

Journal of Material Sciences & Engineering

Open Access

Recent Developments in Quantum Dots/CNT Co-Sensitized Organic Solar Cells

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Abstract

Polymer solar cells (PSCs) are emerging alternative candidates to the standard silicone technology for green and renewable energy generation owing to their flexibility and solution processability. Bulk heterojunction (BHJ) organic solar cells (OSCs) based on conjugated semiconducting polymers as donor (D) and fullerene derivatives as acceptor (A) offer large D/A interfacial area, which overcomes the short exciton diffusion length. Although, recent advances in narrow band gap semiconducting polymers have led to the improvement in power conversion efficiency of organic photovoltaics (OPVs) beyond 10%, inefficient charge separation and low carrier mobility as well as negligible photon harvesting in near-infrared (NIR) and/or infrared (IR) region of the solar spectrum have still remained as bottle neck for ultimate performance of OPVs. Most PSCs only absorb the UV-visible part of the solar spectrum, leading to the low light harvesting efficiency. Hence, solution processed photoactive materials comprising nanostructured semiconducting inorganic quantum dots (QDs) as sensitizer have attracted great attention to improve energy conversion efficiency of the OPVs. This is attributed to the outstanding optoelectronic properties of QDs such as band gap tunability, potential NIR photons harvesting and multi exciton generation (MEG). However, the main shortcoming of inorganic QDs based OSCs is randomly hopping charge transport among discrete QD particles, which can be tackled through hybridization with one dimensional (1D) electrically conductive nanostructured materials such as carbon nanotube (CNT). By this way, CNT particles would behave as support for anchoring the light harvesting semiconductor QDs, leading to the enhancement of the exciton dissociation and charge transport towards the corresponding electrodes. Recently, manufacturing PSCs co-sensitized by QD loaded CNT has been shown as a promising direction to maximize performance of the device. This article reviews the recent developments in enhancement of OPVs" performance by utilization of high efficient light harvesting QDs and/or their hybrid with 1D CNTs.

Keywords: Organic solar cell; Quantum dot; Carbon nanotube; Ternary solar cell; Hybrid solar cell

Introduction

In the past few years, there has been great growth in interest towards organic photoactive (OPV) technology as an alternative to expensive silicon based PV technologies, owing to its low cost of materials, inexpensive large area device production through e.g. ink jet or rollto-roll printing techniques, environmental friendliness, high flexibility, and freedom of form [1,2]. Compared to the conventional silicone based solar cells, polymeric PVs give a wider selection of the photoactive materials to engineer the cell photon harvesting and boost the energy conversion efficiency [3-5]. In organic solar cells, the photoactive layer normally comprises p-doped (electron donor) and n-doped semiconducting materials (electron acceptor) that are blended to desired morphology [6-8]. To maximize charge generation, a large area interface between these two phases is required, which can be achieved by controlling and optimizing the photoactive micromorphology. The developed final microstructure of the coated photoactive layer is controlled by various parameters such as blend composition, rate of solvent evaporation, solution viscosity and rate of crystallization [8-11]. In spite of aforementioned merits of OPVs, they still suffer from lack of acceptable efficiencies [12]. Improvement of OSCs efficiency by various means such as synthesis of new materials, micro morphological optimization and applying advanced strategies such as multi-junction structures, ternary near-IR sensitization and hybrid organic-inorganic systems have been the scope of many researches during last decades [13-21]. The latter strategy will be the focus of this review.

Colloidal semiconductor nanocrystals or quantum dots have great potential for PV applications due to their high absorption coefficient, tunable band gap which is size dependent, multiple exciton generation with single photon absorption, tunable energy levels, slow exciton relaxation and low cost [13-16]. Despite such conceptual merits, QD based organic solar cells have demonstrated poor device performances as a result of randomly hopping charge transport among discrete QD particles. Besides, QDs phase separate from their organic matrix, thus developing a bicontinuous network is difficult.

Improvement in charge carrier separation and transport can be achieved via hybridization of QDs with one dimensional electrically conductive nanostructured materials such as CNT. In this way, CNT particles would behave as support for anchoring the light harvesting semiconductor QDs, leading to the enhancement of the exciton dissociation and charge transport towards the corresponding electrodes [22]. Unique optical and electronic properties of CNT as well as its wide electrochemical stability window, and high surface area render CNT as an excellent moiety in OSCs. As a consequence of such synergistic effect, BHJ polymer solar cells containing CNT/QD nanohybrid have attracted great attentions.

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Received May 29, 2017; Accepted June 12, 2017; Published June 22, 2017

Citation: Soltani R, Katbab AA, and Ameri T (2017) Recent Developments in Quantum Dots/CNT Co-Sensitized Organic Solar Cells. J Material Sci Eng 6: 347. doi: 10.4172/2169-0022.1000347

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To enhance charge generation and transport, many attempts have been reported on the QD loaded CNT sensitized polymeric solar cells (PSCs) [23-25]. High efficiency of these nanohybrid based PSCs is attributed to the enhanced charge separation at the QD-polymer and/ or QD-CNT interfaces, and increased charge transportation within the photoactive layer due to the high intrinsic charge carrier mobility through the interconnected CNT clusters. The use of CNT in this type of device is particularly attractive and effective approach due to the extremely high surface area ~1600 m²/gr which offers a tremendous opportunity for exciton dissociation. Moreover, at low concentration, percolated conductive pathways are formed by the carbon nanotube providing the means for high carrier mobility and efficient charge transport. Hence CNT can serve as an efficient support for anchoring the light harvesting semiconductor QDs. Unlike the well-studied transport issues in QD-CNT based hybrid solar cells, [26] the impact of QD-CNT nanostructures on the morphology of the photoactive layer is less investigated.

Although there are a lot of valuable reviews in the field of organic solar cells [27-30] ternary solar cells [30,31] and hybrid solar cells [32,33] but there exists a lack of deep investigation in hybrid QD based solar cells. In the present review, recent developments in enhancing energy conversion efficiency of polymer solar cells by incorporation of inorganic nanostructured semiconductor sensitizers such as QDs, carbon nanotubes and their hybrid into the photoactive layer is overviewed. The first part discusses the core concept of organic solar cell operation including device physics and architectures, materials used in OSCs and challenges of organic photovoltaics. Then, we present and discuss the reported ternary hybrid solar cells sensitized by quantum dots. Finally hybrid solar cells comprised of carbon nanotubes and carbon nanotubes co-sensitized by quantum dots are addressed in details in the last section.

Overview on Fundamentals and Processing of Organic Solar Cells

Operational principles

In polymer based photovoltaic devices the incident photons are absorbed by the donor materials existing in the photoactive layer, and then bounded electron-hole pairs named exciton are generated which are then splitted into free charges at the interface of donor and the acceptor phases where enough energy for charge separation exists. Finally, the separated electrons and holes are transported to their respective electrodes which need continuous conducting path ways. To enhance the overall power conversion, the efficiency of each individual step should be increased [34]. Schematic diagram of the photocurrent generation mechanism in a so called bulk heterojunction (BHJ) OPV is illustrated in Figure 1.

The most important parameter which needs to be evaluated for quantifying the efficiency of a polymer solar cell upon light illumination is power conversion efficiency (PCE) which represents the efficiency of the cell under illumination and is calculated according to the equation (1). In OPVs, the current flow is zero under dark condition. When a high voltage (higher than open circuit voltage) is applied, the contacts start to inject charge carriers to develop current at forward bias (Figure 2).

Light illumination leads to the creation of additional photocurrent and flow across the junction which has opposite direction compared with the dark current.

$$PCE = \frac{J_{sc}V_{oc}}{P_{in}} \times FF = \frac{Maximum power produced per surface unit}{Total incident light power per surface unit}$$
(1)

 $J_{\rm sc}, V_{\rm oc}, {\rm FF}$ and ${\rm P_{in}}$ denote short circuit current density, open circuit voltage; fill factor and incident light energy flux, respectively. ${\rm P_{in}}$ is standardized at 100 mW cm⁻² under AM 1.5 spectrum, where the simulated spectral intensity matches the sun's intensity on earth's surface at an angle of 48.21° [35]. From the PCE expression, it can be understood that power conversion efficiency of the cell can be maximized by the enhancement of $J_{\rm sc}, V_{\rm oc}$ and FF. $J_{\rm sc}$ can be measured through the equation (2):

$$J_{SC} = \frac{q}{\overline{hc}} \int_{\lambda_{\min}}^{\lambda_{\max}} EQE P_{in}(\lambda) \lambda \, d\lambda \tag{2}$$

Where q is the elementary charge, h and C represent the Planck constant and speed of light respectively, and EQE denotes the external quantum efficiency, which is the ratio of collected charge carriers (electrons) per incident photon at a specific wavelength expressed in nanometers. This value takes into account all the physical phenomena involved during the photovoltaic process. EQE is calculated according to the equation (3).

$$EQE = \eta_{abs} \eta_{diff} \eta_{cc} \eta_{tr} \eta_{cc}$$
(3)

Where η_{abs} , η_{diff} , η_{tc} , η_{tr} , η_{cc} are the efficiencies of photon absorption,



Figure 1: Main steps of photoconversion in a bulk heterojunction solar cell, (a) from a kinetic point of view; and (b) depicted in form of an energy diagram. (i) Generation of singlet exciton by photoabsorption in the electron donor; (ii) exciton diffusion to donor/acceptor interface; (iii) Exciton dissociation by electron transfer from donor to the acceptor; (iv) separation of polaron pair due to material disorder and electric field; (v) charge transport to the electrodes and (vi) charge extraction [2].

exciton diffusion, electron hole separation, carrier transport and charge collection, respectively. The last four parameters are included in one parameter named internal quantum efficiency IQE, with EQE= η_{abs} × IQE. Regardless of the absorption efficiency of the materials, IQE is a relevant representative of cell quality and provides a qualitative assessment of the photoactive potential to separate excitons into free charges and collect them at electrodes.

As can be observed from equation (2) and (3), there are different ways to enhance J_{sc} including harvesting more photons or by shifting the absorption edge of the polymer from the UV-Vis range to the red part of the solar spectrum [36] through introducing a second photo absorber with complementary absorption profile [17].

The V_{oc} is determined by the energy difference between the highest occupied molecular orbital (HOMO) level of the electron donors and the lowest unoccupied molecular orbital (LUMO) level of the electron acceptors and is empirically described by the equation (4). However, the V_{oc} also depends on the morphology of the active layer, as well as on buffer layers at the electrodes and on the electrode work function [37]. It is also reported that V_{oc} is linearly correlates to the charge transfer state energy [38,39].

$$eV_{OC} = (E_{HOMO}^{donor} - E_{IIIMO}^{acceptor}) - 0.3$$
(4)

The fill factor (FF) is characterized according to the equation (5), which is the ratio of current and voltage at the maximum power point to short circuit current and open circuit voltage.

$$FF = \frac{J_{mpp}V_{mpp}}{J_{sc}V_{oc}}$$
(5)

 $\rm P_{mpp}$ is the point that the rectangle defined by $\rm J_{mpp}$ and $\rm V_{mpp}$ is largest in a J-V curve (Figure 2).

The FF depends on various parameters such as morphology, thickness of the active layer and choice of electrodes. Additionally the fill factor is directly influenced by the serial resistance (R_s) of the device. Consequently FF can be maximized by decreasing R_s as a result of minimizing contact and bulk resistances [40].

Common materials

Organic materials with π -conjugated structure are suitable candidates for the fabrication of organic solar cell [26]. These materials are categorized into two groups including electron donors and electron

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acceptors. Recently, developing novel polymers and small molecules as donor and fullerene derivatives as acceptor and non-fullerene acceptors have attracted great attention in order to achieve highly efficient organic solar cell.

Most of the semiconducting polymers are hole conductor and among them, polymers like 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), Poly[2-methoxy-5-(2ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), Poly[2,7-(9,9dioctylfluorene)-alt-4,7-bis(thiophen-2-yl)benzo-2,1,3-thiadiazole] (PFO-DBT), Poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'di-2-thienyl-2',1',3'-benzothiadiazole)], Poly[[9-(1-octylnonyl)-9Hcarbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7diyl-2,5-thiophenediyl] (PCDTBT), pDPP5T-2 a thiophene derivative of diketopyrrolopyrrole (DPP), Poly-(3-hexylthiophene-2,5-diyl) (P3HT), and Poly([2,6'-4,8-di(5-ethylhexylthienyl)benzo[1,2-b;3,3-b] dithiophene]{3-fluoro-2[(2-ethylhexyl)carbonyl]thieno[3,4-b] thiophenediyl}) (PTB7-Th) are the most used and investigated ones. However, those with low band gap and broad absorption spectrum are preferred as a result of their potential to harvest more photons of the solar spectrum. Therefore, great endeavors have been devoted to synthesis of different conjugated polymers with low band gap during last decade [36].

For electron acceptors some polymers such as poly-[2-methoxy-5,2-ethylhexyloxy]-1,4-(1-cy-anovinylene)-phenylene (CN-MEH-PPV), Poly(9,9-dioctylfluorene-alt-benzothiadiazole) (PFO-DBT), Poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] (F8BT), and mostly small molecules like $\mathrm{C}_{_{60}}$ and soluble derivatives of C_{60} and C_{70} , namely $PC_{60}BM$ [17] and $PC_{70}BM$ [41], bis-adduct fullerene derivatives such as Bis-PC70 BM [42], and ICBA [14], and graphene nano sheets [43-45] are vastly studied and used. Fullerenes are considered as the most appropriate electron acceptor due to the ultrafast photo induced charge transfer between electron donors and acceptors, high mobility and better phase segregation to create three dimensional (3D) networks for the transportation of electrons to the electrode [46]. However, fullerene acceptors suffer from synthetic inflexibility, poor absorption in the solar spectrum range, and an inherent tendency to undergo post-fabrication crystallization, resulting in device instability. Consequently non-fullerene acceptors such as perylene diimide monomers, dimers and polymers [47,48], and indacenodithieno thiophene core small molecules (e.g. ITIC [49] and





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IDTBR [50]) are going to become an alternative for fullerene acceptors in OPVs.

Recently, Y. Cao et al. [51] have reported the PCEs of 10.6% for the PTB7-Th:PC₇₀BM (0.35:0.65) single junction solar cells with a Jsc=17.43 mA/cm², Voc=0.825 V and FF=73.78%. Chemical structures of the commonly used materials in OPVs are illustrated in Figure 3.

Device architectures

Besides the choice of donor and acceptor materials, device architecture and arrangement of the photoactive layer components has been shown to play crucial role in energy conversion efficiency of OPV device and its performance [52].

Figure 4 illustrates different types of photoactive layer architecture of OPVs including bilayers, bulk heterojunction and ordered BHJs. Bilayer polymer solar cell were investigated for the first time in 1993 [53] by evaporating a thin layer of C_{60} on top of spin coated Poly [2-methoxy-5-(2-ethylhexyloxy)-1,4phenylenevinylene] (MEHPPV). However, a low overall efficiency was exhibited by this cell due to the low interfacial area between the donor and acceptor phases for this type of morphology.

Bulk heterojunction morphology has been found as the most promising architecture for OPV devices, as it can provide large donor-acceptor interfacial area and conducting channels for both electron and hole carrier. Hence, large enhancement of the J_{sc} parameter was achieved in BHJ devices.

The interfacial area between donor and acceptor plays crucial role in enhancing the exciton dissociation in BHJ based organic cells. The smaller domains, the larger interfacial area is provided between the donor and acceptor phases, and consequently effective exciton dissociation. In organic solar cells the diffusion length of about 10 nm is required before electron and hole are recombined. Hence, to increase the probability of exciton dissociation, the presence of domains with few nanometer sizes are necessary. In other words, the travelling distance from the points where excitons are generated to the D/A interface needs to be of the order of less than 10 nm. On the other hand, a continuous channel of the donor and acceptor components would guaranty the facilitated transport of free holes and electrons toward the cathode and anode electrodes, respectively. However, to achieve such an optimized and ordered BHJ structure, as illustrated in Figure 4c, either nanoimprinting processes or directed self-assembly of block copolymers are essential. These strategies require either specialized instrumentation or more expensive synthesis and processing methods, making them difficult to be implemented in the production of corresponding solar cells [52].

Challenges of organic photovoltaics

In spite of such a huge growth in organic photovoltaics, they still suffer from various issues like losses from the bulk and surface recombination, reduced $V_{\rm oc}$ by insufficient dissociation processes and limitation of the charge carrier mobility and, thus, poor charge extraction at the electrodes.



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Morphology of the active layer is another challenge of OPVs. It needs to be taken into account that optimization of the morphology of the active layer is crucial to achieve the desired efficiency. An ideal morphology should be able to maximize interfacial interaction between the photoactive layer components in order to obtain higher exciton dissociation and also provide domain size within the order of the exciton diffusion length, crystalline domains to facilitate charge mobility and finally create percolated pathways to the electrodes [52,54].

However, the most important limiting factor is the limited absorption window of the conjugated polymers used in photoactive layer construction. Only a small portion of the solar spectrum can be harvested and consequently a lot of energy is lost. Various efforts have been made to tackle the limited absorption through utilizing optical spacers, arranging modules in V-form as well as using Low-bandgap copolymers with enhanced absorption in the red part of the spectrum, though they often lack from lower charge generation or absorb only little in the blue part of the solar spectrum. Another approach is made by using tandem solar cells in which polymers with different band gaps and absorption spectra are involved. However, they are based on a complicated multilayer stack with serious technical issues such as processing of a robust intermediated layer, the coupling of appropriate absorbers as well as optimization of the active layer thickness. Incorporation of materials having complementary absorption characteristics in a single junction device is an elegant, alternative strategy for harvesting more photons, the so called ternary solar cells. Therefore photon harvesting is enhanced in a simple single-junction.

Ternary Solar Cells

The main goal of developing ternary solar cells was to extend the absorption spectra of the large bandgap polymers to cover the full range of the sun's irradiation spectrum. Unlike tandem solar cells, in ternary systems the sensitizer is merely incorporated into the host active layer which simplifies the device fabrication as a single junction solar cell. As a consequence, fabrication of ternary solar cells becomes possible with lower costs, which is an important issue for industrial applications.

Although the used sensitizers in ternary blend systems are generally the donor components, forming D:D:A ternary systems, the acceptor components may be also introduced as sensitizer forming D:A:A ternary systems (Figure 5). Various sensitizers based on low band gap polymers [55-63], small molecules [64-66], dyes [67-69] and nanoparticles [13-21] are employed in the structure of the photoactive layer in combination with donor material which is usually consists of a large bandgap polymer and fullerene derivative as acceptor. Recently, the record PCEs over 12% have been reported for the PBDB-T:IT-M: BisPC₇₀BM (1:1:0.2) ternary solar cells with a Jsc=17.3 mA/cm², Voc=0.95 V and FF=74% [42], which demonstrate the potential of ternary sensitization concept for OPVs' upscaling.

In an ideal photoactive layer the sensitizer not only broadens the absorption width but can also facilitate the exciton dissociation and provide excellent charge transporting properties [70]. Application of nanoparticles in the structure of OPVs' photoactive layer either as a sensitizer or electron accepting component has led to the development of new class of ternary systems named hybrid solar cells.

Among various nanoparticles, colloidal semiconductor nanocrystals or quantum dots (QDs) have shown promising applicability in solution-processed transistors, solar cells, and other optoelectronic devices due to their high absorption coefficient, tunable band gap, multiple exciton generation with single photon absorption, tunable energy levels, slow exciton relaxation and low cost [13-17].

Hybrid QD Based Solar Cells

Introduction to quantum dots

In recent years, significant attention have been given to the

development of quantum dot photo sensitized solar cells because of outstanding photo electronic characteristics of QDs specially their band gap tunability through size variation, and consequently manipulation of the optical and electronic properties of corresponding OPVs. Moreover, non-sensitized organic solar cells can only absorb the UV-Vis part of the solar spectrum, whereas incorporation of QDs into the organic photo active layer enhances the light harvesting efficiency and charge carrier concentration, owing to the potential of the QDs to absorb the near IR photons.

If the particle size of an inorganic crystalline solid stays in the order of nanometer, an interesting optical and electronic behavior can be exhibited. Semiconductors with all three dimensions within the range of 1-10 nm are referred to as "quantum dots" and their electrons exhibit quantum mechanical effects. In bulk semiconductors, electrons are distributed in energy levels very close to each other so that to be considered as continuum, and deals with two bands namely valence and conduction bands which are separated by energy band gap. The band gap is constant and characteristic of a specific material. Excitation of semiconductors with energy higher than their band gap results in separation of electron hole pair in the range of Bohr radius $(r_{\rm Br})$. For typical semiconductors, $r_{\rm Br}$ is in the range of 1-10 nm. Thus for QDs with the size range lower than r_{Br} , physical dimensions of the particle confines the excitons and the created excitons behave in a manner similar to the particles in a box problem. Consequently, the quantum effects such as quantization of energy levels can be displayed in principle [71,72]. Unlike bulk semiconductors which have constant and unique energy levels, the band gap of QDs and their absorption and emission spectra could be altered due to the quantum confinement effect [73]. Generally, the smaller QD dimensions, the larger would be the band gap [4]. Moreover, presence of quantum dots with different sizes in a cell permits to enhance the final efficiency of solar cells as a consequence of widening the absorption spectrum.

Furthermore, multiple exciton generation (MEG) by the absorption of a single photon, slow exciton relaxation, and low cost are distinct characteristics of QDs. MEG leads to the formation of more than one electron-hole pair through the absorption of one photon. Difference between the photon energy and the band gap of the absorbing components results in excess kinetic energy and generation of hot carriers. In all kinds of solar cells except quantum dot solar cells (QDSCs), this excess energy gives rise to thermalization and energy losses. However, in QDSCs, hot carriers are the route of production more than one electron-hole pair through impact ionization (Figure 6) [74]. When QDs are excited with energy higher than their band gap

not only excitons are created, but also can transfer their excess kinetic energy to other absorbing phases, leading to the formation of more electron-hole pairs, which results in increasing the internal quantum efficiency (IQE) greater than 100%. The multiple exciton generation may yield improved efficiencies in photovoltaic devices [33]. Till now, MEG has been reported for various synthesized quantum dots, including PbS, PbSe, PbTe, CdS, CdSe, InAs, InP and Si [75].

Synthesis of quantum dots and deposition techniques

There are two general approaches to synthesize quantum dots, including bottom up and top down. The former is based on the reaction between molecular or ionic precursors in solution phase and is more familiar to chemists [76-78]. However, the latter method which is more familiar to engineers includes carving of bulk semiconductor lithographically or electrochemically into particles with sizes in the range of 1-10 nm [4]. QDs could either be incorporated into the photoactive layers alone, or in combination with other nanomaterials such as TiO₂, ZnO, CNT, etc. Consequently, the method of QD deposition on the surface of the desired substrate is very important. Between various examined approaches in-situ fabrication and also attachment of pre synthesized colloidal QDs, named ex-situ fabrication, are more employed for the production of QDs synthesized photoactive layers, as illustrated in Figure 7. The former is the most accepted technique for QDs preparation due to its less difficulty and low cost. Chemical bath deposition (CBD) [33] and successive ionic layer adsorption and reaction (SILAR) [79] are two well known insitu deposition techniques. These methods are based on the reaction between reactant precursors in solution that react on the substrate. The growth of crystallites is controlled by the time of reaction or number of cycles of the SILAR process. Nevertheless, in these techniques the precise control of the particle size distribution is difficult.

Direct adsorption of pre-synthesized QDs could be carried out through electrophoretic deposition (EPD) which is carried out by applying a DC electric field between two electrodes immersed in a QD suspension. However, tendency of the QDs to aggregate in solution would lead to the uneven and poly-disperse film coverage by the QD aggregates. A majority of the solid-state QD films are prepared by the drop casting or spin coating method. In these methods, a known amount of the colloidal QD suspension is added onto the desired surface, and the film is dried in a controlled way. Another popular exsitu deposition method of QDs is the linker-assisted attachment of QD particles to the oxide surface. This method allows selective attachment of pre-synthesized QDs to an oxide surfaces using a bi-functional linker molecule. The linker molecule must be carefully selected to interact



ISSN: 2169-0022

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positively with the QDs" surface and modify surface defects [80].

Tuning the quantum dots through ligand exchange

Another important parameter in determining the quantum dot properties, besides its size, is its ligand which is a layer of organic surfactant molecules. These monolayers are usually long-chained ligands deposited on the surface of NPs to prevent the particles from agglomeration and enhance their miscibility in the respective solvent. Consequently organic ligands act as stabilizers which assure NP"s dispersibility by van der Waals forces [81]. Commonly used organic ligands during QDs synthesis process are oleic acid (OA) and trioctyl-phosphine oxide (TOPO) since they provide the desired growth conditions as homogeneous nucleation and narrow size distribution; furthermore they passivate dangling bonds which act as trap states. However, for photovoltaic applications, these ligands are not suitable since they are electrically insulating and provide a huge distance between donor and acceptor. Thus, they hinder the charge and/or energy transfer and prevent the decent charge transport.

Circumventing the disadvantages of long-chained ligands can be carried out through replacing the long capping ligands with shorter ones. The most widely used ligands are pyridine, thiols, amines, acids and phosphine oxides [82-84]. Pyridine based ligands show good electron transfer from polymer to the nanoparticle, while it can only partly remove the long-chain ligands due to its weak affinity to the nanoparticle. Unlike pyridines, thiols show strong affinity to the nanoparticle; however, are toxic, harmful to the environment and show only poor stability due to oxidation. The native ligands are completely removed by amines, as tri-butyl-amine or butyl-amine also show the ability to remove the native ligands and belong to the group of short ligands. Acids are appreciated as non-toxic and environmentally friendly materials which form a salt during ligand exchange, removable by centrifugation [85,86]. The inherently high sensitivity of aforementioned ligands to oxygen and moisture could impart electronic instability in the whole colloidal quantum dot solid. Recently, the use of halide components, such as iodide, during the QDs synthesis has been shown to passivate surface traps [87,88] resulting in n-type CQD solids [89]. This partial halide shell provides a very good passivation of the CQD surface resulting in CQD solids with excellent air stability. The effectiveness of such treatment was demonstrated with the fabrication of ambient-stable QD based solar cells [90,91].

In general ligand exchange can be realized via two approaches including in situ (in colloidal phase during synthesis) and post synthetic (in solid phase after the BHJ layer deposition) ligand exchange methods. In the first method, the NPs in solution are exposed to an excess of the desired ligands, followed by an antisolvent which removes the displaced pristine compounds. However, in the case of post synthetic replacement, the ligand is infiltrated into the solid BHJ film, which as well is followed by a rinse of an antisolvent [92].

It is worth knowing that the choice of ligand drastically influences different parameters such as film morphology, charge separation, electron mobility and charge transport, energy levels of the nanoparticle relative to the vacuum level, trap density and absorption spectrum of the polymer [92-97].

Hybrid QD based solar cells

Enhancing the PCE of polymer solar cells have been challenged during the last few years by incorporating nanocrystal quantum dots with high light harvesting potential into the solution processable polymer PVs, by which J_{sc} is significantly increased as the light absorption spectra is extended beyond the visible range. Three major quantum dot based solar cell configurations including QD assemblies, QD sensitized solar cells and QDs dispersed in organic semiconductor/ polymer matrices are presented in Figure 8.

The principle for the energy conversion by QD sensitized polymer solar cells is similar to BHJs. In another words, light is absorbed by the photoactive layer which leads to the formation of excitons and free charge carrier generation at the interface of both semiconductor constituents. Various polymer-QD hybrid solar cells have been fabricated using semiconducting polymers like MEH-PPV [98], P3HT [99], PTB7 [100], PTB7-Th [101] and poly[2,6-(4,4-bis-(2-ethyhexyl)-4Hcyclopenta [2,1-b;3,4-b0]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCDTBT) [102,103], and semiconductor nanocrystals such as CdSe,



CuInS₂, CdS, InP [100], ZnO [101], CdSeTe [17] and PbSe [104] or PbS [98]. Photovoltaic characteristics of various QD sensitized polymeric solar cells have been briefly presented in Table 1. Dual characteristic of QDs as electron donor and/or electron acceptor in combination with various polymers is also other merits of these devices. Most importantly, these organic-inorganic hybrid devices, based on solution processable materials, have` the potential of construction on the flexible substrates with low production cost at large scale by employing roll-to-roll printing techniques.

Although fullerene derivatives exhibit to be efficient in transporting electrons, they do not show any absorption features within the visible range of the solar spectrum. In contrary, QDs demonstrate high absorption coefficients as well as good electron conductivity, suggesting a good substitution for fullerene. They can also being used in combination with fullerene to improve solar cell efficiency. In 2013 Park et al. [105] utilized CdSe nanoparticles as sensitizer for the P3HT: PCBM host system. They studied the effect of ligand exchange from pristine long chain oleic acid to the ring-shaped pyridine on photophysics and photovoltaic properties of hybrid solar cells. The overall device performance was best for ternary P3HT:PCBM:CdSe ternary cells after CdSe ligand exchange, showing a PCE of 2.96% compared to 2.85% for OA capped nanoparticles in ternary application and 2.74% for the binary P3HT:PCBM reference. Jeong et al. [101] fabricated hybrid ternary solar cells consisting of PTB7-Th, PC71BM, and ZnO NP. When only 1wt% ZnO NP was added to the binary BHJ PTB7-Th:PC₇₁BM layer, J_{SC} and FF were noticeably improved, and V_{OC} was kept constant. As a result, the PCE of ternary hybrid solar cells increased from 9.13 for the reference device to 9.54% for the sample comprising 1wt% ZnO NPs. The enhanced performance was due to the improved charge transport, as supported by the trend of dark J-V curves and series resistances, which could be made by the better chain stacking of PTB7-Th components in the presence of small amount (1 wt%) of ZnO NP. Han et al. [100] added 5 wt% InP QDs into the PTB7:PC71 BM host matrix and reported a maximum PCE of 8.4% for the ternary device due to the increase in $\boldsymbol{J}_{\rm SC}$ and FF by the synergy effect of InP QDs and the used Poly [(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) interlayer. In 2016 our research group fabricated hybrid solar cells based on pDPP5T-2 electron donating polymer, $PC_{61}BM$ and cadmium selenide telluride $(CdSe_{X}Te_{1-X})$ QDs and evaluated the photovoltaic performance and optoelectronic properties of the prepared devices as a function of QDs loading. The power conversion efficiency of the fabricated hybrid solar cells was improved up to 5.11% for the device containing 4 wt% of $CdSe_{X}Te_{1-X}$ QDs which found to be mainly due to the enhancement in short circuit current density resulted from the enlarged light harvesting potential of the photoactive layer [17].

In spite of all explained advantages of QD sensitized organic solar cells, they suffer from important shortcomings including inefficient transportation of photo induced charge carriers as a result of random hopping, insulating characteristics of most of ligand materials used to modify the surface of QDs for their stabilization in solutions, and also QD tendency to phase separate from the organic matrix [14].

Many researchers have put efforts to enhance the charge carrier splitting and transportation by hybridization of QDs with one dimensional nanostructured materials such as ZnO nanowires [15] or conductive carbon nanotubes [13,14,16,22]. Such ideal 1D nanomaterial's can be benefited since they have potential to serve as support for light harvesting QDs through surface absorption. They also can behave as acceptor to promote exciton dissociation or form a path for transportation of charges towards their respective electrodes. These would lead to the increase of photo conversion efficiency of QD based hybrid solar cells.

Hybrid solar cells based on carbon nanotubes

Carbon nanotubes are allotropes of carbon with a cylindrical structure. They consist of graphitic sheets rolled up into a cylindrical shape. The most widely used CNTs are either single-walled (SWNT) or multi-walled (MWNT) structures. SWNT structure can be thought as a single graphite layer wrapped into a cylinder. The cylinder can be rolled up in different ways, represented by a couple of indices (n,m), called the chiral vector ($C_h=na_1+ma_2$). Tubes having n=m are called "armchair" and those with m=0 "zigzag". All the others are "chiral" nanotubes as indicated in Figure 9. MWNTs consist of concentric tubes of graphite. The interlayer distance is close to the distance between graphene layers

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Electron donor Electron acceptor		OD (Lineard)	V _{oc} J _{sc}		FF	PCE	Reference	
	QD (Ligand)	[V]	[mA/cm ²]	[%]	[%]			
pDPP5T-2 PCBM	-	0.58	13.78	61.56	4.88	[17]		
	CdSeXTe1-X (p-methylthiophenol)	0.57	14.73	60.99	5.11			
	DODM	-	0.78	17.66	66.3	9.13	[400]	
PIB/-IN	PCBM	ZnO (octanoic acid)	0.78	18.15	67.4	9.54	[100]	
	DODM	-	0.575	13.2	60	4.9	[404]	
PIBI	PCBIVI	InP (OA)	0.676	13.9	62.5	6.4	[101]	
РЗНТ РСВМ	-	0.622	7.35	0.59	2.74			
	CdSe (OA)	0.624	7.67	0.59	2.85	[105]		
		CdSe (Pyridine)	0.644	7.5	0.61	2.96		
PCPDTBT	-	DDT conned DbC	-	11.15	-	-	[402]	
-	-	BDT capped PbS	-	11.06	-	-	[102]	
	-	ZnO	0.04	1.3	27.5	0.02		
-	CdS/ZnO Hybrid	0.31	1.6	43.4	0.24	[46]		
PSHI	P3H1	CdSe/CdS/ZnO	0.675	4.2	51.8	1.5	[15]	
	-	Heterojunction						
P3HT	-	hexanoic acid treated	0.61	6.04	56.2	2.09	.09	
PCPDTBT	-	CdSe	0.58	8.16	55.3	2.65	[103]	
	DODM	-	0.57	7.51	0.48	2.06	[00]	
P3HI	PCBM	CdSe (pyridine)	0.6	8.15	0.62	3.05	[99]	

Table 1: Photovoltaic characteristics of hybrid solar cells comprising various types of QDs.



in graphite, approximately 3.4 Å.

Carbon nanotube has unique features such as high electrical conductivity, mechanical strength, thermal and optical properties, extraordinary length to diameter and hence very high surface area. Nanotube ropes are attracted by strong Vander Waals forces, leading to the physical structure of this material. Electrical properties of metallic CNTs is 1000 times greater than copper. Configuration of SWCNTs strongly affects its electrical properties i.e. if n=m, the nanotube has metallic character but, if the subtraction of n and m is multiple of 3, nanotube exhibits semiconducting optoelectronic behavior with a very small band gap. Otherwise, the nanotube is a moderate semiconductor and its gap is a function of the tube's diameter. Structural defects of CNT particles influence the electrical properties of the tubes, so that a defect in some conducting CNTs can cause the surrounding region to become semiconducting and generally the conductivity of the CNT is lowered.

All mentioned characteristics make CNTs potentially useful in a lot of fields such as electronics, photovoltaic, optics, medicine, biosensors, as fillers in polymer matrices and many other applications.

Incorporation of CNTs into the photoactive layer of organic photovoltaic has been found as a promising approach to increase the power conversion efficiency since charge transport can be effectively improved through conductive pathways provided by CNTs as a result of its high aspect ratio [106,107]. The photovoltaic characteristics of recently prepared hybrid solar cells containing various types of CNT are summarized in Table 2. CNT was first used as an electron acceptor in combination with poly (3-octylthiophene) (P3OT) in 2002. Although the solar cell efficiency showed to be improved in comparison with the cell based on P3OT alone, the final efficiency was still lower than the cells fabricated with PCBM [108]. This lower efficiency was attributed to the presence of inevitable metallic sites in the structure of CNT which gives rise to the recombination of the electron-holes and hence short circuiting the cell. Salim et al. [109] reported the effects of the incorporation of semiconducting single-walled nanotubes (sc-SWNTs) with high purity on the efficiency of BHJ organic solar cell based on regioregular rr-P3HT:PCBM. They reported that sc-SWNTs could organize the polymer phases, confirmed by the increase in crystallite size, the red-shifted absorption characteristics and the enhanced hole mobility. They reported an improved PCE up to approximately 4% (8% higher than its reference device) by incorporating sc-SWNTs. They also demonstrated higher thermal stability of BHJ OSCs upon incorporation of sc-SWNTs. Landi et al. [24] constructed devices composed of 1 wt% SWNTs dispersed into P3OT matrix, and claimed a photo response with low current density, but relatively high open circuit voltages (1V). Andre's et al. [110] tried to incorporate different types of carbon nanotubes (single wall, double wall and multi wall carbon nanotubes)

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Electron donor	Electron acceptor	Type of CNT	V _{oc}	J _{sc} [mA/cm²]	FF [%]	PCE [%]	Reference
			[V]				
РЗНТ	PCBM	-	0.63	9.56	61	3.69	[109]
		sc-SWNT	0.63	9.91	64	3.98	
P3HT	PCBM	-	0.557	7.114	54.2	2.15	[117]
		B-CNTs	0.277	6.452	30.2	0.54	
		N-CNTs	0.302	6.863	28.1	0.58	
P3HT	PCBM	FSWCNT (oxygen functionalized)	0.52	5.53	0.49	1.8	[119]
P3HT	PCBM	alkyl-amide	0.56	14.79	0.52	4.39	[120]
		SWCNT	0.6	10.45	0.5	3.18	
P3HT-Py/MWCNT	P3HT-PCBM	MWCNT	0.58	8.83	52	2.64	[126]
MWCNT-P3WT		-	0.57	6.8	56	2.17	
P3HT	PCBM	esterified SWCNT	0.668	11.14	0.522	3.66	[121]
		-	0.583	12.1	0.542	4	
P3HT	PCBM	SWCNT-CONHTh	0.55	5.6	0.58	1.78	[122]
		SWCNT	0.55	4.95	0.52	1.41	
		-	0.55	3.77	0.48	1	
P3HT	PCBM	MWCNT-COOH	0.6	8.34	60.97	3.05	[118]
		MWCNTs	0.54	5.8	44.42	1.39	
		-	0.6	7.18	65.3	2.86	

Table 2: Photovoltaic characteristics of hybrid solar cells containing various types of CNTs.

into organic solar cells based on P3HT matrix and have reported that interaction between CNTs and polymer phase causes local orientation of the polymer segments, and hence induces nucleation for the crystallization of P3HT. Moreover, these interactions allow charge separation of the photo generated excitons within the polymer, and also enhancement of the electron transport towards the electrode via CNT conductive pathways. As a result of CNT incorporation, the power conversion efficiency enhanced by three orders of magnitude compared to the counterpart device without CNTs. However, they reported that there is no clear connection with the number of walls or diameter of the nanotubes, consequently the important variables to consider are the purity and defect density of the CNTs, and therefore, the metallic to semiconducting ratios. Zaminpayma et al. [111] have studied the effect of the extent of interfacial interaction between SWNTs and conjugated polymers including poly(2-methoxy-5-(3-7-dimethyloctyloxy)-1,4-phenylene-vinylene) (MDMO-PPV), P3HT, and poly[(9,90dioctylfluorenyl-2,7-diyl)-co-bis (N,N0-(4,butylphenyl)) bis (N,N0phenyl-1,4-phenylene) diamine] (PFB) on the device performance by means of molecular dynamic simulation. Based on their calculations, the interaction intensity between the SWNTs and P3HT was higher than CNT/MDMO-PPV. Their results exhibited that the interfacial interaction energy is influenced by SWNT diameter, and the specific monomer structure of the polymers, but chirality of CNT structure and temperature showed to have less impact on the device performance.

Based on Radbeh et al. [112], the performance of organic solar cells can be also improved via ordering the CNT particles perpendicular to the electrodes as better paths for the charge carrier transport toward the corresponding electrodes could be provided.

Although utilization of CNTs as an electron acceptor material has been tried by various researchers, the overall cell efficiency is still low in comparison with the cells based on fullerenes. This could be attributed to the presence of unavoidable metallic sites on surface of CNT particles which leads to the short circuiting the cell. Kanai and co-workers [113] have used density functional theory (DFT) calculations to assess the interface between P3HT and semiconducting/metallic CNTs and the potential of such combinations for the high efficiency solar cells. Their results demonstrated that the semiconducting tubes could form an ideal type-II heterojunction and thus may be a suitable replacement for the fullerenes in the organic solar cells, while in the case of the metallic tubes their calculations indicated a sizable charge recombination to the ground state as a result of chemical potential equilibration.

The short circuit problem of CNTs has been tackled by introducing low concentration of CNTs in combination with other electron acceptors such as PCBM or C_{60} . Thus, the main role of CNTs is to enhance the efficiency of charge transport and it can also act as an exciton dissociation center. Jousselme and coworkers [114] have tried to prepare solutions of single and multi-walled carbon nanotube blended with P3HT and PCBM, using new method to avoid sonication, with homogeneous dispersion of CNT particles throughout the matrix. Photovoltaic devices based on P3HT:PCBM (1:1) mixture comprised of 0.1 wt% multi-walled carbon nanotubes has showed efficiency of 2.0% compared to counterpart cell without CNT which exhibited conversion efficiency of 0.7%. Su and co-workers [115] investigated the enhancement of light absorption and charge carrier transport of a P3HT:PCBM heterojunction by introducing acid washed MWNTs. Their results exhibited that the 0.01 wt% MWNTs doped P3HT:PCBM photovoltaic device had an PCE improvement of 29% as a result of induced alignment of P3HT chains which led to the more absorption of the solar spectrum as well as a better hole transport. Kim and coworkers [116] have explored the effect of incorporating nitrogen-(N) or boron-(B) doped MWNT on the performance of P3HT:PCBM solar cells. Unlike un-doped metallic multi wall CNTs which cause undesired electron-hole recombination, N or B doped CNTs which are uniformly dispersed in the active layer can enhance electron and hole transport, respectively, and eventually help carrier collection. In particular, incorporation of 1.0 wt% B-CNTs resulted in balanced electron and hole transport, and reached a power conversion efficiency improvement from 3.0% (conventional control cells without CNTs) to 4.1% (37% PCE enhancement). Keru et al. [117] studied the influence of B- and N-doped carbon nanotubes on the performance of P3HT:PCBM. Even though boron- and nitrogen-doped CNTs are known to have different properties of p-type and n-type, respectively, both hybrid devices showed similar photovoltaic characteristics. In

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both cases, the devices recorded low power conversion efficiencies compared to the standard P3HT:PCBM device. The doped-CNTs were metallic in nature as a result of the low concentration of substitutional boron in B-CNTs and pyridinic-nitrogen species in N-CNTs which was reported as the main reasons for similar poor performance of the two corresponding ternary devices.

Unfortunately high tendency of carbon nanotubes to form aggregated structures prevents their uniform dispersion throughout the polymer matrices which can lower the efficiency of CNT polymer solar cells compared to their fullerene counterparts. For better dispersion of CNT in polymer matrices, various types of covalent and non-covalent functionalization have been suggested and tried. The tips and sidewalls of CNT can be functionalized through covalent bonding. Acidic solutions such as HNO₃, HNO₃+H₂SO₄, H₂SO₄ in conjunction with KMnO₄ are usually used to functionalize the tips and the defects of tubes with carboxyl (-COOH) and alcohol (-OH) groups [118]. Various photovoltaic cells based on combination of P3HT, PCBM and functionalized SWNT (FSWCNT) has been fabricated by Singh et al. [119]. Their reports indicated that incorporation of FSWCNT onto the P3HT: PCBM blend matrix enhanced the absorption intensity as well as charge collection efficiency, with performance 18 times higher than that observed for P3HT: FSWCNT (0.1%) and twice than P3HT: PCBM based cells (0.9%). Hong and co-workers [120] have examined the effect of incorporation of alkyl-amide functionalized CNT into the P3HT: PCBM solar cells. The ternary solar cells exhibited a remarkable 40% PCE enhancement (from 3.2 to 4.4%) compared to the binary solar cell without CNT. This is attributed to the high dispersion state of functionalized CNT throughout the polymeric matrix, and hence enhanced charge mobility as well as wider photo absorption spectrum. Functionalization of CNTs by other means has also been attempted by binding pendant thiophene rings or ester groups on the surface of SWCNT. In both cases, the enhancement of the photovoltaic response was believed to be due to the more efficient dispersion of the modified SWCNTs resulting in a more homogenous photoactive layer [121,122].

CNT destruction through defect creation via disruption of sp² hybridization is the main drawback of covalent surface modifications, whereas non-covalent surface modifications are advantageous as the sp² conjugated structures and electronic performance of CNTs are preserved. Non-covalent modification of CNTs for the application in organic solar cells is typically carried out through the usage of organic mediating molecules range from low molecular weight molecules to supramolecules and polymers. The mediating molecules alter the intrinsic properties of CNTs by either adsorbing onto or wrapping the CNTs [123]. Chen and co-workers [124] have investigated the influence of hydroxyl groups attached to the P3HT (HOC-P3HT-COH) on the reduction of the domain size of the PCBM crystals in P3HT matrix. They reported that HOC-P3HT-COH acts as compatibilizer and increase the physical attachment of PCBM to P3HT, leading to the less aggregated structure, and hence higher surface area and exciton dissociation rate. Thermal stable polymer solar cell with high performance (PCEs of 4.06%) was achieved using 5% HOC-P3HT-COH in P3HT:PCBM matrix. However, high loading level would reduce the final efficiency due to the creation of complete miscible blend in the active layer. Giulianini et al. [125] have reported a detailed experimental evidence for the rrP3HT helical wrapping on the surface of CNTs by atomic resolved UHV-STM images. They were able to confirm that the wrapping is constrained by the coiling angle and the nanotube diameter, resulting in the extension of the polymer chain to chain distance. Two different strategies for the increase of the CNT dispersion in solution and in P3HT thin films have been proposed by Boon et al. [126]. They modified P3HT end group into a formaldehyde function through Vielsmeier–Haack reaction and then changed this group to imine bonds by reactive mixing with the CNTs carrying surface amine groups. Physisorption of P3HT chains on the surface of CNTs lead to a much better dispersion of MWCNTs in solution and in the solid state. This non-covalent approach led to the 22% increase in solar cell efficiency in comparison to the cell without P3HT-Py/ MWCNT.

Hybrid solar cells based on CNT decorated with QD nanostructures

To enhance the charge carrier separation and transport properties of the semiconductor quantum dots incorporated in organic matrices, their hybridization with semiconducting one dimensional carbon nanotubes would be beneficial [127]. Carbon nanoropes not only serve as support for anchoring the QDs, but also provide electron transport highways to direct the flow of photo-generated carriers to their corresponding electrodes. The one dimensional nanostructured CNTs with high aspect ratio and unique electrical conductivity has been shown as an excellent scaffold to be loaded by QDs such as ZnO, CdS, CdSe, InP, PbS, PbSe applicable in hybrid solar cells [128-130]. Generally, there are two approaches for the deposition of QDs on CNTs, including in-situ and ex-situ methods. In both methods, deposition of the QDs can be carried out by either covalent or noncovalent attachment. Facility and low cost are the benefits of the former technique; however; precise control of the QDs size distribution is complicated. Schornbaum et al. [131] have developed a method for non-covalently attachment of PbSe QDs on SWNTs without any linker molecule or chemical modification of the SWNTs through insitu synthesis of QDs by using hot injection method. Das et al. [132] have synthesized PbS SWNT nanohybrids through in-situ mixing of lead nitrate and sodium sulfide solutions in ethanol under ultrasound irradiation and using 1,2 benzene-di-methane-thiol (1,2-BDMT) as stabilizer.

However, the ex-situ fabrication methods include the ex-situ preparation of QD particles and their absorption on the CNT surface by molecular linkers, covalent attachment or through direct physical adsorption. The main advantage of the ex-situ assisted deposition of nano crystal is that the QDs are synthesized prior to deposition, with well controlled shape and size using capping agents. Nevertheless, when simple physical mixing is applied long deposition times, low photocurrents due to the isolating effect of the ligands and inefficient deposition of QDs on CNTs backbone is the minimum shortcomings of this approach. Das et al., [133] proposed a method for the attachment of commercially obtained oleic acid stabilized monodispersed PbS QD with the size of 2.7 nm onto the surface of CNT prefunctionalized by an aromatic dithiol (1,2-BDMT). They believed that the aromatic part of 1,2-BDMT attaches to the CNT by π - π stacking interactions and the thiol part replaces oleic acid on the surface of QDs, leading to the non-covalent attachment of the QD to the CNT. Efficient electron transfer from the QDs to CNTs was proved by quenching of the PbS photoluminescence (PL) spectrum.

Enhanced efficiency, solution processability, low cost and large area coverage of hybrid solar cells based on QD/CNT nanostructures and conjugated polymers have been recently reported [23]. The superior efficiency of this type of hybrid solar cells originate from the fast charge separation at QD-polymer and/or QD-CNT interfaces as well as enhanced charge transport throughout the photoactive layer due to the high electron mobility.

Shukla et al. [13] reported substantial enhancement in the external quantum efficiency by incorporating simple mixture of PbSe QD and CNT onto the P3OT based OPV cells as a result of significantly improved charge transfer between CNTs and QDs. However, in this approach controlled deposition of QDs is complicated and agglomeration is inevitable. Consequently, covalent functionalization of CNT [133], QDs [16] or both of these two nanomaterial's [22] has been studied. Cho et al. [134] have shown that by thiol covalent modification of SWNT, a large number of PbSe QDs are attached on the surface of CNT. Their results indicated efficient harvesting of IR photons, followed by fast charge transfer, and enhanced conduction in the poly vinyl carbazole (PVK) polymer blended with PbSe-SWNT nanostructure's, leading to more than 100% increment of EQE. Wang et al. [22] deposited PbS QDs on the surface of MWCNTs via simple mixing of pre synthesized high quality PbS QDs and oleylamine (OLA) pre functionalized MWCNTs. Results revealed enhanced electron transfer from photo excited PbS QDs to MWCNTs. Incorporation of as synthesized PbS QD/MWNT Nano architectures into the P3HT as an effective hole conducting polymer resulted in the high PCEs of 3.03% as compared to 2.57% for the standard OPV cell based on P3HT:PCBM. A PCE enhancement around 31% has been reported by Lee et al. [14] for the solar cell based on P3HT:ICBA and hybrid nanosystem comprising indium phosphite (InP) QDs/N-doped multi walled carbon nanotubes (NCNTs). They reported that both V_{oc} and J_{sc} enhanced with the nanohybrid materials comprising InP QDs and metallic N-doped CNTs in which QDs promote exciton dissociation and CNTs enhanced the transport of the separated electrons. Such a synergistic effect successfully improved the PCE from 4.68% (reference cell with pure P3HT:ICBA active layer) to 6.11%. A simple method for the fabrication of composite based on polymer/CdSe QD/CNT under visible light irradiation has been developed and reported by De et.al. [16]. For this purpose, a mixture of 5-mercapto-2,2-bithiophene (BTSH) covalently modified CdSe QDs (BTSCdSe) solution with CNT was employed. Subjection of the prepared mixture to the visible light irradiation results in the photo induced hole transfer from the CdSe QD core to the BTS ligand and consequently polymeric QDs on the CNT surface were formed. They have claimed wrapping of BTSCdSe around the CNT surface due to the π - π interactions between thiophene groups of polymer and CNT. Dependence of photoluminescence quenching kinetics through charge transfer or resonance energy transfer on the distance between QD and CNT surface was speculated by Peng et al. [135]. In their work, the heterostructure of dual wall CNT (DWNT) and CdSe QD capped with short amino thiol linker (AET) was synthesized. Results indicated that long lived charge separated states were formed within two components, which was induced by AET hole trapping ligands and fast charge transfer to the DWNT. They also found that precise control on the surface chemistry and distance between QDs and DWNTs has a significant effect on the various kinetic pathways.

Covalent functionalization has also been employed for in-situ deposition of QDs on nanotubes. Kim and coworkers [15] have reported the fabrication of P3HT based solar cell co-sensitized by the CdSe/CdS/ZnO NW nanohybrids with significant improved PCE. The cell has been assembled in four steps including: deposition of ZnO nano arrays on the ITO substrate, SILAR deposition of CdS QDs on ZnO nanowires, CBD deposition of CdSe QDs on CdS layer and finally infiltration of P3HT solution into the CdSe/CdS/ZnO arrays by spin coating. Significant improvement of the solar cell efficiency was achieved as a result of enhanced open circuit voltage, efficient transfer of electrons through one dimensional ZnO nanowires and holes via polymeric network, and a broader absorption spectrum. The fabricated hybrid cell exhibited incredible durability of the cell performance compared to that of liquid based, quantum dot sensitized solar cells.

covalent functionalization, non-covalent surface Unlike modification of CNT is beneficial as the sp2 conjugated and the electronic structures of CNTs are retained. Thus many researchers prefer this method for the deposition in-situ or ex-situ of QDs on the CNT surface [132]. Weaver et al. [136] have investigated current responses of the cell made of a Nano composite based on MWNTs/ thiol derivative perylene compound/CdSe QDs. Ex-situ fabricated QDs and Ethanethiol Perylene Tetra-carboxylic Di-imide (ETPTCDI) play the role of photon harvester and transfer their excited electrons or holes to CNTs, which increased the overall photon harvesting efficiency of the nanocomposite. ETPTCDI can act as a linker molecule and significantly increases the adhesion between QDs and CNTs throughout bonding between QDs and thiol groups of ETPTCDI and π - π interactions between ETPTCDI and CNTs. Recently our research group designed and fabricated a new solution processed nanohybrid system comprising of single-wall carbon nanotubes loaded by PbS QDs capped with an epitaxial ligand shell of methyl-ammonium lead iodide perovskite clusters (MA₄PbI₆) by solution mixing of acid functionalized SWNTs with high quality PbS/PbI₆ QDs [137]. Our obtained results revealed that incorporation of the synthesized PbS/ PbI₆-SWCNT nanohybrid system to the host active layer enhanced the absorption spectrum of the P3HT:PCBM significantly. Moreover, the solar cells generated by as synthesized Nano architectures showed improved PCE by around 15% over standard P3HT:PC₆₁BM solar cells. This was mainly due to the enhancement of J_{sc} as a result of higher photon harvesting by methyl ammonium lead iodide cluster capped PbS QDs and facilitation of exciton dissociation as well as improved electron transport by SWCNTs. Importantly, we investigated the microstructure of our hybrid blend systems by using GIWAXS method to get insights into the influence of loading the QDs on SWCNTs on the Nano scale morphology and its correlation to the charge transport and device performance. The GIWAXS results revealed an enhanced P3HT crystallinity in both in-plane and out of plane directions upon implementation of the synthesized PbS/PbI₆-SWCNT Nano architectures into the P3HT:PCBM host matrix compared to the only PbS/PbI₄-incoporated counterpart. This fact contributed to the improved transport properties and enhancement of the absorption strength in the PbS/PbI_e-SWCNT-incorporated hybrid solar cells. Table 3 summarizes the photovoltaic characteristics of recently prepared hybrid solar cells based on various types of QD-CNT Nano hybrids.

Summary and Outlook

The concept of employing semiconductor Nano crystals in polymeric solar cells has been found as a promising approach to extend the absorption spectrum of semiconductor polymers and, consequently, enhance the light harvesting properties and performance of the device. The power conversion efficiency of these systems still lag behind their inorganic counterparts due to randomly hopping charge transport of QD particles and QDs phase separation. One dimensional nanostructure such as carbon nanotubes can serve as support for anchoring the light harvesting semiconductor QDs to prevent their disruptive influence on the nano-scale morphology, as the charge acceptor to promote exciton dissociation and as the charge transport highway to direct the flow of photo generated charge carriers to the electrode. Various in-situ/ex-situ and covalent/non-covalent

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Electron donor	Electron acceptor	QD-CNT nanohybrid	V _{oc}	J _{sc}	FF	PCE	Reference
			[V]	[mA/cm ²]	[%]	[%]	
P3OT	-	CdSe-SWNT complexes (SWNT- COOH), CdSe-aminoethanethiol	0.75	0.00016	-	-	[24]
P3HT	-	ZnO	0.04	1.3	27.5	0.02	[15]
	-	CdS/ZnO Hybrid	0.31	1.6	43.4	0.24	
	-	CdSe/CdS/ZnO Heterozunction	0.675	4.2	51.8	1.5	
P3HT	PCBM	PbS (OA)-MWNT(OA) hybrid	10.81	0.54	54	3.03	
		-	0.882	0.54	54	2.57	[22]
P3HT ICBA	ICBA	-	0.75	10.7	58.3	4.68	[14]
		InP	0.76	11	51.8	4.33	
	-	N-doped CNT (NCNT)	0.77	11.2	61.3	5.29	
	-	InP:NCNT	0.79	11.9	65	6.11	
P3HT	PCBM	-	0.57	8.77	62.84	3.17	[137]
		PbS/Pbl _e -SWCNT ₂₀	0.58	9.67	64.22	3.63	

Table 3: Photovoltaic characteristics of hybrid solar cells containing various types of QD-CNT nanohybrids.

methods have been employed to deposit QDs on the surface of CNTs. The QD-CNT nanostructures have been successfully applied to the organic based solar cells. However, getting a deeper insight into the working principles of these systems, their charge transport kinetics and morphology formation as well as using the highly efficient organic matrices instead of P3HT:PCBM are crucial to achieve high efficiency QD-CNT based hybrid solar cells and all these importance need to be further investigated.

Acknowledgments

The authors gratefully acknowledge the support of the Cluster of Excellence "Engineering of Advanced Materials (EAM)" at the University of Erlangen-Nuremberg, which is funded by the German Research Foundation within the framework of its "Excellence Initiative". This work has been partially funded by the Iranian Ministry of Science Research and Technology. T. A. acknowledges the support of the Synthetic Carbon Allotropes (SFB953), Solar Technologies go Hybrid (SolTech), and Bavarian Equal Opportunities Sponsorship - Förderung von Frauen in Forschung und Lehre (FFL).

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