



# Bulk heterojunction polymer solar cell and perovskite solar cell: Concepts, materials, current status, and opto-electronic properties

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## ABSTRACT

Recently, the demand for sustainable and clean energy resources has led to an intense growth in the development of different types of solar cells. Among all types of photovoltaics, polymer solar cells and perovskite solar cells have received extensive attention because of their potential for achieving cheap, light weight, facile and fast fabricated devices. Bulk heterojunction polymer solar cells have been considered for about two decades, while perovskite ones have introduced just for 7 years. Comparison of these devices indicates a higher performance for perovskite solar cells. This review starts by comparative introducing of configurations, materials, mechanisms, fabrication methods, crystalline natures, band gap tuning, and the current status of the photovoltaic performances of polymer and perovskite solar cells. We emphasize the importance of the optoelectronic properties of the absorber layers including absorption coefficient, exciton binding energy, exciton dissociation, exciton and charge carrier lifetimes, charge carrier mobility, and exciton and charge diffusion lengths. Suggestions regarding needed improvements and future research directions in the field of polymer and perovskite solar cells are provided.

## 1. Introduction

In recent years, the demand for sustainable and clean energy resources has led to an intense growth in the development of solar cells that directly convert sun light into electricity. Solar cell is one of the most promising technologies for harvesting the sun energy as the largest noncarbon-based natural source. Photovoltaic technology should meet three factors of efficiency, stability, and low cost to reach the industrial demonstration (Krebs, 2008). Silicon photovoltaics as the first generation solar cells are stable, with long lifetime around 25 years and power conversion efficiencies (PCE) as high as 20%, but their fabrication processes are too complex and expensive (Krebs, 2008). Photovoltaic uptake has been growing to introduce sufficient alternatives to the conventional solar cells. The lowest cost and simplest fabrication method for solar cells is solution processing that provides roll-to-roll printing as a beneficial method for large scale production. Some of the most promising technologies utilized for decreasing the manufacturing costs of solar cells are based on solution process,

including dye-sensitized solar cells (DSSCs) (Ghadiri et al., 2010), QD-sensitized solar cells (QD-SSCs) (Ghoreishi et al., 2014), small molecule organic or polymer solar cells (Arabpour Roghabadi et al., 2016a, 2016b, 2016c; Ghasemi Varnamkhasti et al., 2012; Tavakkoli et al., 2011), and perovskite solar cells (PSCs) (Arabpour Roghabadi et al., 2016a, 2016b, 2016c). Among all types of photovoltaics, bulk heterojunction polymer solar cells (BHPSCs) and PSCs have received extensive attentions because of their potentials for achieving cheap, facile and fast fabricated, and light weight solar cells. BHPSCs have been considered for about two decades, while PSCs have introduced just for 7 years. Comparison of these two types of photovoltaics shows a higher performance for PSCs. In this review, first, a history of both devices is reported and their configurations and mechanisms are introduced. The common applicable materials for their layers are presented and compared. In addition, the opto-electronic properties of their absorber layers are reviewed and compared.

There are several points that should be mentioned:

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1. This review mainly focuses on the comparative introducing of two types of third generation solar cells that are polymer and perovskite (PSK) based devices.
2. This review searches the reason for the available gap between the performances of the two categories in the opto-electronic properties of their active layers.
3. To compare the photovoltaic performances of BHPSCs and PSCs, some of the high efficient devices from these two categories are selected and presented.
4. Although both BHPSCs and PSCs could be fabricated based on different structures such as single junction and multi junction devices, in this review, the single junction configuration is mostly attended.

## 2. History

### 2.1. Bulk heterojunction polymer solar cells (BHPSCs)

The use of organic (small molecules, polymers) and organic–inorganic materials in the optoelectronic devices such as solar cells and organic light emitting diodes has rapidly grown due to their light weight, low cost, and facile fabrication technologies. BHPSCs are almost nano-film devices that their active layers are based on semiconductor polymers. In 1993, the first polymer heterojunction solar cell based on Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]/Buckminsterfullerene (MEH-PPV/C60) was made by Sariciftci et al. (1993). In this two-layer device, the heterojunction which formed at the interface of MEH-PPV as a donor and C60 as an acceptor, led to a PCE of 0.04%. Several two-layer heterojunction solar cells were made by varying donor and acceptor materials and optimizing the structures. Increasing the donor-acceptor interface for achieving an efficient charge separation led to introduce the bulk heterojunction architecture. In this structure, donor and acceptor are mixed together to form a bi-continuous interpenetrating network with a high interfacial area. In 1995, Yu et al. fabricated the first BHPSC by blending MEH-PPV polymer with C60 (Yu et al., 1995). The performance improvement, achieved by using the bulk heterojunction configuration, has introduced this configuration as a standard architecture for these devices. Up to now, numerous BHPSCs were made based on this architecture by varying conjugated polymers as donors and utilizing different types of acceptors such as fullerene derivatives, non-fullerene derivatives, and nanoparticles. Nowadays, the PCE of single-heterojunction polymer solar cells reached up to 13% (Fig. 1) (Zhao et al., 2017).

The most developed conjugated polymers for BHPSCs can be divided in three categories: poly(phenylenevinylene) derivatives (PPV) (Yu et al., 1995), poly(thiophene) derivatives, and polyfluorene derivatives (Krebs, 2008). Fig. 2a shows the chemical structures of some of the used polymers and acceptors in BHPSCs. In the early stage of polymer photovoltaic research, devices were made by PPV derivatives with band gaps larger than 2 eV (Yu et al., 1995). The best achieved

PCE for polymer devices based on PPV derivatives is around 6% (Mustapha et al., 2016). The second category, poly(thiophene) derivatives with lower band gap ( $\leq 2$  eV), is the group that widely used in polymer photovoltaics especially poly(3-hexylthiophene) (P3HT) with a band gap of 1.9 eV. In poly(thiophene) based devices, the PCE reached up to 13% (Zhang et al., 2016a, 2016b; Zhao et al., 2017). Polyfluorene derivatives are the third family of conjugated polymers used in BHPSCs with high thermal stabilities. However, their absorption ranges are limited by their high band gaps, they are promising candidates for achieving high  $V_{OC}$  because of their low highest occupied molecular orbital (HOMO) levels (Halls et al., 2000; Svensson et al., 2003).

Different types of acceptors are used in BHPSCs which can be divided into the organic acceptors and inorganic acceptors (Fig. 2b). Organic acceptors include fullerene derivatives (e.g. PCBM and indene- $C_{70}$  bisadduct (IC<sub>70</sub>BA) (Fan et al., 2012; Xu et al., 2013)), non-fullerene derivatives including small molecules (e.g. ITIC (Zhao et al., 2016a, 2016b, 2016c, 2016d), TPE-DPP (Liu et al., 2016a), D4 (Rananaware et al., 2016), N7 (Raynor et al., 2016)), and conjugated polymers such as Cyano-PPV (Yu and Heeger, 1995) and HP-PDI (Zhang et al., 2017). The common utilized inorganic acceptors are quantum dot nanocrystals such as CdSe (Arabpour Roghabadi et al., 2017a, 2017b; 2016a, 2016b, 2016c) and PbS (Lu et al., 2016) and metal oxide nanostructures such as ZnO (Yong-June Choi et al., 2011) and TiO<sub>2</sub> (Li et al., 2011a). However, the optoelectronic properties of the inorganic acceptors can be in the higher levels than the organic ones, devices with the organic acceptors achieved better performance. Because, there are fundamental differences between the process parameters and the nature of the charge collection in the polymer/PCBM, polymer/non-fullerene derivatives, and polymer/nanocrystals heterojunctions (Li et al., 2011b). Although the bulk inorganic semiconductors have high carrier mobilities, polymer/inorganic nanocrystals films possess low carrier mobilities because of the abundant surfaces and complex interfaces (Roghabadi et al., 2016). The limited absorption of solar spectrum, difficult functionalization for modifying the energy levels, morphological instability, and comparatively high production cost of fullerene derivatives have led the research progress to use non-fullerene acceptors (Rananaware et al., 2016). There are several non-fullerene acceptors based on organic small molecules such as DPP derivatives that exhibited PCEs up to 13%. It was proposed that more efficient novel non-fullerene acceptors will be developed and much higher PCE values will be obtained in the near future (Chen and Zhang, 2017; Raynor et al., 2016; Zhao et al., 2017).

### 2.2. Perovskite solar cells (PSCs)

Organic–inorganic hybrid PSKs were first used as visible-light sensitizers in dye-sensitized liquid-junction solar cells in 2009. In these devices, the dye pigment in DSSCs was replaced with two organic-inorganic hybrid halide-based PSKs,  $CH_3NH_3PbBr_3$  and  $CH_3NH_3PbI_3$ . Extremely unstable devices were achieved with PCEs around 3% that were much lower than the PCEs of the devices based on Ru-based molecular dyes (Jung and Park, 2015; Kojima et al., 2009; Petrović et al., 2015). Therefore, the PSK sensitizers did not attract much attention due to the obtained low efficiency and stability. Two years later, the PCE of the perovskite-sensitized photocells reached 6.5% by optimizing the thickness of photoanode and modifying interfaces. It was shown that how to form the PSK sensitizer on the thinner TiO<sub>2</sub> film (Im et al., 2011). These works were not cited until reporting the fabrication of more efficient and stable PSC in 2012. In fact, the main problem in these liquid-junction-sensitized devices was their short lifetime (a few minutes), because the PSK was easily dissolved in liquid electrolyte. This problem encouraged the researchers to concentrate on the solid-state hole transporting materials (HTM). In 2012, the device with 9.7% PCE was made by utilizing 2,2',7',7'-tetrakis-(N,N-dimethoxyphenylamine)-9,9'-spirobifluorene (spiroMeOTAD) as a solid-state HTM (Kim et al., 2012). After obtaining this advance, hybrid organic-inorganic PSKs were significantly attended by researchers. Because of the hybrid

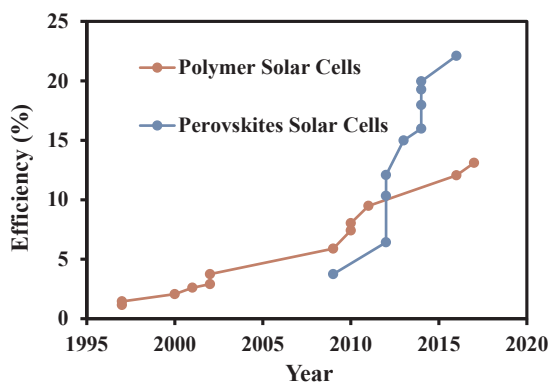


Fig. 1. Progress in BHPSCs and PSCs efficiencies (NREL).

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