Carbon Nanotubes for Organic Solar Cells

Power conversion efficiency with an interdigitated bulk heterojunctions structure.

IDEAL INTERDIGITATED HETER-ojunctions are considered to be the best solution for high-performance organic solar cells. However, the implementation of the ideal interdigitated structure is difficult. In this article, the general application of carbon nanotubes (CNTs) in organic solar cells is first discussed followed by the investigation of electrical roles of CNTs in organic solar cells. Based upon the current research results, we propose a novel inverted interdigitated structure for organic photovoltaic cells, which can be implemented by vertically aligned carbon nanotubes (VA-CNTs). The power conversion efficiency of organic solar cells with this interdigitated structure, verified by simulation, exceeds the state-of-the-art performance.

ORGANIC SOLAR CELLS

Harvesting solar energy using photovoltaic technology is widely recognized as an essential component of future global energy production [1]. Among the variety of platforms for converting solar energy into useful electricity, polymer-based organic photovoltaic systems, although still in their infant stage, hold the promise for large-scale commercialization. Compared with solar cells made of inorganic materials, organic photovoltaic cells are less expensive, considering that organic solar cells can be fabricated onto the substrate by high-throughput, low-cost fabrication methods such as

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roll-to-roll painting, simple brushing, or ink jet printing [2]–[4].

The research on organic photovoltaics dates back to 1959 when Kallman and Pope reported the first organic solar cell made of anthracene, which can only produce 0.2-V open-circuit voltage with energy conversion efficiency at about $2 \times 10^{-4}\%$ [5]. The major breakthrough in organic solar cells was achieved 20 years ago by Tang in his seminal work [6], which introduced the donor–acceptor bilayer device configuration. The power conversion efficiency of organic solar cells has been further improved by the so-called bulk heterojunction configuration at nanoscale (Figure 1) in which the donors and acceptors are blended together to maximize the interfacial area between them [7].

The basic operation of organic solar cells made of bulk heterojunctions can be summarized as follows: because of the low dielectric constant of organic materials, excitons (tightly bound electron–hole pairs) are initially created in the conjugated polymer after photoexcitation; subsequently, excitons diffuse to the donor/acceptor interface and dissociate to charge-transfer excitons, which can either undergo geminate recombination or be separated to free electrons and holes; then, free carriers are either transported through segregated phases and finally collected by electrodes or lost via recombination during transportation.

The major factors that limit the power conversion efficiency of organic
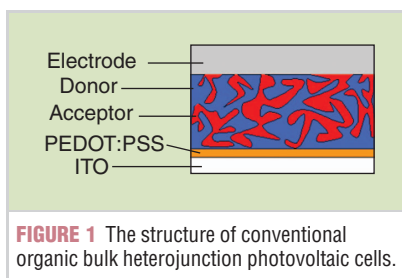
solar cells include high-exciton binding energy (0.2–0.6 eV); short-exciton diffusion length (10–20 nm); spectral mismatch problem—large gap (absorber's band gap) between the lowest unoccupied molecular orbital (LUMO) level and the highest occupied molecular orbital (HOMO) level of the organic absorbers; low open-circuit voltage—narrow gap between acceptor LUMO level and donor HOMO level of the blend (effective band gap of the blend); and low carrier mobility. The discovery of the photoinduced electron transfer from conjugated polymers to fullerene molecules [8] solved the problem of high-exciton binding energy. The photoinduced electron transfer is indeed ultrafast, resulting in a quantum yield of photoinduced charge generation of nearly 100% [9]. The introduction of bulk heterojunctions solved the problem of short diffusion length as the disordered and networked domains offer sufficient interface area for excitons to quickly find an interface to be disassociated. Simulation study [10] has shown that, under current technology, 10%

power conversion efficiency is possible by optimizing the band gap, i.e., the energy levels of HOMO and LUMO of the donor and acceptor materials.

Figure 2 shows the schematic energy potential diagram of the conjugated polymer poly-3-hexylthiophene (P3HT) as a donor and phenyl-C61-butyric acid methylester (PCBM) as an acceptor as well as an ideal donor [11]. As shown in Figure 2, a higher open-circuit voltage is possible if the HOMO level of the donor can be lowered or the LUMO level of the acceptor can be increased [12]. The efficiency can also be improved by reducing the band gap of the donor material, such as poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) [13], and therefore to cover more spectrum of the sunlight.

A recent study reports a power conversion efficiency of 6% using a polymer with band gap of only 1.6 eV [14]. Unfortunately, ideal donor is still not yet available. While research groups in material science and chemistry continue searching for low band gap materials with appropriate HOMO and LUMO levels [15], [16], other research groups spend their efforts on developing tandem organic solar cells to solve the spectral mismatch problem [4], [17], [18]. Nevertheless, the little improvement in the efficiency in tandem solar cells is shadowed by the high cost and complexity in fabricating such tandem devices. Researchers are still
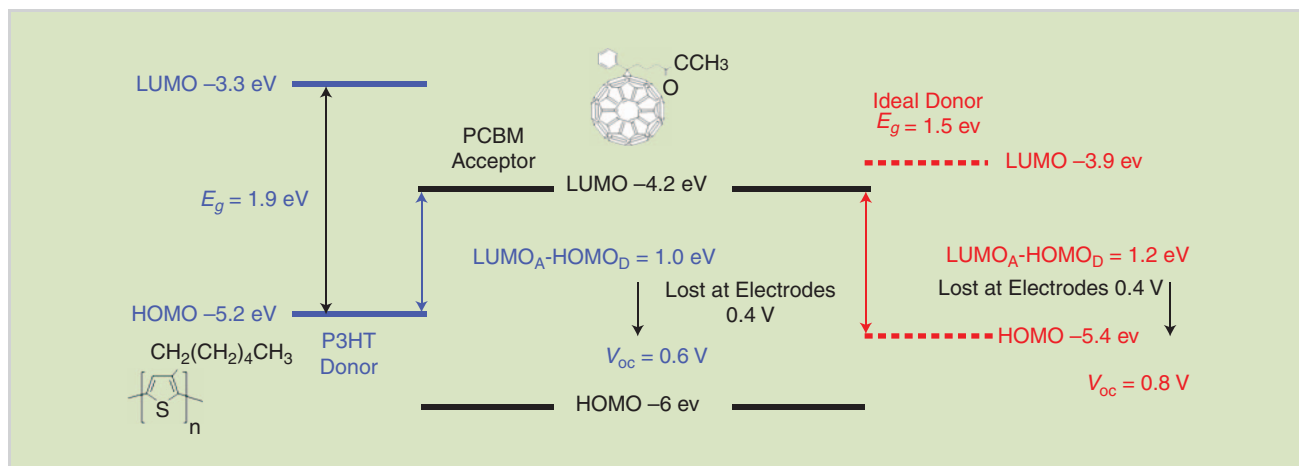

FIGURE 2 Schematic energy potential diagram of P3HT:PCBM and ideal-donor:PCBM bulk heterojunction organic solar cells.

> Harvesting solar energy using photovoltaic technology is being widely recognized as an essential component of future global energy production.

making efforts to search for the possible ways to overcome those limiting factors for best power conversion efficiency.

CARBON NANOTUBES AS ELECTRODE MATERIALS

Indium tin oxide (ITO)-coated glass is commonly used as transparent electrode in solar cells. However, ITO glass is expensive in fabrication and mechanically brittle, which increases the fabrication cost and limits the flexibility of solar cell devices [19], [20]. Moreover, because of the rough surface of ITO glass, it is imperative to coat other materials with the buffer layer such as poly (3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) in organic solar cells to smoothen the ITO surface. This buffer layer not only makes the fabrication procedure complex [20] but is also prone to degradation.

Fundamental studies have shown that CNTs are promising nanoelectronic elements that outperform conventional electronic materials [21]–[27]. Recently, it is reported that a continuous film of single-walled CNTs (SWCNTs) with high purity could replace ITO glass as a transparent electrode in solar cell devices [28]. Compared with ITO-coated glass by vacuum sputtering, it is much easier to fabricate transparent SWCNTs electrodes to reduce the photovoltaic fabrication cost in the near future. Other advantages of transparent CNT electrodes include the relatively flat surface (10-nm roughness) and the mechanical flexibility [19]. The flexibility of CNT electrodes will pave the way to fabricate organic solar cells by roll-to-roll painting. However, the relative high sheet resistance (100 Ω) and low transmittance of CNT film in the visible region need to be further balanced and optimized [29].

CNTs AS ACCEPTOR MATERIALS

The first investigation of CNTs in organic solar cells as acceptor materials can be traced back to 2002 when Kymakis and Amaratunga blended SWCNTs with poly (3-octylthiophene) (P3OT) to fabricate solar cell devices [30]. They claimed that there are mainly two effects of SWCNTs in the organic photovoltaic device: 1) to facilitate exciton dissociate at the interface between P3OT and SWCNTs and 2) to provide ballistic pathway for carrier to be transported. However, the power conversion efficiency of P3OT/SWCNTs devices is extremely low (<0.1%). The claimed reason is that there is not enough interface area between P3OT and SWCNTs to sufficiently dissociate exciton due to the insolubility and low concentration of SWCNTs in polymer (<1%) [31]. To tackle this problem, CNTs were further functionalized to increase the solubility and then used to fabricate the homogeneous thin-film organic solar cells with high concentration of CNTs [32]. However, the improvement is limited, probably due to the increased carrier recombination in the functionalized CNTs. So far, no organic solar cells using CNTs as acceptors have been reported as highly efficient. The main reason is that CNTs are donorlike materials when they are blended with the semiconducting polymers. This will be discussed in the "Electrical Role of CNTs" section.

CNTs AS ADDITIVES

It is a consensus now that the performance of organic solar cells with bulk heterojunctions is critically dependent on the nanoscale morphology of the active layer: the phase separation between donors and acceptors and the formation of interconnected percolation networks [33]. It has been found that carrier mobility can be improved by ameliorating the nanoscale morphology of the active layer through thermal annealing [34]–[37] and solvent annealing [37]–[39] to improve the crystallinity and phase separation. The annealing has to be controlled in such a way that the interfacial area between the donor and acceptor should not be significantly reduced by phase separation. Therefore, the improvement is limited because of the fact that, after annealing treatment, the carriers are still transported through the disordered organic materials, which are much slower compared with those in solid-state materials.

As the increased carrier mobility by annealing is largely attributed to the formation of percolation pathways, introduction of CNTs is also expected to increase the carrier mobility and hence improve the power conversion efficiency [30], [40]. When CNTs are blended into the active layer, free carriers can be transported through the ballistic pathways provided by CNTs [41]. Experimental studies including ours [42]–[44] have shown that the performance of organic solar cells can be dramatically enhanced after the introduction of the proper amount of CNTs to the active layer.

In our work [44], we have observed about 50% overall performance boosting when the proper amount of SWCNTs is introduced into the active layer of P3HT:PCBM bulk heterojunctions organic solar cells. As shown in Figure 3, the short-circuit current is increased by about 30% for the device with nominal 1% (the concentration is not the actual value but the value in preparing the initial solution) SWCNTs concentration in comparison with the device without SWCNTs. However, it has also been observed that adding too much SWCNTs decreases the performance of organic solar cells. When more than nominal 3% SWCNTs are added, the performance drops significantly. After further analysis, we inferred that, under low concentration of SWCNTs, the benefit of ballistic pathways provided by the CNTs outperforms the detrimental effect

of electron–hole recombination inside metallic SWCNTs and hence leads to improved performance of solar cells; under high concentration of SWCNTs, the excessive electron–hole recombination inside metallic SWCNTs severely deteriorates the performance of solar cells. Therefore, the key to using CNTs as additives to organic solar cells is to obtain pure semiconducting CNTs, which is still a major technical challenge.

ELECTRICAL ROLE OF CNTs

Our study [44] revealed that a proper concentration of CNTs increases the performance of CNT-incorporated organic solar cells, but we still lack the fundamental understanding of the electrical role of CNTs (whether they are donors or acceptors). To our knowledge, there still exists a debate on the role of CNTs in organic solar cells [45]. Some groups [31], [41], [46] assume that CNTs work as acceptor materials and, as a result, the photoexcited electrons
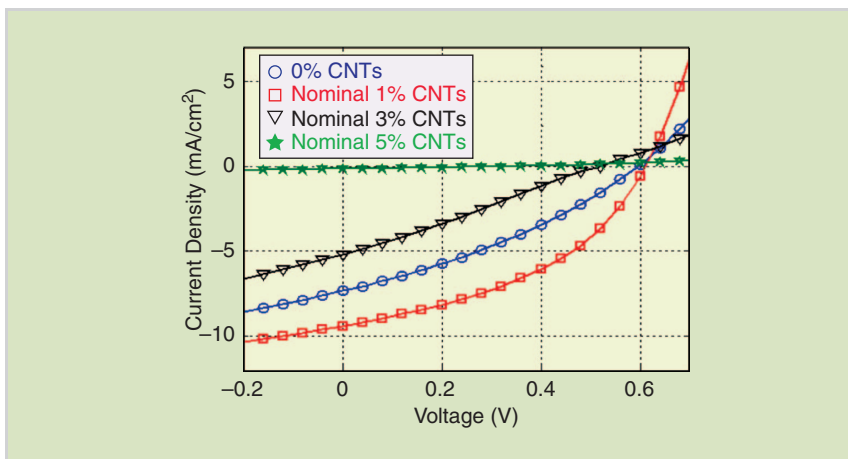

FIGURE 3 The current–voltage (J–V) characteristics of four devices were measured under an illumination intensity of 100 mW/cm^2.

will finally go to nanotubes and then be extracted by the external circuit, while others [40], [47] believe that nanotubes are donor materials and hence holes are collected by CNTs, and the hole mobility is increased.

Using a single-pass mode Kelvin probe force microscope, we have investigated

the electrical role of CNTs in P3HT:PCBM organic solar cells [48]. In our study, CNT bundles were deposited on top of the active layer to expose CNTs to the probe. Figure 4(a) is the topography of SWCNTs on top of P3HT:PCBM blended film in the dark. The surface potential images in the dark [Figure 4(b)]
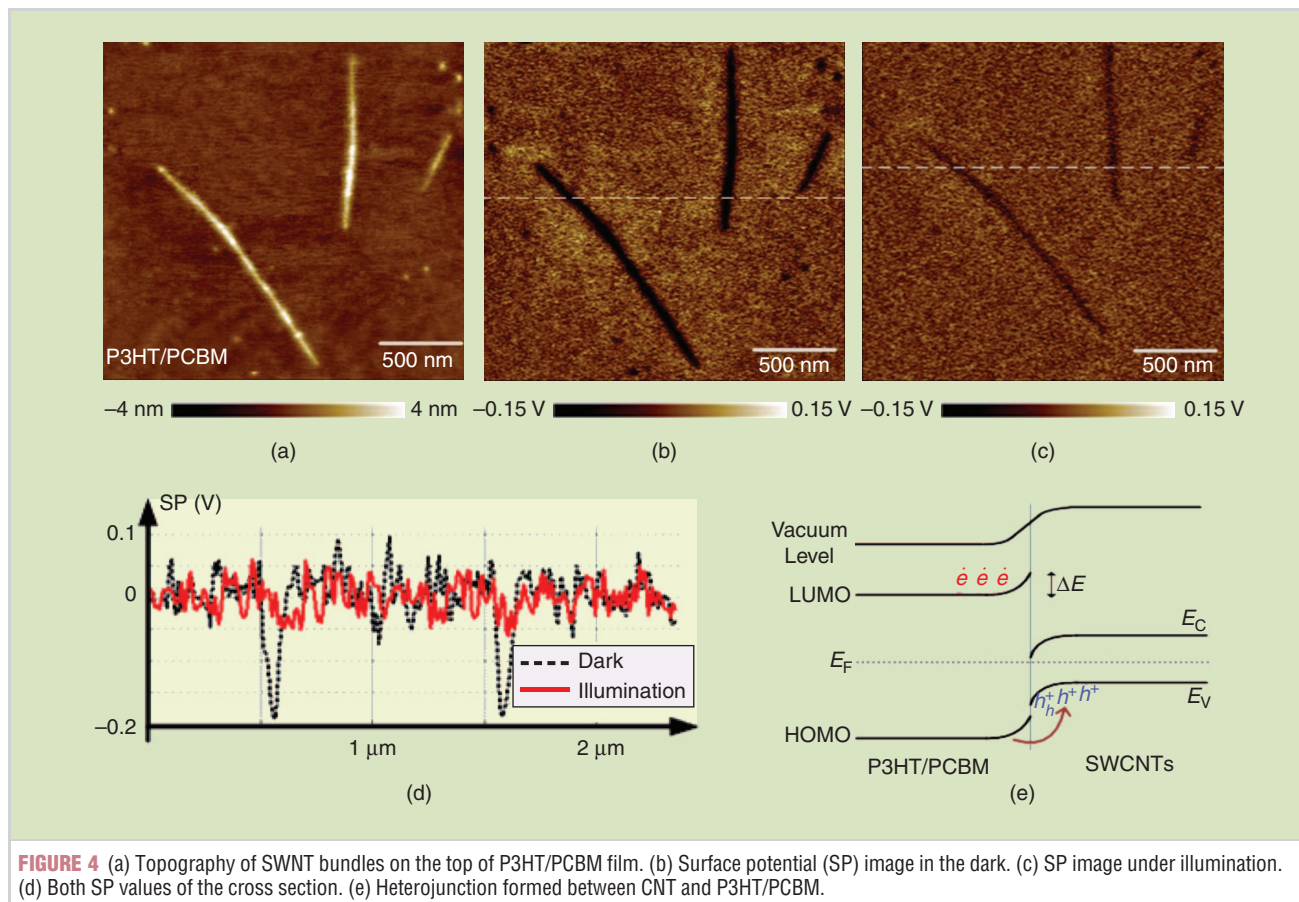

FIGURE 4 (a) Topography of SWNT bundles on the top of P3HT/PCBM film. (b) Surface potential (SP) image in the dark. (c) SP image under illumination. (d) Both SP values of the cross section. (e) Heterojunction formed between CNT and P3HT/PCBM.

and under illumination [Figure 4(c)] as well as their surface potential values of the cross section [Figure 4(d)] indicate that surface potential contrast between SWCNTs and P3HT/PCBM under illumination almost disappeared. Specifically, surface potential contrast decreases from 0.19 V in the dark to 0.04 V under illumination. The significant decrease of surface potential contrast between SWCNTs and P3HT/PCBM under illumination can only be explained when more holes are transported from the active layer (P3HT/PCBM) to SWCNTs due to the built-in potential generated by the heterojunction between CNTs and P3HT/PCBM blend, as shown in Figure 4(e). The Kelvin probe force microscopy study on P3HT:PCBM/SWCNTs demonstrated that photoinduced holes are transported to SWCNTs, while electrons are blocked because of the heterojunctions, and thus, SWCNTs work as donors. Therefore, introducing CNTs to the active layer of organic solar cells primarily increases hole mobility.

FUTURE RESEARCH OF CNTs FOR ORGANIC SOLAR CELLS

A fundamental issue of organic solar cells made of bulk heterojunctions is the lack of congruence in achieving simultaneous high efficiencies for light absorption, exciton dissociation, and charge carrier collection. The blending of donor and acceptor significantly increases their contact interface and therefore increases the exciton dissociation efficiency. However, free carriers must be transported through the phase-separated domains (either hoping or tunneling) inside the disordered blend. To minimize the recombination loss, the blend thickness has to be designed with a tradeoff between the light absorption and the carrier collection such that enough photons can be absorbed while the photoexcited charge carriers travel a small distance before extraction. Another tradeoff is on the nanoscale morphology of the blend, which has to be tuned such that it creates enough interconnected pathways for efficient extraction of charge carriers while still maintaining enough interfaces for dissociation of excitons. Even with finely tuned nanoscale morphology, the power
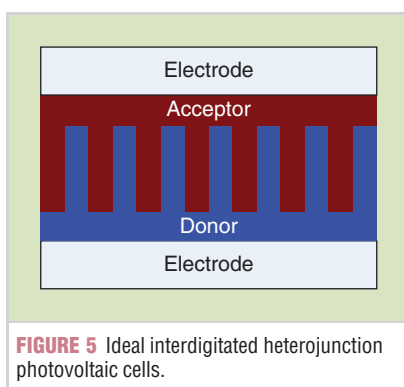

FIGURE 5 Ideal interdigitated heterojunction photovoltaic cells.

conversion efficiency is still limited because of the insufficient light absorption due to the thin active layer (less than 100 nm).

To overcome the incongruence of bulk heterojunctions, ideal interdigitated heterojunctions, as shown in Figure 5, are considered to be the best solution for high-performance organic solar cells [49]. The two phases of donor and acceptor are interdigitated in percolated highways to ensure high mobility of charge carrier transport with reduced recombination in the bicontinuous pathways. The two phases are interspaced with an average length scale of around or less than the exciton diffusion length (10–20 nm). A pure donor phase at the hole-collecting electrode and a pure acceptor phase at the electron-collecting electrode are placed to act as diffusion barriers for the wrong sign charge carriers at the respective electrodes. However, such a well-organized nanostructure is a great challenge to implement.

In recent years, several groups have attempted to mimic the ideal interdigitated heterojunctions based on porous titania [50], zinc oxide nanorod arrays [51], [52], TiO_2 nanotubes arrays [53], as well as $ZnO–TiO_2$ core–shell nanorod arrays [54]. Unfortunately, none have reported high power conversion efficiency on these devices. Vertically aligned (VA) organic polymer nanowires [55], [56] may be a good solution to make real interdigitated heterojunctions [57], [58] for organic solar cells, but these organic nanowires suffer from low carrier mobility [59].

Another critical issue of organic solar cells with bulk heterojunctions is

the short lifetime. Traditionally, the electrode made of aluminum is very much prone to oxidation, and the aluminum atoms can easily diffuse into the active layer to degrade the polymer quickly. The degradation of the interface between ITO and PEDOT:PSS also occurs frequently [60], [61]. A practical way to minimize the device degradation is an inverted structure that incorporates metal oxides such as TiO_x and MoO_3 as a diffusion barrier and use high work function metals such as Ag and Au as an anode electrode [62]–[65].

Here, we propose a novel inverted structure of organic photovoltaic cells with interdigitated bulk heterojunctions [Figure 6(a)], which can be implemented by VA-CNTs. In this structure, a layer of semiconducting polymer (polythiophene) is electrochemically polymerized on VA-CNTs to block electrons. The donor–acceptor blend is infiltrated into the gaps between these polymer-coated VA-CNTs. A layer of TiO_x on top of the blend is deposited to block holes and absorb ultraviolet light to protect the active layer. The advantages of devices based on such interdigitated heterojunctions include but are not limited to the following.

1) The proposed interdigitated structure is more practically realistic to be implemented than the ideal interdigitated heterojunctions and other interdigitated structures.

2) The interdigitated structure effectively decouples the light absorption length and the charge collection length such that both can be tuned independently for obtaining the best device performance. For example, by maintaining the spatial distance between VA-CNTs, the effective collection length can be fixed, while the effective absorption length can be increased by simply increasing the length of the CNT (device thickness). On the other side, the effective collection length can be tuned by varying the space among VA-CNTs without significantly affecting absorption.

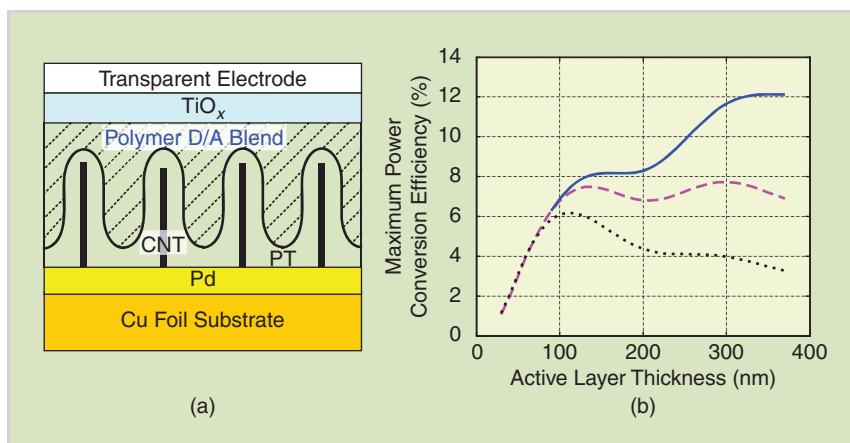3) The inverted structure will enable a longer lifetime of the device by avoiding the problem of degradation.

FIGURE 6 (a) An inverted organic photovoltaic cell with interdigitated bulk heterojunctions (BHJs) based on PCPDTBT:PCBM ([6,6]-phenyl C61-butyric acid methylester) implemented by polythiophene (PT:polythiophene)-coated VA-CNTs. (b) Comparison of power conversion efficiency of PCPDTBT:PCBM devices in three scenarios with respect to device thickness: black-dotted line for planar devices under current condition; magenta-dashed line for planar devices with hole mobility matches P3HT:PCBM devices; blue-solid line for devices with interdigitated BHJs under mobility-matched condition.

Our simulation study [Figure 6(b)] suggests that the power conversion efficiency of organic solar cells with the proposed interdigitated bulk heterojunctions can exceed 12% when a small band gap polymer donor, PCPDTBT, is used. However, such structure requires VA-CNTs to be well controlled over spacing and length. This calls for further study on the growth of VA-CNTs.

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