Hybrid Organic-Inorganic Solar Cells: Recent Developments and Outlook

A. A. D. T. Adikaari, D. M. N. M. Dissanayake and S. R. P. Silva

Abstract—Solution processed photovoltaic devices are an attractive alternative to costly inorganic semiconductor based conventional photovoltaics. Solution processable organic photovoltaic systems are affected by low carrier mobility, lifetime issues under ambient conditions and limited optical absorption due to the high bandgaps of organic materials. Nanostructured inorganic materials promise to alleviate some of these drawbacks, by enabling the hybrid systems to perform better in a commercial perspective. This review examines four key areas of hybrid organic-inorganic photovoltaic systems. These are metal oxide-organic, carbon nanotube-organic, semiconductor nanowire-organic and semiconductor nanocrystal-organic systems, which are showing growing importance and potential in the literature. Recent advances in terms of device performance for these respective topics are reviewed, along with an outlook for each hybrid system.

Index Terms—Photovoltaic cells, Organic compounds, Hybrid Systems, nanotubes, nanomaterials, solar cells

I. INTRODUCTION

PHOTOVOLTAICS (PVs), better known as solar cells, have become a viable alternative for electrical power generation in recent years. This process has been further expedited with the increasing concerns on fossil fuel based sources due to carbon emission. PVs have been used for energy conversion for over a half a century, the uptake worldwide has been slow due to the relatively high cost of energy generated in comparison to fossil fuels. With mounting concerns on climate change, it is now an opportune time to move the use of solar energy from a lifestyle decision one of national and international significance for the long term stability of the earth’s eco system.

A number of techniques for photon to electricity conversion has been attempted over the years and the use of semiconducting materials has been the most successful. Semiconductors absorb photons when exposed to light and excite electrons to higher energy states, creating mobile electrons and holes. These charge carriers are swept across the device by utilizing a built-in electric field, generating a flow of electrons through a load which can be used immediately or can be stored for later consumption. The most widely used and available technique has been silicon p-n junction solar cells due to their efficiencies (8-20%), abundance and reliability. Although silicon PVs dominate over 90% of the market share [1], the energy intensive, costly fabrication processes have kept the cost of energy produced high, preventing the mass uptake of the technology. Therefore, cheaper alternative PV technologies have been highly sought after and organic material based technologies have come to the forefront after the last decade. Organic materials are cheaper, and not as-energy intensive in terms of the production process. Further, the possibility of device fabrication from solution makes the technology very attractive from a potential commercial perspective. However, the efficiencies and lifetimes of organic PV devices are inferior to their conventional inorganic semiconductor counterparts and too low for commercial viability at present.

Early research on organic PV systems was derived from the conventional p-n junction architecture, with organic materials replacing p-type and n-type materials as charge donors and acceptors. The development of organic PV devices was initiated by the discovery of ultrafast charge transfer between poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene (MEH-PPV) and buckminsterfullerene (C60)] by Sariciftci et al. [2] in 1992. The initial PV devices are known as bilayer systems, due to the deployment of electron donors and acceptors as thin layers of tens to hundreds of nanometres [3]. Unlike free charge carriers in inorganic semiconductors, absorbed photons create electron-hole pairs known as excitons in organic semiconductors, so that dissociation of the charges is necessary before collection at the electrodes. Exciton dissociation is believed to occur at interfaces between materials with different electron affinities and ionization potentials, where the electron is accepted by the material with larger electron affinity and the hole by the material with lower ionization potential. A bilayer structure therefore is limited by the depth of the optical absorption as well as excitation diffusion length, limiting the achievable efficiency of the system. Hence, interpenetrating donor-acceptor networks formed from a phase-segregated mixture of two semiconducting organic materials were proposed to overcome this problem [4, 5].
These interpenetrating networks are now known as bulk-heterojunction active layers.

Initial bulk-heterojunction PVs were all-polymer based which were later expanded to polymer/small molecule systems [6]. Bulk heterojunction PV devices fabricated have shown steady progress over the years [7-9], in terms of device efficiency, reaching a high of 6.7% in 2009 for a single junction device [10].

Performance of bulk-heterojunction systems have been enhanced using a number of advances. These aspects fundamentally fall into two categories; enhancement of short circuit current density ($J_{sc}$) and open circuit voltage ($V_{oc}$). Secondary aspects have also been addressed which yield better fill factors leading to higher efficiencies. Some of these advances have been achieved by utilisation of inorganic nanoscale material systems in organic structures, essentially rendering these devices “hybrid”. This review concerns with three key areas of hybrid organic-inorganic PV systems. These are metal oxide-organic, carbon nanotubes (CNT)-organic and semiconductor nanowire-organic systems. In addition, bilayer hybrid systems have had considerable research effort in infrared PV systems [11]. Therefore, a fourth category of semiconductor quantum dot-organic systems are also reviewed as part of this hybrid PV devices review.

The metal oxide-organic hybrid device systems are dominated by work on TiO$_2$ and ZnO based systems. However, most of the literature on TiO$_2$ deals with dye-sensitized PV devices, which are not within the scope of this review. Therefore, TiO$_2$ based hybrid PVs discussed here do not utilise any sensitizers and only use the material as an electron transport layer of the hybrid system. The review on TiO$_2$ follows a review on ZnO based hybrid PVs, followed by a semiconductor nanowire hybrid system section. A third category of CNT hybrid systems is reviewed next and three main applications of CNTs in organic PV systems are discussed. CNTs in the active layer, as a charge collection interface at the electrode and as the transparent electrode are the three applications discussed.

The review attempts only to discuss organic-inorganic hybrid PV device research, and present performance parameters of the investigated devices. Therefore, a large quantity of literature on charge transport between materials is excluded from this study. PVs are fundamentally characterised using a key set of parameters, obtained through current-voltage characteristics under simulated solar irradiation. The measurements are performed according to international standards, such as “IEC 60904-1:2006, PV devices-Part 1: Measurement of PV current-voltage characteristics” or the relevant national standards. The simulation experiments are expected to be performed with AM 1.5G illumination (IEC 60904-3:2008), which yields an overall power density of 1000W/m$^2$.

The current-voltage characteristics are collected preferably through an electronic load, which allows extracting the $V_{oc}$, $J_{sc}$, current density ($J_{mp}$) and the voltage ($V_{mp}$) at the maximum power point. This data is used to calculate the fill factor (FF) and the power conversion efficiency ($\eta$) of the device under test, parameters which are fundamental for comparison of competing technologies. Fig. 1 shows a typical current density-voltage (J-V) curve for an organic solar cell, illustrating the fundamental parameters of a PV device.

It can be seen that not all the measurements reported on PVs are performed under standard illumination and therefore makes comparison of performance difficult. In this review, the measurements reported with the types of illumination other than AM1.5G are referred to as nonstandard measurements, highlighting the difficulty in comparison.

II. METAL OXIDE-ORGANIC MATERIAL PVs

A. Titanium Dioxide Based Hybrid PV

Nanostuctured TiO$_2$ has been studied as a PV material since the 1980s, establishing the basis for dye-sensitised solar cells [12]. Compared to dye-sensitised solar cells, the solid nanostructured TiO$_2$-polymer solar cell has the advantage of utilising the complete heterostructure for exciton dissociation, potentially leading to thinner devices, since the entire polymer-filled pore volume is available for exciton generation, rather than only a dye monolayer at the TiO$_2$ surface. Further, the rigid structure of TiO$_2$ offers better mechanical stability compared to the organic PVs [13].

The bulk heterojunction concept for organic PVs utilises disordered nanostructures, as a trade-off for the ease of fabrication by mixing donor and acceptor phases. The porous structure of nanostructured TiO$_2$ has been investigated as an electron acceptor layer with organic photoactive polymers as the hole conductor extensively [14]. Early work on TiO$_2$ hybrid PVs used metal phthalocyanines as the photoactive polymer [15]. The PV performance of these initial devices are poor with efficiencies ~0.01%. Subsequently, poly ($\rho$-
phenylene vinylene) (PPV) was utilized to fabricate nanocomposites with TiO₂, although the device performances were not drastically improved [16, 17]. A report on SWCNT:MEH-PPV nanocomposite on TiO₂ as the photoactive layer is available, however without enhanced performance [18]. A 0.18% efficient glass/indium doped tin oxide (ITO)/TiO₂/MEH-PPV/Au device has been reported in 2001, however with white light illumination [19]. Subsequent improvements on device design with nanocrystalline TiO₂ has resulted in 0.58% efficient TiO₂/MEH-PPV bilayer devices with a Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), a conducting polymer layer, at the Au electrode [19-21]. A similar system with aligned TiO₂ nanowires has also been reported with a maximum device efficiency of 0.4% under standard test conditions [22]. Similar independent studies with photoactive polymers, poly(3-octylthiophene) (P3OT) (0.06% [23]) and sodium poly[2-(3-thienyl)-ethoxy-4-butylsulfonate] (PTEBS) (0.13% [24]) as the photoactive layers on TiO₂ have been reported however, device measurements with nonstandard light sources for solar simulation.

Use of Poly (3-Hexylthiophene) (P3HT) as the photoactive polymer was reported subsequently [25], again with Solar simulation performed with nonstandard methods. Attempts have been made to utilize TiO₂ nanoparticles in a P3HT/ [6,6]-phenyl C₆₁ butyric acid methyl ester (PCBM) blends yielding a maximum efficiency of 1.5% [26]. A recent report on P3HT/TiO₂ hybrid device yield a 1.7% efficiency through a ligand exchange onto the TiO₂ nanorods enhancing the efficiency, compared to the previous attempts [27].

High efficiencies have been reported for TiO₂ hybrid system with an inverted bulk heterojunction architecture, utilizing TiO₂ as an additional electron transport material with a P3HT:PCBM system. Vertically oriented TiO₂ nanotube arrays on transparent, conducting fluorine doped tin oxide (FTO) coated glass substrates, has been utilised for the inverted cells, which are reported to enhance light absorption and charge collection capability compared to a thin layer of TiO₂. The highest efficiency attained for this system under standard solar simulations is 4.1% [28], with other independent work reporting efficiencies of 2.7% [29], 2.5% [30] and 1.5% [31]. It has also been reported that inverted TiO₂/P3HT:PCBM bulk heterojunction devices show improved stability against oxygen [32]. Use of self assembled monolayers (SAMs) between the TiO₂ and the electrode also has been reported to yield good efficiencies, with C₆₀ SAMs resulting in 3.8% efficient devices [33].

The most notable TiO₂ hybrid PV was reported very recently, for a poly [N-900-hepta-decanyl-2, 7-carbazole-alt-5, 5-(40, 70-di-2-thienyl-20, 10, 30-benzothiadiazole) (PCDTBT) in bulk heterojunction composites with the fullerene derivative [6, 6]-phenyl C₆₁-buturic acid methyl ester (PC₆₁BM) as the electron acceptor. With a TiO₂ optical spacer arrangement, a 6.1% efficiency has been observed which is the highest efficiency reported for TiO₂/organic hybrid device [34]. Table I shows the most notable titanium oxide-organic hybrid PV device parameters with respective references.

Outlook

Although considerable effort has been placed on improving TiO₂ dioxide based organic hybrid PV devices, the best performing been in conjunction with the P3HT:PCBM bulk heterojunction systems. The ability of forming ordered nanostructures with TiO₂ together with randomly phase separated P3HT:PCBM has the potential for reaching maximum internal quantum efficiencies for this system simultaneously benefiting from the improved device stability. In addition, the ability of TiO₂ to work as an optical spacer while aiding electron collection from the acceptor is set to attract considerable attention. Also, the observed stability improvement with the utilisation of TiO₂ requires further understanding in order to maximise the effect in hybrid PVs.

B. Zinc Oxide Based Hybrid PV

Although ZnO has been studied for more than half a century, renewed interest in research is evident, especially on nano-scale structures. ZnO is a direct wide band gap (3.3 eV at 300 K) II-VI compound semiconductor [35]. ZnO can be grown with simple crystal-growth technologies, resulting in potentially lower costs for ZnO-based devices. High-quality ZnO films can be grown at relatively low temperatures less than 700°C. Further, there are additional properties which make ZnO preferable over other wide-band-gap materials. ZnO can be doped substitutionally and by controlling the

<table>
<thead>
<tr>
<th>Year</th>
<th>Architecture</th>
<th>Vₒc (V)</th>
<th>Jₐc (mA/cm²)</th>
<th>FF (%)</th>
<th>η (%)</th>
<th>Device Area (cm²)</th>
<th>Spectrum (mW/cm²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1996</td>
<td>Glass/ITO/TiO₂/ZnPc/Au</td>
<td>0.34</td>
<td>0.15</td>
<td>28.6</td>
<td>0.01</td>
<td>1.00</td>
<td>AM 1.5/100</td>
<td>[15]</td>
</tr>
<tr>
<td>2001</td>
<td>Glass/ITO/TiO₂/MEH-PPV/Au</td>
<td>1.10</td>
<td>0.40</td>
<td>42.0</td>
<td>0.19</td>
<td>0.03</td>
<td>-/100</td>
<td>[19]</td>
</tr>
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<td>2005</td>
<td>Glass/ITO/TiO₂/MEH-PPV/PEDOT:PSS/Au</td>
<td>0.64</td>
<td>2.10</td>
<td>43.0</td>
<td>0.58</td>
<td>0.04</td>
<td>AM 1.5/100</td>
<td>[21]</td>
</tr>
<tr>
<td>2005</td>
<td>Glass/ITO/PEDOT:PSS/P3HT:PCBM/NC-TiO₂/Al</td>
<td>0.50</td>
<td>5.63</td>
<td>48.0</td>
<td>1.50</td>
<td>0.06</td>
<td>AM 1.5/90</td>
<td>[26]</td>
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<td>2006</td>
<td>Glass/ITO/PEDOT:PSS/P3HT:PCBM/NC-TiO₂/Al</td>
<td>0.64</td>
<td>12.40</td>
<td>51.0</td>
<td>4.10</td>
<td>0.31</td>
<td>AM 1.5G</td>
<td>[28]</td>
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<tr>
<td>2006</td>
<td>Glass/ITO/PEDOT:PSS/P3HT:NC-TiO₂/TiO₂/Al</td>
<td>0.75</td>
<td>3.49</td>
<td>65.0</td>
<td>1.70</td>
<td>0.10</td>
<td>AM 1.5/100</td>
<td>[27]</td>
</tr>
<tr>
<td>2006</td>
<td>Glass/ITO/TiO₂/Ni/TiO₂/MEH-PPV/TiO₂/Al</td>
<td>0.59</td>
<td>10.96</td>
<td>42.0</td>
<td>2.71</td>
<td>-</td>
<td>AM 1.5G</td>
<td>[29]</td>
</tr>
<tr>
<td>2006</td>
<td>Glass/ITO/TiO₂/C₆₀/P3HT:PCBM/PEDOT:PSS</td>
<td>0.62</td>
<td>10.60</td>
<td>57.2</td>
<td>3.78</td>
<td>-</td>
<td>AM 1.5/100</td>
<td>[33]</td>
</tr>
<tr>
<td>2007</td>
<td>Glass/ITO/PEDOT:PSS/P3HT:PCBM/Al</td>
<td>0.75</td>
<td>66.0</td>
<td>6.10</td>
<td>0.13</td>
<td></td>
<td></td>
<td>AM 1.5G</td>
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</table>
doping level, electrical properties can be changed from insulator through n-type semiconductor to metal while maintaining optical transparency that makes it useful for transparent electrodes in flat-panel displays and solar cells [36].

The major obstacle in widespread use of ZnO is the difficulty in achieving a p-type material, while undoped ZnO show n-type behavior. ZnO is reported to have an impressive array of nanostructural forms. Nanowires, nanorods, nanobelts, nanocombs, nanosaws, nanosprings, nanocoils and even nanotubes are some of these structures [37]. The versatility of the material indicates a number of potential areas of application in PVs. The main thrust of interest has been on organic PV devices.

**ZnO in Organic PVs**

Early reports of ZnO-organic hybrid PVs are of a bulk heterojunction nature using ZnO nanocrystals (NCs) made by hydrolysis [38, 39]. ZnO NCs: poly[2-methoxy-5-(3′,7′-dimethyl-octyloxy)-1,4-phenylenevinylene] (MDMO-PPV) active layer devices on a PEDOT:PSS hole extraction layer on ITO coated glass has shown 1.6% efficiency under standard test conditions [38]. The solar simulation used is nonstandard [39]. ZnO nanorod/P3HT system has also been reported to show 3.3% efficiency at AM 1.5G illumination. Glass/ITO/ZnO NCs/P3HT:PCBM/PEDOT:PSS/Ag hybrid structures are reported to yield stable devices up to a month at 0.29% efficiency under standard test conditions [40].

Subsequent research by the same group has investigated the replacement of NCs with nanorods, synthesized by heating solutions of NCs. However, an improvement in device performance has not been observed, postulated to be due to the poor solubility of rods compared to NCs in organic solvents [40]. Also, the same group reports the performance of NC ZnO:P3HT bulk heterojunction devices, with a maximum efficiency of 0.9% with 0.7 V \(V_{oc}\) and 2.2 mA/cm\(^2\) \(J_{sc}\). Similar work from another group report 0.2% efficient ZnO nanorod/P3HT devices on ITO with PEDOT:PSS hole extraction layer before Au electrodes [42].

TABLE II

<table>
<thead>
<tr>
<th>Year</th>
<th>Architecture</th>
<th>(V_{oc}) (V)</th>
<th>(J_{sc}) (mA/cm(^2))</th>
<th>FF (%)</th>
<th>(\eta) (%)</th>
<th>Device Area (cm(^2))</th>
<th>Spectrum ((mW/cm^2))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2004</td>
<td>Glass/ITO/PEDOT:PPS/MDMO-PPV:ZnO NC/Al</td>
<td>0.81</td>
<td>2.40</td>
<td>59</td>
<td>1.60</td>
<td>0.10</td>
<td>-</td>
<td>[38]</td>
</tr>
<tr>
<td>2006</td>
<td>Glass/ITO/PEDOT:PPS/P3HT:ZnO NC/Al</td>
<td>0.69</td>
<td>2.19</td>
<td>55</td>
<td>0.92</td>
<td>0.10</td>
<td>-</td>
<td>[39]</td>
</tr>
<tr>
<td>2006</td>
<td>Glass/ITO/ZnO:ZnO nanofibres/P3HT:Ag</td>
<td>0.44</td>
<td>2.20</td>
<td>56</td>
<td>0.53</td>
<td>0.10</td>
<td>AM 1.5/100</td>
<td>[41]</td>
</tr>
<tr>
<td>2007</td>
<td>Glass/ITO/PEDOT:PPS/P3HT:ZnO/LiF/Sm/Al</td>
<td>0.83</td>
<td>10.00</td>
<td>43</td>
<td>2.03</td>
<td>0.10</td>
<td>AM 1.5/100</td>
<td>[44]</td>
</tr>
<tr>
<td>2008</td>
<td>Glass/ITO/ZnO NCs/P3HT:PCBM/PEDOT:PPS/Ag</td>
<td>0.62</td>
<td>11.17</td>
<td>54</td>
<td>3.78</td>
<td>-</td>
<td>AM 1.5/100</td>
<td>[51]</td>
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<tr>
<td>2008</td>
<td>Glass/ITO/PEDOT:PPS/P3HT:PCBM/ZnO/MUA/Al</td>
<td>0.65</td>
<td>11.10</td>
<td>63</td>
<td>4.60</td>
<td>-</td>
<td>AM 1.5/100</td>
<td>[53]</td>
</tr>
<tr>
<td>2009</td>
<td>Glass/ITO/PEDOT:PPS/P3HT:ZnO:Al</td>
<td>0.75</td>
<td>5.20</td>
<td>52</td>
<td>2.00</td>
<td>-</td>
<td>-100</td>
<td>[50]</td>
</tr>
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</table>

The best performing organic-inorganic hybrid PVs with ZnO are inverted structures where the transparent electrode act as the electron collecting electrode [51]. Glass/ITO/ZnO NCs/P3HT:PCBM/PEDOT:PSS/Ag hybrid structures are reported to show 3.3% efficiency at AM 1.5G illumination. This inverted device structure is also reported to be much more stable than the conventional P3HT:PCBM bulk heterojunction solar cells. The increased stability is believed to be due to reduced oxygen permeability, reducing the oxygen related degradation of the active layer of the polymer based solar cell structures.

A completely different approach on the use of ZnO in organic systems was reported by Gilot et al. [52]. They suggested that insertion of an optical spacer between the active layer and the reflective electrode results in a redistribution of the optical electric field, enhancing device performance. Development of this concept has resulted in a number of highly efficient ZnO based hybrid device structures. The optical spacer ZnO, treated with a SAM has been reported to be the best case with...
Glass/ITO/PEDOT-PSS/P3HT:PCBM/ZnO/SAM/Al devices showing 4.6% efficiency at standard test conditions [53]. The SAM used in this instance is mercaptopendecanoic acid (MUA). It has also been reported that ZnO is highly effective to tailor unfavourable work functions of metals such as Ag for organic PVs, using the optical spacer design. It has been observed that favourable metals, such as Ag, from a manufacturing point of view, can be used as electrode material retaining 80% of device efficiency with a ZnO optical spacer layer [54].

An all-solution processed poly-(3-carboxydithiophene) (P3CT) based bulk heterojunction system has also been attempted with low efficiencies ~0.2% under standard test conditions. The Glass/ITO/ZnO/ZnO:PC3T/PEDOT-PSS:Ag hybrid devices are reported to be stable up to 4 days showing 80% of the initial efficiency after 100 hours [55]. An inverted hybrid device with vertically aligned ZnO nanowires, in a Glass/ITO/ZnO/C60/CuPc/PEDOT-PSS:Ag configuration has also been reported yielding a device efficiency of 0.53% at standard test conditions [56].

Table II shows the most notable ZnO-organic hybrid PV device parameters with respective references.

Outlook

Use of ZnO as a bulk electron transport material in hybrid systems has more potential compared with TiO2. Also, ZnO competes as an optical spacer material with TiO2, where much effort has been concentrated. Apart from the existing applications, a number of other uses can be identified for ZnO as well. ZnO may be able to contribute to photocurrent generation through bandgap engineering. Already, a knowledge base exists on band gap modulation using Mg and Cd alloying. Impurity-created states resulting in enhanced optical absorption at lower energies would be another potential area of interest. Ohmic-contact metallization should be one of the main goals in improving device performance, in the successful utilization of ZnO in organic PVs. Although a low resistance Ohmic contact on wide-band-gap semiconductors can be obtained by thermal annealing, surface roughness and structural degradation of the interface can be induced during the thermal annealing process, resulting in poor device performance and reliability. Also, organic material systems are highly susceptible to heat, resulting in poor performances upon exposure to temperatures above a couple of hundred degrees. Therefore, it may in some instances be preferable to develop low-resistance Ohmic contacts without the use of a thermal annealing process.

Another aspect which warrants detailed analysis is the enhanced stability of ZnO/polymer hybrid devices. The stability of the devices may increase due to two main aspects. Use of ZnO can increase the effective area of the cell, resulting in better yield for a given volume of absorber layer. Reduced amounts of sensitive organic material should lead to better stability in performance.

III. Carbon Nanotube-Organic PVs

Carbon nanotubes have been identified as a revolutionary material system with the potential to transform the electronics industry. Single wall carbon nanotubes (SWCNTs) comprise of a single graphene cylinder, with typical diameters in the range 0.4-3.0 nm. Multi-wall carbon nanotubes (MWCNTs) comprise of several co-axially fixed tubes of different radii with an inter-tube separation close to the inter-plane separation in graphite (0.34-0.35 nm) [57]. MWCNTs have diameters as large as 100 nm. However, for organic PV device applications, diameters less than 20 nm are preferred due to the ~100 nm organic layer thickness in these device structures. The cylindrical, covalently bonded structure of carbon nanotubes are extremely strong with a tensile strength comparable to steel, at only a fraction of the density of Al [58]. They are efficient conductors of charge, with high heat transmission capacity, which is useful for thermal management of hybrid PV devices. Here we categorise the application of CNTs to three main areas, and discuss a comprehensive but non exhaustive review of reported device performances. Attempts have been made to incorporate carbon nanotubes into the active layers, as a charge collection layer at the electrodes and as a possible replacement for transparent electrodes. These aspects are reviewed separately under the following sections.

A. CNTs in the Active layer

Early research on CNT-organic hybrid systems were confined to charge transfer analysis between photoactive organic materials and CNTs [59]. Use of SWCNTs in an electron acceptor role was first reported by Kymakis and Amaratunga in 2002, with P3OT as the donor [60]. This early work with ITO and Al as electrodes resulted in poor device parameters, with best efficiencies of 0.1%. Later, poly(phenylenethynylene) (PPE) as the donor layer was investigated with SWCNTs as the acceptor, however with minute efficiencies and a Voc of 0.1 V and Jsc of 29 μA/cm2 [61]. These results have been improved to devices yielding 0.05% efficiency [62]. Also, poly[(2-methoxy,5-octoxy)1,4-phenylenevinylene] (MO-PPV)/SWCNT systems have been reported with nonstandard solar simulation and device efficiencies as low as 0.004% [63]. Another polymer used with SWNTs as the acceptor is a poly-hexylthiophene drivative. Bulk heterojunction cells with this material has been fabricated resulting in a power conversion efficiency of 0.52%. This work is also with nonstandard illumination, making comparison difficult. The polymer is reported to have advantages over P3HT due to the ease of fabrication and better stability against moisture and oxygen [64].

Double wall carbon nanotubes ( DWCNTs) as the acceptor material in a bulk heterojunction configuration has also been attempted, with P3OT as the acceptor material albeit with very low device efficiency at 0.001% [65]. Use of MWCNTs as the electron acceptor has also been attempted, however with insignificant device efficiencies [66]. Acid functionalized MWCNTs have been used in PTEBS, a water soluble
polymer, leading to 0.5% efficient hybrid devices [67]. The MWCNT content was 1 to 7.5% by weight in these composites, and the authors report reduced series resistances leading to better fill factors with the incorporation of MWCNTs.

A study on the use of P3HT with all three types of CNTs has been performed, however, the device characterisation is nonstandard, therefore meaningful comparisons cannot be made [68].

With the success of polythiophene-fullerene derivative bulk heterojunction solar cells after 2005 [7], attempts have been made to incorporate CNTs in the active layer of P3HT:PCBM systems. The most successful devices have shown 2.0% efficiency with 0.1% by weight MWCNTs in the active layer. An increase of $J_{sc}$ and a reduced $V_{oc}$ are reported for these devices although the reference device performance is poor for a typical polythiophene/fullerene derivative bulk heterojunction system. The most successful devices have shown 2.0% efficiency with 0.1% by weight MWCNTs in the active layer of P3HT:PCBM devices after 2005 [7], attempts have been made [68].

TABLE III

<table>
<thead>
<tr>
<th>Year</th>
<th>Architecture</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>Device Area (cm²)</th>
<th>Spectrum (mW/cm²)</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>2002</td>
<td>Glass/ITO/P3OT/P3OT:SWCNT/Al</td>
<td>0.75</td>
<td>0.12</td>
<td>40</td>
<td>0.04</td>
<td>-</td>
<td>AM 1.5/100</td>
<td>[60]</td>
</tr>
<tr>
<td>2005</td>
<td>Glass/SWNT/PEDOT:PPS/ P3HT:PCBM/Ga</td>
<td>0.50</td>
<td>6.50</td>
<td>30</td>
<td>0.99</td>
<td>0.07</td>
<td>-/100</td>
<td>[84]</td>
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<td>2006</td>
<td>PET/SWNT/PEDOT:PPS/P3HT:PCBM/Al</td>
<td>0.61</td>
<td>7.80</td>
<td>52</td>
<td>2.50</td>
<td>0.04</td>
<td>AM 1.5G/100</td>
<td>[86]</td>
</tr>
<tr>
<td>2006</td>
<td>Glass/ITO/PEDOT:PPS/ PTEBS/MWCNT/C60/Al</td>
<td>0.57</td>
<td>1.52</td>
<td>62</td>
<td>0.55</td>
<td>0.10</td>
<td>AM 1.5/100</td>
<td>[67]</td>
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<tr>
<td>2007</td>
<td>Glass/ITO/MWCNT/P3HT:PCBM/LiF/Al</td>
<td>0.50</td>
<td>4.00</td>
<td>47</td>
<td>0.93</td>
<td>0.08</td>
<td>AM 1.5/100</td>
<td>[79]</td>
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<tr>
<td>2007</td>
<td>Glass/ITO/PEDOT:PPS/ P3HT:PCBM:MWNT:LiF/Al</td>
<td>0.57</td>
<td>9.33</td>
<td>38</td>
<td>2.00</td>
<td>0.28</td>
<td>AM 1.5/100</td>
<td>[69]</td>
</tr>
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<td>2007</td>
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<td>0.54</td>
<td>2.69</td>
<td>49</td>
<td>0.75</td>
<td>0.16</td>
<td>AM 1.5/95</td>
<td>[70]</td>
</tr>
<tr>
<td>2007</td>
<td>Glass/ITO/PEDOT:PPS/P3HT:SWCNT:LiF</td>
<td>0.48</td>
<td>1.93</td>
<td>42</td>
<td>0.52</td>
<td>0.25</td>
<td>-/70</td>
<td>[64]</td>
</tr>
<tr>
<td>2008</td>
<td>Glass/ITO/PEDOT:PPS/ P3HT:PCBM:SWCNT/Al</td>
<td>0.55</td>
<td>4.95</td>
<td>52</td>
<td>1.40</td>
<td>0.05</td>
<td>AM 1.5/100</td>
<td>[72]</td>
</tr>
<tr>
<td>2009</td>
<td>Glass/ITO/PEDOT:PPS/ QTF12:PCBM:DWCNT:Lif/Al</td>
<td>0.56</td>
<td>2.37</td>
<td>37</td>
<td>0.50</td>
<td>0.28</td>
<td>AM 1.5/100</td>
<td>[71]</td>
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<td>2009</td>
<td>N type Si/MWCNT/SWNT/P3OT:Al</td>
<td>0.44</td>
<td>6.16</td>
<td>36</td>
<td>0.98</td>
<td>-</td>
<td>AM 1.5/-</td>
<td>[76]</td>
</tr>
<tr>
<td>2009</td>
<td>Glass/ITO/MWCNT/P3OT:PCBM:Lif/Al</td>
<td>0.61</td>
<td>7.30</td>
<td>62</td>
<td>2.70</td>
<td>0.35</td>
<td>AM 1.5G/100</td>
<td>[81]</td>
</tr>
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<td>2009</td>
<td>Glass/ITO/ODA-SWCNT:P3HT:PCBM:BCP:LiF</td>
<td>0.52</td>
<td>7.66</td>
<td>44</td>
<td>1.76</td>
<td>0.80</td>
<td>AM 1.5G/100</td>
<td>[this work]</td>
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Fig. 2. J-V characteristics for the ODA-SWCNT:P3HT:PCBM active layer device (circles: dark, squares: AM1.5G illumination).
What is evident from this experiment as well as previous work is that CNTs as active layers lead to lower $V_{oc}$ likely to be due to weak diode creation in the large area hybrid structure, due to the thin active layer of the system. Much work is needed to ascertain if the CNTs in the active layer can enhance the charge collection, either through exciton dissociation or enhanced charge transport.

B. CNTs as a charge collection interface at the electrode

A number of attempts have been made to utilize CNTs as a hole extraction layer at the transparent electrode of organic PV devices turning them into hybrid systems. SWCNTs have been incorporated at the ITO electrode by dip coating the ITO coated glass substrates and ITO coated glass substrates with a PEDOT:PSS layer, before completing the devices with a P3HT:PCBM active layer. Both these cells are reported to be highly efficient, (4.9%) however, the J-V characteristics are nonstandard making it difficult to compare device performance with existing literature [78]. Attempts have been made to grow MWCNTs directly on to ITO coated glass substrates using chemical vapour deposition [79]. Devices fabricated with P3HT:PCBM active layers on top of these ITO/MWCNT substrates result in a maximum efficiency of 0.93%, affected by an increased absorption upon MWCNT growth on the ITO coated glass substrate.

Use of a MWCNT-tetrasulfonate copper phthalocyanine nanocomposite has also been reported as a hole extraction layer for bulk heterojunction devices. Its application as a high work function hole-extracting material has resulted in 1.25% efficient P3HT:PCBM hybrid PVs by spin coating the nanocomposite before fabrication of the active layer on ITO [80]. Similar work compares the performance of PEDOT:PSS, acid functionalized MWCNTs and SWCNTs as hole extraction layers [81]. It has been shown that thin films of partially oxidized MWCNTs and SWCNTs are equally effective at facilitating hole-extraction in efficient (2.7%) P3HT:PCBM bulk-heterojunction hybrid solar cells, also achieved with PEDOT:PSS hole extraction layers.

Use of transparent MWCNT sheets as an interlayer anode electrode for tandem cells have also been reported. The work interconnects a P3HT:PCBM cell on an ITO coated glass substrate, with a copper phthalocyanine:C$_60$ cell on top through the use of MWCNT layer sandwiched by PEDOT:PSS, resulting in device efficiency of 0.31% [82].

C. CNTs as the transparent conductive oxide

Transparent electrodes from SWCNTs have been investigated as a potential replacement of the transparent electrode for the thin film PV devices after Wu et al. reported large area films in square centimeters [83]. The films were soon utilized in P3HT:PCBM bulk heterojunction systems replacing the conventionally used ITO electrodes yielding devices with nearly 1% efficiency [84]. These devices had low FF (0.30), although they were lower for ITO based reference devices as well. The device employed a PEDOT:PSS layer on top of the SWCNT layer, as a hole extraction layer. This work has been enhanced by subsequent research, where SWCNTs are blended in PEDOT:PSS for electrode fabrication [85]. Using PEDOT:PSS as the host material, better dispersion of functionalized single wall carbon nanotubes are reported to have achieved increasing efficiency for P3HT:PCBM devices to 1.3%. The FFs are also reported to show a slight improvement from 0.3 to 0.4. Subsequently, using a film transfer process, SWCNT films were fabricated with sheet resistivity at 200Ω/□. Coated with a PEDOT:PSS layer, these films result in 160Ω/□ sheet resistivity and P3HT:PCBM devices yield 2.5% efficient cells compared to devices fabricated with ITO which are 3% efficient [86]. The use of a flexible substrate for this work, poly-(ethylene terephthalate) (PET) makes the work relevant from a manufacturability point of view. Similar work with spray coated SWCNT electrodes followed by with PEDOT:PSS and P3HT:PCBM and Al has resulted in 1.5% efficient devices [87]. Devices without the PEDOT:PSS layer perform poorly at the reduced efficiency of ~0.5%. A 1.3% efficient P3HT:PCBM bulk heterojunction device has also been reported with a MWCNT transparent electrode on glass, starting with a freestanding MWCNT sheet [88].

Table III shows the most notable CNT-organic hybrid PV device parameters with respective references.

Outlook

The outlook for CNT-organic hybrid structures depends on increased functionality of the nanostructures, which would then be able to be utilized in organic systems with the required design criteria. Although CNTs promise much, consistent & repeatable techniques are necessary for good control of film thickness and CNT distribution from a number of solvent bases. These aspects are extensively studies at the moment, and advances can be expected from electrode applications as well as intermediate charge transport layers in hybrid PVs.

IV. SEMICONDUCTOR NANOWIRE ORGANIC PVs

Recent work on hybrid organic/inorganic systems involves the use of nanowires as electron acceptors [89]. Silicon nanowires grown on a silicon substrate has been transferred in to a P3HT:PCBM bulk heterojunction active layer, before deposition of an Al electrode. These devices are 1.9% efficient, but are much lower than the typical 4% for such systems [90]. Another system utilizes P3OT:MWCNT blend with Si nanowires grown on a Si wafer with best efficiency of 0.6% [91]. Si nanowires directly grown on ITO coated glass substrates have been used for Si nanowire/P3HT:PCBM hybrid cells with 0.43% efficiency [92]. CdS nanowire/MEH:PPV hybrid cells on FTO coated glass substrates have also been attempted with device efficiencies at 1.62% [93].

Outlook

Application of nanowires in organic PV systems is becoming an area of significant interest. With the use of
silicon and other semiconductor nanowires being highly photoactive, enhanced charge transport while contributing to the photocurrent can be expected from these hybrid devices. This will further raise the potential of these devices in terms of power conversion efficiency.

V. SEMICONDUCTOR QUANTUM DOT ORGANIC PVs

Semiconductor NCs with dimensions comparable to the exciton-Bohr radius of the material show vastly different properties to the bulk. This results from the change of the electronic configuration due to effects of quantum confinement. Most notably, the energy of the lowest excitonic state is observed to change inversely with the NC size. Furthermore, the densities of states become more discrete in nature demonstrating a molecular-like absorption of light. Such optical tuneability can be utilized to realize novel optoelectronic devices such as light emitting diodes, lasers and PVs. Photoactive organic materials possess high optical bandgaps which limits the light absorption capability. It is believed that the use of NCs could potentially address this critical limitation by increasing the spectral sensitivity of hybrid devices to match the solar spectrum, and increase the power conversion efficiency [11]. To this end such hybrid PV devices have reported efficiencies up to 2.8% [94, 95]. However, the NCs utilized in these reports are limited to wide bandgap Cd based chalcogenides that do not harvest near infra-red photons ($\lambda > 750$ nm) which comprise $\sim 47\%$ of AM1.5G spectrum. A possible solution for this problem is the use of narrow bandgap NCs such as Pb chalogenides (PbS, PbSe). Synthesis of PbS NCs has been reported in detail, and has been utilised for fabrication of hybrid PV devices successfully [96]. The high ionization potential of the PbS NCs (5.2 eV [97]) together with its lower band gap ($-1$ eV) makes it an attractive option to be used as a photoelectron acceptor in a hybrid device configuration. C$_{60}$ is often used as an electron acceptor with organic polymers and small molecular materials demonstrating ultrafast charge transfer rates [2]. Furthermore, the lower electron affinity of C$_{60}$ (4.5 eV [98]) can make an effective heterojunction with PbS NCs for exciton dissociation. The first experiments on this regard were carried out by fabricating bilayer devices between the PbS NCs and C$_{60}$ [99]. Oleic ligand capped PbS NCs were spin coated on ITO coated glass followed by the deposition of a C$_{60}$ layer to obtain bilayer devices. Due to the insulating nature of oleic ligands coupled with the large NC separation (~4 nm) resulted in a reduced $J_C$ of 11 $\mu$Acm$^{-2}$ under AM1.5G illumination. The $J_C$ was improved up to 340 $\mu$Acm$^{-2}$ by thermal annealing at 300 $^\circ$C, partially removing the capping ligands, studied by X-ray photoelectron spectroscopy. However, along with the desired ligand pyrolysis, thermal annealing was observed to damage the NC structure mitigating further improvement of the photocurrent. Despite the low efficiency, (0.015%), these devices showed for the first time an infrared photosensitivity up to 1600 nm with external quantum efficiency (EQE) of 0.025% in a Pb NC based hybrid device.

Subsequently, the as-synthesized oleic acid ligands were exchanged to shorter butylamine as a possible route to improve charge transport between the PbS NCs [100]. In addition, the shorter ligand capped NCs formed smoother films (2.48 nm RMS roughness) compared to oleic acid capped NCs (10.65 nm RMS roughness) on PEDOT:PSS coated ITO substrates. This, believed to be caused by chemisorption between the butylamine moiety and the PSS groups, made possible the deposition of thin films of NCs (~100 nm) without pinholes reducing shorting. The deposited NC films were further pre-treated by immersing in methanol, which removed the residual ligands resulting in a dramatic increase of the $J_{SC}$ up to 5 mA/cm$^2$ and thirty fold improvement of efficiency (0.44%) in fabricated NC/C$_{60}$ bilayer device [101]. Furthermore, an improvement in the EQE of 35% in the visible range and 5% EQE in the infrared regime was also observed. Fig. 3 illustrates a cross sectional transmission electron micrograph of the device.

A simplified model considering the photon absorption and exciton dissociation at normal incidence of light through a bilayer of NCs and C$_{60}$ has been used to estimate the maximum $J_{SC}$ expected from this configuration [136]. Under AM1.5G an approximate $J_{SC}$ of 15 mAcm$^{-2}$ is predicted using this model for the above mentioned layer thickness. Experimentally, one third of the maximum current density was obtained from the PV devices and the difference is attributed to losses in exciton dissociation and charge extraction, respectively. Better control of the active layer thickness and optimized removal of residual ligands is expected to enhance the $J_{SC}$ closer to the maximum.

However, the crucial factor affecting the overall efficiency in these NCs hybrids device is the low $V_{OC}$. The optimized PbS NC/C$_{60}$ described in [97] demonstrated a $V_{OC}$ of 0.23 V under AM1.5G. The maximum attainable $V_{OC}$ in an excitonic PV device is known to be the difference between lowest unoccupied and highest occupied molecular orbitals of the acceptor and the donor respectively [102]. Using this method the theoretical maximum $V_{OC}$ between PbS NCs and C$_{60}$ was estimated to be 0.7 V [97]. The disparity between the experimentally obtained $V_{OC}$ and the theoretical maximum is
suggested to be due to the formation of an interfacial dipole layer between the PEDOT:PSS and the PbS NCs [97]. Therefore, modification of the interfaces with appropriate electrical dipoles is a possible route to improve the $V_{oc}$ and was further explored.

Since the hole accepting interface is believed to govern the $V_{oc}$ in the PbS NC/C$_{60}$ devices, interfacial modifications were attempted during our most recent investigations. To increase the potential energy of the extracted hole, an increase of work function at the ITO/PbS NC interface was needed. Thermally deposited thin film (2 nm) of polytetrafluoroethylene (Teflon) was used as an interfacial layer for this purpose. Teflon demonstrates a high work function and has been used previously for interfacial modification in organic PV devices [103]. However use of Teflon is limited due to its low charge conductivity, extremely high surface energy and resistance towards chemical bonding.

Fig. 4 shows the comparison of the J-V characteristics of PbS NC/C$_{60}$ based devices using a 2 nm layer of Teflon as an interfacial layer measured under AM1.5G. The reference ITO/PEDOT:PSS/PbS NC/C$_{60}$/BCP/Al device, without the Teflon layer, has a $V_{oc}$ of 0.23 V, agreeing with our earlier work. Incorporating a 2 nm film of Teflon between the ITO and PEDOT:PSS increased the $V_{oc}$ by 50 mV to 0.28 V. However, the presence of a charge barrier in the form of insulating Teflon is observed to decrease the $J_{sc}$ (0.96 mA/cm$^2$) compared to the reference device (1.15 mA/cm$^2$). As can be seen qualitatively from fig 5, the FF of the Teflon incorporated device dropped to 0.33 from the 0.42 obtained for the reference. The importance of using a PEDOT:PSS layer spin coated on top of Teflon is evident from the resistive nature of ITO/Teflon/PbS NCs/PCP/Al device characteristics. PEDOT:PSS acts as a buffer layer on top of the 2 nm film of Teflon passivating its porous nature increasing the shunt resistance. Additionally, chemisorption between the PEDOT:PSS and the PbS NCs enabled the uniform film formation for improved device performance. Even though an improvement of $V_{oc}$ is observed by the incorporation of a Teflon layer, the reduction of the $J_{sc}$ and fill factor resulted in an overall poor efficiency of 0.09% with respect to the 0.11% for the reference device. All the same this technique opens the possibility for a deeper study of the interfacial modification in hybrid devices as a possible method to improve device performance.

Outlook

Utilization of infrared region of solar spectrum in solution processable PVs is currently studied extensively. Band gap tunable semiconductor NCs have been used to this end with organic electron accepting material, albeit with very low device efficiencies. It can be expected that these low energy photon harvesting hybrid devices can find applications as parts of tandem architectures, contributing towards commercial, organic-inorganic hybrid PVs. Fundamental drawback in fabricating such tandem architectures lie in the poor transport characteristics of the NCs and insufficient understanding of the charge/energy transfer between the organic-NCs. Furthermore, the toxic nature of the materials comprising these NCs may also pose a major obstacle to the development of this field. However, the prospects of fabricating extremely high efficiency PVs, harnessing the property of multi-carrier generation in NCs, will continue to strongly drive NCs based hybrid PV research in the future. Other non-toxic forms on NCs will also emerge which could potentially replace current heavy metal containing NCs.

VI. CONCLUSION

A comprehensive review of organic-inorganic hybrid PV devices is presented. Fig. 5 illustrates the progression of notable hybrid PVs over the last decade, which are extracted from tables I, II & III. Although a vast array of literature is available for different photoactive material systems/device architectures, the most successful hybrid system to date has been the bulk-heterojunction system. Most of the materials discussed have been investigated with polythiophene/fullerene derivative bulk heterojunction systems, resulting in a maximum of 6.1% for a TiO$_2$ optical-spacer utilized bulk heterojunction solar cell with PCDTBT.

Fig. 5. Progress of hybrid PVs from year 2000, in terms of efficiency.

TiO$_2$ and ZnO compete for the similar applications in these systems, with reports of stability increase of the hybrid
devices once incorporated. Use of ZnO as an electron acceptor has potential as well, considering the added benefits of stability and ease of fabrication.

Use of CNT in organic systems has shown some progress. However, much work is still necessary for the CNTs to be controllably dispersed in solvents. Once good control of the CNTs is achieved, it is envisaged that CNTs will play a major role in addressing engineering problems of organic PVs towards a solution processable, printable future. The ongoing research on QDs for longer wavelength light harvesting is also showing promise, and provides more opportunities for integration into solution processable hybrid photovoltaics.

REFERENCES


