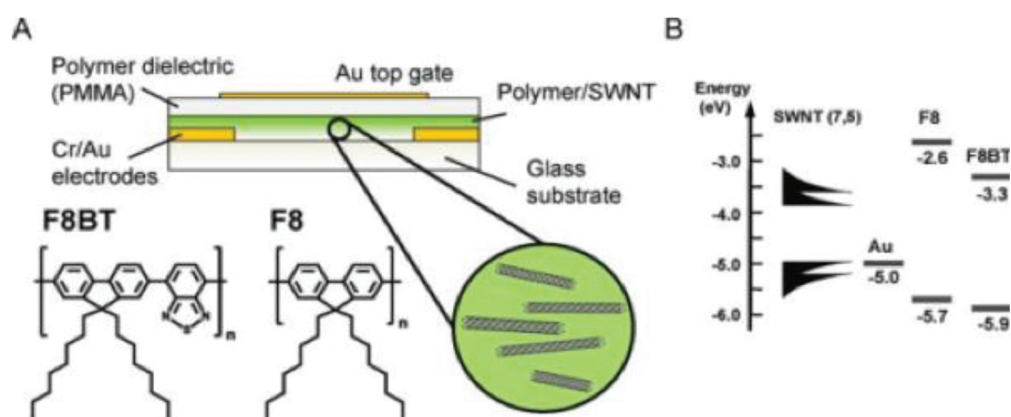


Figure 5. (A) Schematic illustration of bottom contact/top gate polymer field-effect transistor with carbon nanotubes dispersed in the semiconducting polymers F8BT and F8. (B) Energy level diagram of a semiconducting SWNT with (7, 5) chirality, gold (injecting electrode), and HOMO/LUMO levels of both F8 and F8BT. Reprinted from [134] with permission. Copyright © 2011 American Chemical Society.

Divya et al. [134] investigated the use of a diketone ligand, 4,4,5,5,5-pentafluoro-3-hydroxy-1-(phenanthren-3-yl)pent-2-en-1-one (Hpfppd), containing a polyfluorinated alkyl group, by covalently immobilizing it onto the multi-walled CNT host via carboxylic acid functionalization pathway. The resultant nanocomposite displayed intense red emissions with an overall quantum yield of 27% under a wide excitation range from UV to visible (~330–460 nm), making it prime candidate for application in OLEDs.

Indium tin oxide (ITO) features a high transmittance at a low sheet resistance [127] and is ubiquitously employed as an OLED anode but not without drawbacks. ITO is brittle and can suffer from cracks that lead to electrical shorting; it can serve as a source of oxygen that diffuses into emissive layers, while it has insufficiently high work function of ~4.7 eV [129, 135].

On this front, SWNT sheets have been considered as viable alternative and were studied for possible use as anodes in OLEDs, **Figure 6** [136]. Some recent prototypes exhibited brightness of $\sim 2800 \text{ cd m}^{-2}$ that was comparable to that of OLED featuring ITO anodes.

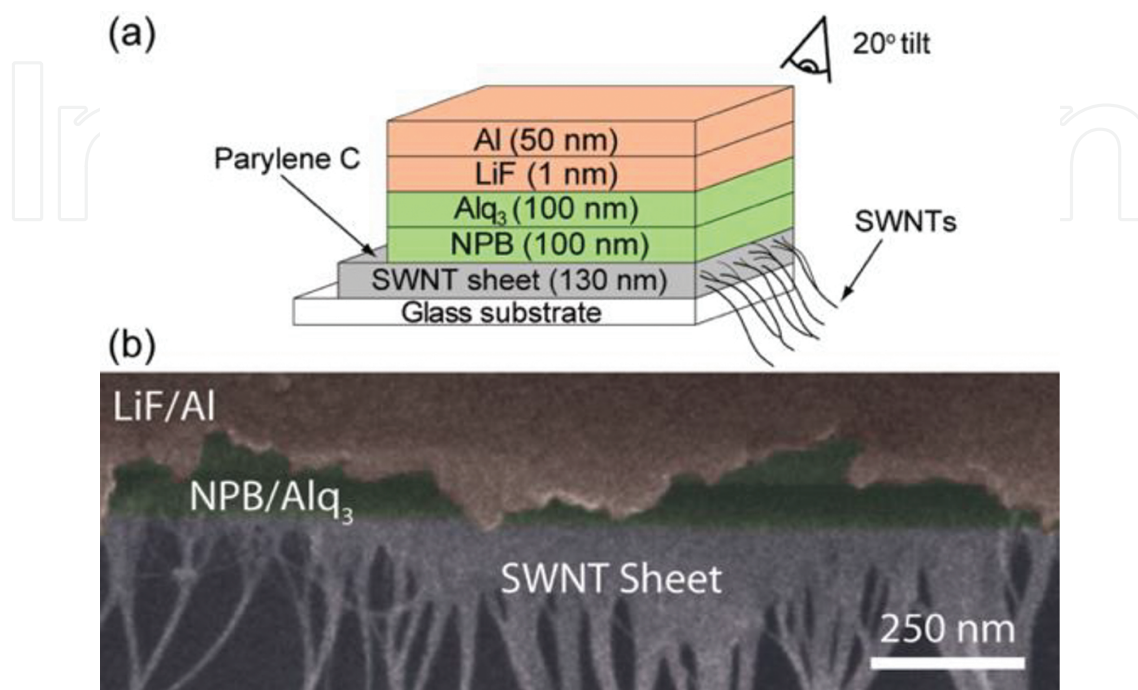


Figure 6. (a) Schematic of the SWNT OLED device and (b) corresponding cross-sectional scanning electron microscopy image at a broken edge taken at a 20° angle from the surface normal. Reprinted from [136] with permission. Copyright © 2006 American Institute of Physics.

Zhang et al. [137] showed arc-discharge nanotubes were overwhelmingly better electrodes than HiPCO-nanotube-based films in all of the critical aspects, including surface roughness, sheet resistance, and transparency. Arc-discharge nanotube films that were PEDOT passivated showed high surface smoothness and featured sheet resistance of $\sim 160 \text{ } \Omega/\text{sq}$ at 87% transparency.

Parekh et al. [138] was able to improve the conductivity of transparent SWNT thin films by treating the samples with nitric acid and thionyl chloride. Geng et al. [139] was able to achieve a fourfold sheet conductance improvement by exposing SWNT films produced by spray technique to a nitric acid with the treated samples demonstrating sheet resistance of ~ 40 and $70 \text{ } \Omega/\text{sq}$, at 70 and 80% transmittance, respectively. To break interdependence of the sheet conductance and the transparency, a magnetic field was applied during drop-casting of SWNT-polymer films onto ITO-coated glass and ITO-coated PET substrates [140]. This led to sample de-wetting and enhancement in the electrical conductivity of the films. For a functionalized SWNT-PEDOT:PSS film formed on an ITO-coated PET substrate, a sheet resistance of $90 \text{ } \Omega/\text{sq}$ at 88% transmittance was obtained. SWNT-PEDOT:PSS composite devices formed on PET substrate were proposed as a way to combat the problem, with the films featuring a sheet resistance of $80 \text{ } \Omega/\text{sq}$, and having a transmittance of 75% at $\sim 550 \text{ nm}$. The ratio of DC to optical

conductivity was higher for composites with mass fractions of 5560 wt% than for nanotubes only films. For ~80-nm-thick composite filled with 60 wt% arc discharge nanotubes, this conductivity ratio was maximized at $\sigma_{DC}/\sigma_{OP} = 1$, with the transmittance (at 550 nm) and sheet resistance of 75 and 80 Ω/sq , respectively. These composites also have excellent electromechanical stability, with <1% resistance change over 130 bend cycles.

As outlined above, CNTs/polymer composites could be incorporated into conducting polymers as the buffer layer, or in the form of plain sheets as flexible anode electrode in OLEDs. The characteristics exhibited by the CNTs/polymer composite as the transport layer in OLEDs have been observed to change with the polymer system as influenced by the nature of the polymer–nanotube interactions. Additionally, nanotube sheets can serve as transparent electrodes in OLEDs which make them a viable alternative to the conventional ITO electrodes.

4.3. Infrared sensors

“*Infra*” from Latin means “*below*”; thus, IR refers to a spectral range beyond the red boundary of the visible electromagnetic spectrum, which corresponds approximately to ~0.8 μm . Since all objects emit IR radiation, the effect is known as a black body radiation, seeing in the dark or through obscured conditions, by detecting the IR energy emitted by objects is possible. IR imaging has therefore become a cornerstone technology for many military and civilian applications including night vision, target acquisition, surveillance, and thermal photovoltaic devices. Biomedical imaging and light-activated therapeutics represent another critical area that particularly benefits from high tissue transparency to IR light. Despite a recent progress in the field of IR sensing and imaging, high cost, requirement for cryogenic cooling, and spectrally limited sensitivity still remain the main disadvantages of this technology today.

Two primary methods of IR detection exist: energy and photon detection. Energy detectors respond to temperature changes generated from incident IR radiation through changes in material properties. Energy detectors, the well-known examples of which are bolometers, pyroelectric, and thermopile detectors, are normally low cost and primarily used in single-detector applications; such applications include fire and motion detection systems as well as automatic light switches and remote thermometers. In contrast to energy detectors, light interacts directly with the semiconductors in photon detectors to generate electrical carriers. More specifically, incident light with energy greater than or equal to the energy gap of the semiconductor drives the semiconductor out of equilibrium by generating excess majority electrical carriers. This translates into a change in the net resistance of the detector. The well-established examples of photon detector materials are lead sulfide (PbS), lead selenide (PbSe). Since these detectors do not function by changing temperature, they respond much faster than energy detectors and in principle can be sensitive to a single photon, if used, for instance, in conjunction with the emerging class of single electron devices. Both, increased sensitivity and reduced response time provided with the use of small bandgap semiconductor materials, have recently led to the development of advanced and very sophisticated IR detection systems, which are of high technological relevance today.

The higher the temperature of an object, the larger the amount of thermal radiation it emits, while its peak intensity also shifts to a shorter wavelength. The demonstrated strong spectral

dependence of thermal radiation on the temperature, also known as a Wien's law, necessitates the use of materials with optimized sensitivity at multiple wavelengths for two primary reasons: (1) to increase sensitivity and (2) to enable highly selective military/civilian target identification and acquisition. Until recently, the problem was addressed through simultaneous use of several materials with peak sensitivity corresponding to different wavelengths. As fabrication and processing change dramatically from one material system to another, engineering of wavelength-specific and ultra-sensitive IR detectors currently remains uneconomical.

A recent progress in the field of nanotechnologies, and in particular, in the area of non-lithographic fabrication of multi-functional nanomaterials such as quantum wells, wires, dots and CNTs opens new opportunities for advancing IR sensing technology beyond today's confines. Unlike semiconductor alloys, the effective energy bandgap of nanomaterials and particularly CNTs can be easily tailored by simply changing their size which enables engineering of future IR-devices with expected spectral range of operation: from ~ 15 to ~ 0.6 μm (i.e., from ~ 0.1 to 2eV). Furthermore, as electron scattering is suppressed in materials featuring one-dimensional electronic configurations, nanotube-based IR photo-detectors are expected to demonstrate orders of magnitude improved sensitivity at room temperature as compared with the detectors operating on thin films or quantum wells. This property could potentially mitigate the requirement for cryogenic cooling currently implemented in most IR photon-type sensing devices.

For IR-detection application, aligning of many nanotubes would be highly critical from two points of view: to increase packing density of nanotubes and thus device sensitivity and to realize polarization sensitive IR optical devices. In contrast to conventional semiconductors, conjugated polymers provide dramatic benefits for engineering active optical nano-electronic and photonic devices; this includes reduced processing cost, excellent physical flexibility, and large area coverage. Until now, application of polymers in electronic devices was primarily limited to a visible range of electromagnetic spectrum [142, 143]. While stability of most polymers represents a barrier to their use as UV sensors, extending their use in the IR range becomes possible by implementing CNTs for both light absorption and free carrier generation. The exciton dissociation rate can be increased by introducing heterojunctions or applying external electric fields. The former can be realized by incorporating p-type nanotubes into n-type polymer matrix, such as PPy (pyridine-2,5-diyl) conjugated polymer, which is also known to exhibit relatively high resistance to oxidation.

Composites of CNTs/polymer feature relatively high absorption in a wide spectral range of ~ 0.2 – 20 μm and an emissivity coefficient close to unity while. Moreover, such composites are resistive to hard radiation damages and can work in high magnetic fields [144]. Unlike MWNTs and graphene which possesses featureless visible/NIR absorption, semiconducting SWNTs in particular exhibit strong and discrete absorption in the visible/NIR region owing to first optically active interband transition (S_{11}) with its energy scaling inversely proportional to the nanotube diameter. Lu et al. [148] reported a very large photocurrent in the device comprising semiconducting single-walled carbon nanotube (s-SWCNT)/polymer with type-II interface,

Figure 7. The detector featured significantly enhanced NIR detectivity of $\sim 10^8$ cm \cdot Hz $^{1/2}$ /W, which is comparable to that of the many conventional uncooled IR sensors, **Figure 8.**

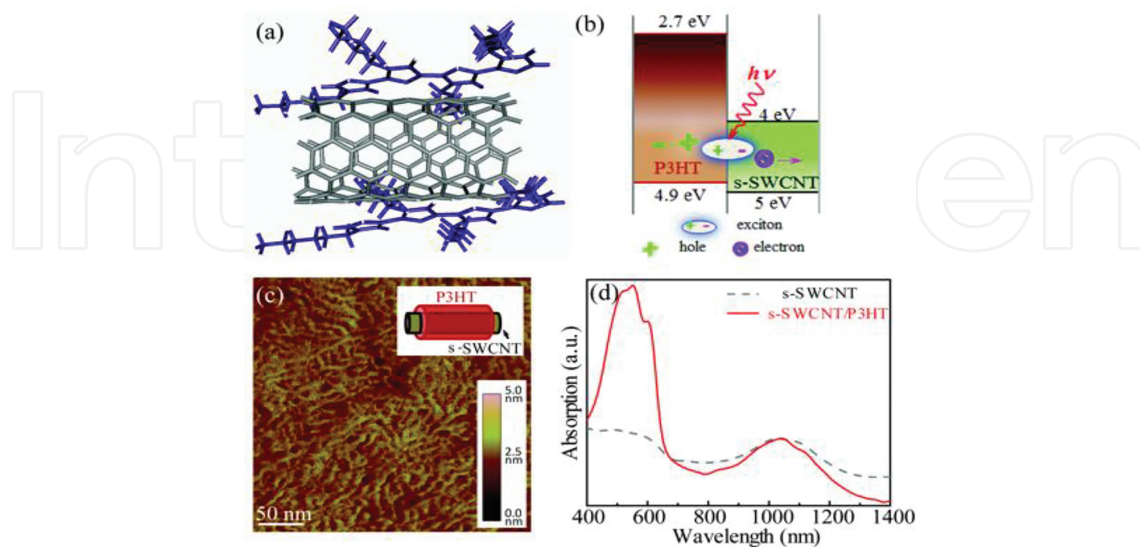


Figure 7. (a) Diagram of s-SWCNT/P3HT nanohybrid. (b) Band structure of the s-SWCNT/P3HT type-II heterojunction. (c) AFM image of s-SWCNT/P3HT. (d) Optical absorbance spectra of s-SWCNT and s-SWCNT/P3HT. Reprinted from [148] with permission. Copyright © 2012 American Chemical Society.

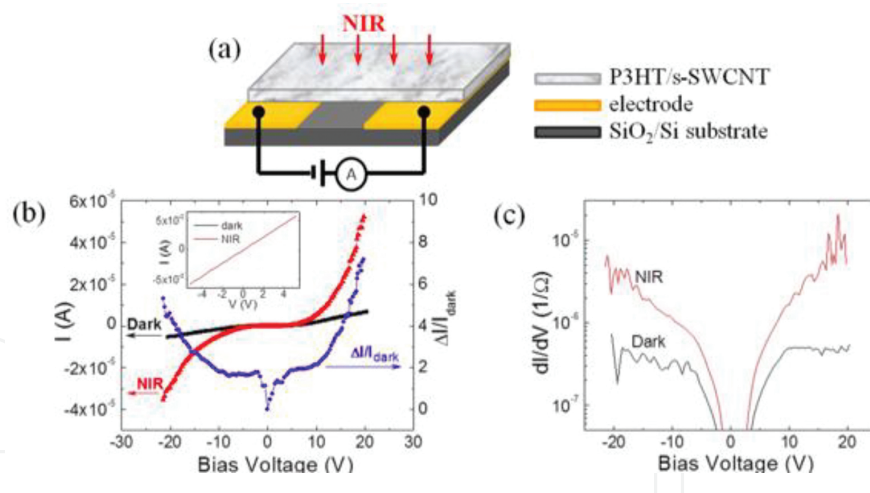


Figure 8. (a) Brief diagram of the electrical setup for IR detections. (b) Representative V–I curves of s-SWCNT/P3HT in dark and under NIR illumination of 2 mW/mm 2 . The inset shows the voltage-biased V–I curves of s-SWCNT control sample. (c) Differential conductance dI/dV of s-SWCNT/P3HT: The data were calculated from (b). Reprinted from [148] with permission. Copyright © 2012 American Chemical Society.

Among other composites, polyaniline–CNTs composite thin film sensors showed an IR photosensitivity enhancement of more than two orders of magnitude under ambient conditions [144]. The attained enhancement in the sensitivity (bolometric effect) is attributed to a higher heat generation by CNTs and large temperature dependence of the resistance of

polyaniline. In another study, Aliev [143] built an uncooled bolometric sensor based on SWNTs/polymer composite with voltage responsivity of ~ 150 V/W. Another, all-printed NIR sensor was engineered by Gohier et al. [146] by depositing multi-walled CNTs on a flexible polyimide substrate; the sensor showed ultra-high responsivity of ~ 1.2 kV/W. A strong dependence of the device response on the surrounding atmosphere was though noted and attributed to desorption of water molecules that negatively affected the photosensitivity. Glamazda et al. [147] reported on a strong bolometric response in SWNT–polymer composite featuring higher degree of internal alignment. A better alignment dramatically increased the temperature sensitivity of the resistance explained within the framework of fluctuation-induced tunneling theory. A spectrally flat mid-IR responsivity of 500 V W⁻¹ was observed and is among the highest reported for nanotube-based bolometers.

Author details

T. Hosseini and N. Kouklin*

*Address all correspondence to: nkouklin@uwm.edu

Departments of Electrical Engineering Computer Science, University of Wisconsin-Milwaukee, Milwaukee, USA

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