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Review Article

Review of Polymer, Dye-Sensitized, and Hybrid Solar Cells

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The combination of inorganic nanoparticles semiconductor, conjugated polymer, and dye-sensitized in a layer of solar cell is now recognized as potential application in developing flexible, large area, and low cost photovoltaic devices. Several conjugated low bandgap polymers, dyes, and underlayer materials based on the previous studies are quoted in this paper, which can provide guidelines in designing low cost photovoltaic solar cells. All of these materials are designed to help harvest more sunlight in a wider range of the solar spectrum besides enhancing the rate of charge transfer in a device structure. This review focuses on developing solid-state dye-synthesized, polymer, and hybrid solar cells.

1. Introduction

Nowadays, the population and technology are growing rapidly. Countries and other emerging economies are experiencing shortage of fossil fuel resources as experienced by many other developed countries. Due to shortage of raw material of nonrenewable energy, it is most important to develop inexpensive and clean energy sources to meet human demand. Solar energy is well known as one of the clean and available energy sources. The free radiation energy obtained from the sun can be used in many applications. The importance of solar energy application can be seen rapidly in the field of electronic devices such as photovoltaics, which is continuously growing from year to year.

The photovoltaic device converts sunlight into electrical energy. Inorganic semiconductors based solar cells dominate about 70% of world market today. The most popular one is silicon-based solar cells that have high stability along with high power conversion efficiency [1]. Along with that, the second-generation solar cell consists of thin films such as CdTe, CIGS, and amorphous silicon capturing 25% of the world market. Meanwhile, works in the production of organic photovoltaic cells (OPVs) and dye-sensitized solar cells (DSSC) are still in the development phase [2]. OPVs have attracted much attention in recent years due to their ease of fabrication and manipulation, flexibility, and low cost. Nevertheless, the efficiency of OPVs at the moment is low because of the limited range of absorption of organic materials, poor charge transport, and poor stability. Hence, more studies should be conducted to improve the stated problems in terms of materials innovation and device's structure optimization [1]. One of the most promising devices is based on bulk-heterojunction polymer solar cells. Normally, the active layer of bulk-heterojunction solar cell consists of different conjugated polymer, which acts as an electron donor and blends with an electron acceptor based on fullerene derivatives such as [6,6]-phenyl-C_{61}-butyric acid methyl ester, PCBM. By tuning the morphology of this layer, we can increase the device efficiency. The type of material used as active layer should be closely matched to the maximum peak of the solar spectrum, which is ~670 nm to get high power conversion efficiency (PCE) [3].

2. Organic Solar Cell

A few decades ago, considerable attention has been paid to the research in the production of conductive polymers and organic molecules [4]. When the scientists began to think to produce a new solar cell, they chose to construct the device using organic materials as shown in Figure 1. This structure is known as bilayer solar cell.

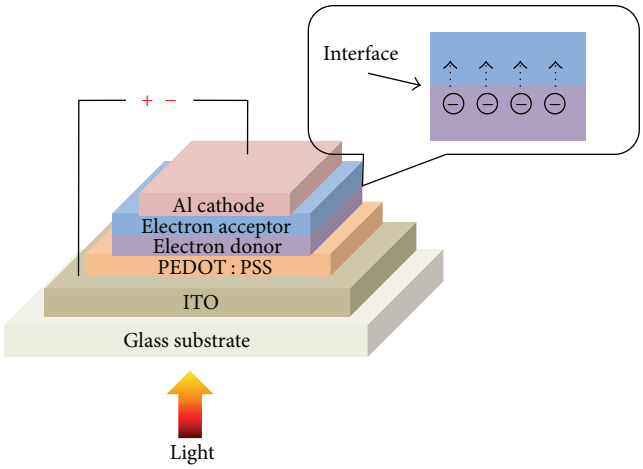

Figure 1: Typical device structure of bilayer solar cell. The charge dissociation only occurs at the interface layer between the donor and acceptor material.

The typical device structure of a bilayer solar cell has a sandwiched architecture and it is fabricated layer by layer. As a basic solar cell, the device consists of four layers such as anode layer, contact material of poly(3,4-ethylenedioxythiophene) : poly(4-styrenesulfonate) (PEDOT : PSS), the active layer, and the cathode. The fundamental mechanism of OPV can be explained by photoexcitation and charge separation at the interface when the energy is sufficient, as shown in Figure 1. Photogenerated excitons diffuse through the donor to the interface between the donor and the acceptor. The excitons at the interface dissociated into electrons and holes. Subsequently the electrons diffuse through the acceptor material towards the cathode. Subsequently the electrons enter the external circuit to generate electrical flow and complete the cell.

One of the reasons for using organic materials is to reduce environmental problems, which is the major concern nowadays. At the same time, using organic materials should reduce production costs, provide a large surface area for light absorption [5], and consume less energy. Organic solar cell is divided into two types—polymer solar cell and small molecule solar cell. These two types of organic electronics materials are essential for light absorption and charge flow. General differences between these solar cells are the materials used in accordance with their constituent molecules, either small or large (polymers), as well as their preparation technique. Spin coating or ink-jet printing is the common technique to fabricate polymer solar cell, whereas small molecule solar cells are processed by thin film deposition techniques in vacuum condition [4].

2.1. Bulk-Heterojunction Solar Cell. The concept of bulk-heterojunction solar cell (Figure 2) was introduced to improve the performance of organic bilayer solar cells (Figure 1). This is because, in the organic bilayer structure, only a small number of excitons are collected at the interface of donor and acceptor materials [6]. In contrast to bilayer structure, the active layer (a layer where the charge dissociates into electron and hole) in the bulk-heterojunction structure is extended. This is a result of mixing an electron donor and an electron acceptor together. This is to increase light absorption and improve efficiency of the optical thickness of the film while maintaining the current flows [4, 7, 8]. In other words, the separation of charge in the bulk-heterojunction structure occurs in the whole surface of active layer compared to the bilayer structure that only occurs in the interlayer. Thus, the tendency of excitons dissociation is higher in the bulk-heterojunction type.

The major issue for OPV is to find suitable materials of the active layer to improve the interface, charge separation, excitation, and efficiency. A polymer based on 2,1,3-benzothiadiazole and pyrrolo[3,4-C]pyrrole-1,4-dione has been found to be suitable for improving the efficiency of OPV [9].

2.1.1. Polymers Based on 2,1,3-Benzothiadiazole (BT). This class of BT derived polymers, poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] or PCPDTBT, was introduced as the first low bandgap polymer in organic solar cell [4, 5]. PCPDTBT is a subclass of π-conjugated polymers having alternating carbon single and double bonds. It has received much attention for photovoltaic applications since the discovery of their conductive properties by Chiang et al. [10]. PCPDTBT becomes a promising active layer material recently due to its desired bandgap of ~1.5 eV. This compound can extend its spectral absorption near the infrared region, which can increase the overall photovoltaic performance of the solar cells. The active layer mixed of PCPDTBT and PCBM has been reported to give a power conversion efficiency of 3.2% [4]. The combination of PCPDTBT and PCBM was found to improve the electron transfer as well as the light trapping. Following optimized morphology of the blend PCPDTBT : PCBM using diiodooctane (DIO) or 1,8-dithiooctane (ODT), the efficiency increases to ~5% [7]. Compared to the popular polymers such as poly(3-hexylthiophene-2,5-diyl) or P3HT with an optical band gap of 1.9 eV, photons harvesting in the solar spectrum, particularly for the long-wavelength red and infrared region, is not so effective. The cell only exhibits 2.6% power efficiency. Therefore, the result is that using material with ideal band gap is one of the key factors to enhance efficiency [8]. Many effects such as light trapping and electron transfer as well as electron mobility influence the efficiency of the solar cells. In a previous study, PCPDTBT : PCBM bulk-heterojunction composites were compared to those of P3HT : PCBM composites because of their photophysics similarity [11]. It was pointed out that when PCPDTBT was fully optimized with PCBM, photovoltaic efficiency above 5% could be achieved because of the superior transport properties of polythiophene-based materials and the better match of the spectral response to the solar emission spectrum. Table 1 shows the comparison of different elements in a protective layer and their J_{sc}, V_{oc}, FF, and MPP (maximum power point), respectively.

Another polymer with 2,1,3-benzothiadiazole (BT) that has been widely used is poly(2,6-(*N*-(1-octylynonyl)dithieno[3,2-*b*:20,30-*d*]pyrrole)-*alt*-4,7-(2,1,3-benzothiadiazole)), PDTPBT, which exhibited lower bandgap and higher HOMO

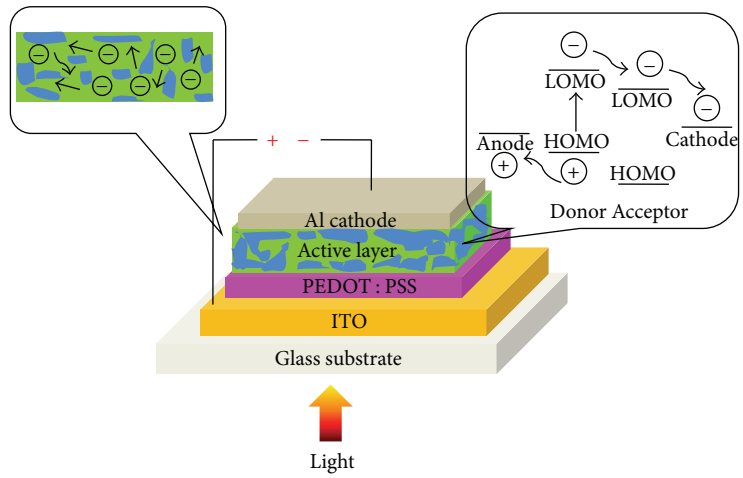

Figure 2: Typical device structure of bulk-heterojunction solar cell. The charge dissociation occurs at the whole surface of the active layer.

Table 1: Photovoltaic properties of PF10TBT : PCBM, P3HT : PCBM, and PCPDTBT : PCBM solar cells under 1 sun white light illumination [63].

Photoactive layer	Type	J_{sc} (A/m^2)	V_{oc} (V)	FF (%)	MPP (mW/cm^2)
PF10TBT : PCBM	Conventional	67.3	0.96	61	4.0
	Inverted	66.1	0.95	59	3.7
P3HT : PCBM	Conventional	87.6	0.57	66	3.2
	Inverted	91.5	0.59	60	3.2
PCPDTBT : PCBM	Conventional	91.8	0.61	50	2.8
	Inverted	91.4	0.58	50	2.6

PF10TBT: poly[2,7-(9,9-didecylfluorene)-*alt*-5,5-(4,7-di-2-thienyl-2,1,3-benzothiadiazole)].

level 1.4 eV and −4.6 eV, respectively, compared to PCPDTBT. However, due to its high HOMO level, less V_{oc} can be exhibited from PDTPBT : PCBM based solar cell. This factor limits the photovoltaic performance tremendously. The high HOMO level of the active layer implied that the electrons excited are high where many electrons have enough energy to migrate, but the reduced V_{oc} will affect the overall efficiency of the cell. Furthermore, the idea of inserting the thiophene units to modify the 4- and 7-positions of BT named as [5,5-(4,7-di-2′-thienyl-2,1,3-benzothiadiazole)] or DTBT is to gain high efficient photovoltaic effect like PCPDTBT. Several DTBT based conjugated polymers are shown in Figures 3 and 4 and according to the previous studies, all the DTBT polymers exhibited PCEs about 5–7% as listed in Table 2 [9]. Interestingly, the highest values of V_{oc} in OPV cells are achieved from PCPDTBT 0.62 V [7], poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)], PCDTBT 0.88 V [12], and poly[4,8-bis(2-ethylhexyl-2-thenyl)-benzo[1,2-b:4,5-b′]dithiophene-alt-5,5′(4′,7′-di-2-thienyl-2′,1′,3′benzothiadiazole)], PBDTDTBT 0.92 V [13]. The outcome indicated that by blending DTBT, V_{oc}, and the efficiency of the cells can be improved. As a result, the structure is modified and the electron transfer is improved. At the same time, more light is captured and the HOMO level of the cells is improved leading to higher V_{oc} and efficiency in OPVs.

2.1.2. Pyrrolo[3,4-C]pyrrole-1,4-dione- (DPP-) Based Polymers. Strong absorption bands in the visible range originate from the DPP and its derivatives. Bürgi et al. [14] reported that the DPP-based polymers have a mobility of 0.1 cm^2 V^{-1} s^{-1} for both holes and electrons. Since 2008, many low bandgap polymers were successfully synthesized and one of them was polythiophenes diketopyrrolopyrrole, PTDPP [9]. By extending the conjugation of the backbone through Suzuki cross-coupling polymerization, this polymer achieved about ~1.3 eV of bandgap and 4.7% of efficiency. Another good example from DPP-based polymer is PPDTDPP which possesses a bandgap of ~1.40 eV and efficiency of 4% which is shown in Table 2. The corresponding LUMO and HOMO of each polymer given in Table 2 are illustrated in Figure 5.

3. Dye-Sensitized Solar Cells

There are two types of dye-based solar cells. First is dye-sensitized solar cell, DSSC, shown in Figure 6. The basic structure of a DSSC involves a transparent network n-type semiconductor of TiO_2. The surface area of the network is designed to be huge and is covered everywhere with a monolayer of a dye. The dye acts as the absorber and the electrolyte is then used to permeate the resulting coated network structure to set up a conduit between the dye and anode (platinum, Pt). The dye absorbs light producing excitons, which dissociate at the dye-semiconductor interface,

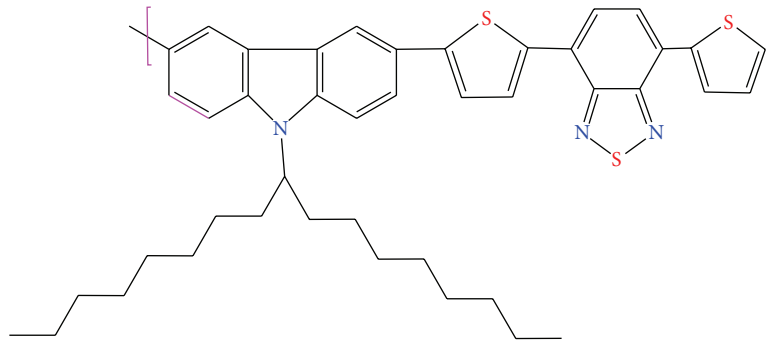

Figure 3: The molecular structure of PCDTBT [66].

Table 2: Properties and device characteristics of polymers.

Polymer	E_g (eV)	HOMO (eV)	LUMO (eV)	J_{sc} (mA/cm^2)	V_{oc} (V)	PCE (%)	Reference
PCPDTBT	1.40	−5.30	−3.57	16.2	0.62	5.5	[7]
PCDTBT	1.88	−5.50	−3.60	10.60	0.88	6.10	[12]
PBDTDTBT	1.75	−5.31	−3.44	10.70	0.92	5.66	[13]
PTDPP	1.30	−5.17	−3.16	11.80	0.65	4.70	[64]
PPDTDPP	1.40	−5.10	−3.40	11.30	0.61	4.00	[65]

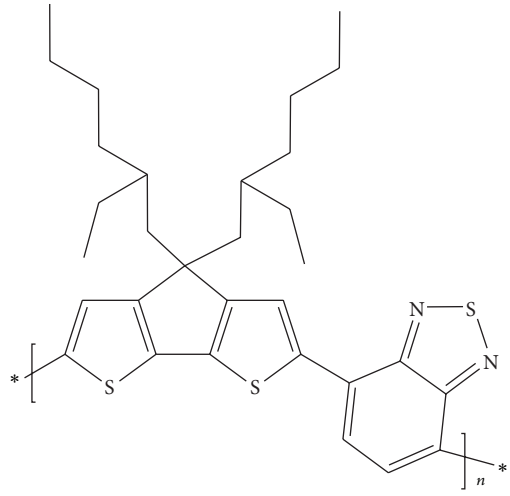

Figure 4: The molecular structure of PCPDTBT [67].

resulting in electrons for the semiconductor and oxidized dye molecules that must be reduced and thereby generated by the electrolyte. The transparent semiconductor network provides the path to the cathode (transparent conducting oxide, TCO) for the electrons. The liquid electrolyte is the pathway from the anode for the reducing species, which provide electrons for the oxidized (hole-bearing) dye molecules.

Second is the solid-state dye-sensitized solar cell, ss-DSC, in Figure 7. As with DSSC, the basic process of this kind of solar cells needs at least four key components, which are light absorption (dye), exciton diffusion, exciton dissociation, and electron transport to anode and cathode. In an organic solar cell, van der Waals forces attach the molecules. When the cell absorbs light, excitons are formed. Due to electrostatic binding of excitons, they will not easily dissociate to electron-hole pair unless the excitons gain sufficient energy for dissociation. After the dissociation process, the electron is transferred to the lowest unoccupied molecular orbital (LUMO), leaving behind a hole. Within that time, the electric field causes the electron to move to the electrode. The final electric current yield from solar cell depends on the total number of the collected charges in the electrode. This number corresponds to the fraction of photons absorbed, the fraction of electron-hole pairs that dissociated, and the total charges that reach the anode and cathode, respectively. The charge carriers need a net driving force to reach the electrodes. This force is produced by the gradient in the electrochemical potentials of electrons and holes [15]. Dye helps to cover the defect in nanostructure by injecting more electrons and prevent charge recombination. Dyes typically have light-harvesting portion to attach to the semiconductor surface. Another portion is acidic ligands to increase the solubility in solution and reduce aggregation [16]. Sometimes when aggregation occurs, the dye molecules are tightly packed that cause their wavefunction to overlap. This will affect their electronic character that often causes quenching between the dyes molecules in the excited state before electron can be transferred [17]. Finally, electrons and holes move to the anode and cathode to generate electricity.

3.1. Dye in Dye-Sensitized Solar Cell. Instead of using liquid electrolyte in dye-sensitized solar cells, solid-state dye-sensitized solar cells (ss-DSCs) use solid hole conductors that are typically made from either small molecules or semiconducting polymers. The problem faced by ss-DSCs is incomplete light harvesting, which reduces the internal quantum efficiency and results in lower current densities

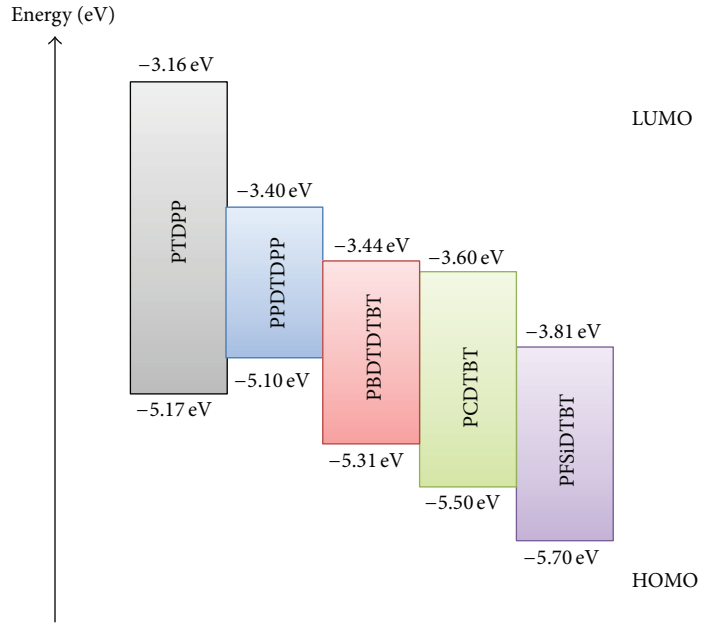

Figure 5: The corresponding energy diagram of the polymers given in Table 2.

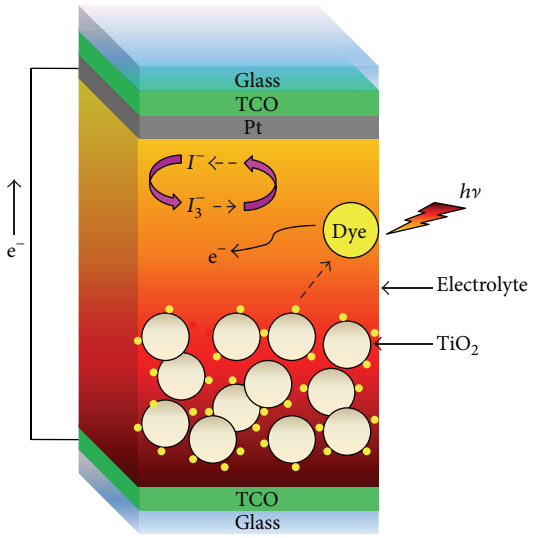

Figure 6: Dye-sensitized solar cell, DSSC.

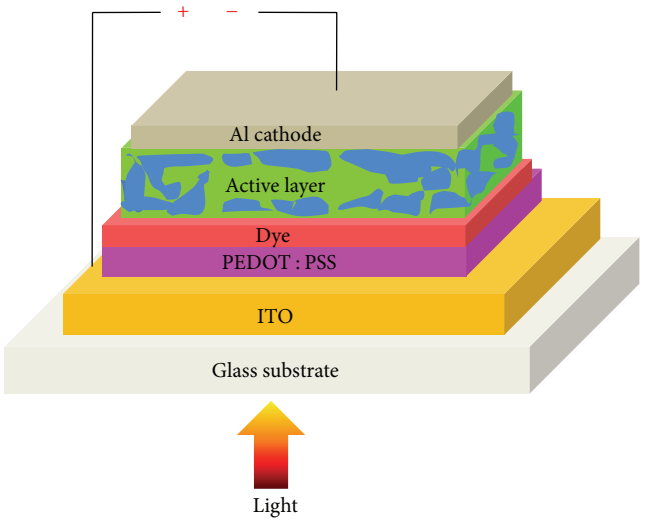

Figure 7: Solid-state dye-sensitized solar cell, ss-DSC.

than liquid-based dye-sensitized solar cells [17]. This type of solar cell also suffers from unsuitable use of p-type materials as a hole collector. This is because of the nonavailability of common p-type material. Other problems include high degradation rate of p-type material, difficulty in depositing at low temperature (high temperature will destroy the dye), and interface issues between the hole collector and the dye and the most crucial is to find an ideal dye as photosensitizer with suitable bandgap with less degradation.

In order to improve the efficiency of the cell, all the problems mentioned needed to be solved. The problems can be tackled by modifying the structure of the electron collector and enhancing the surface area increasing the light absorption. By modifying the structure, the interface between the layers can be improved. Finally, a suitable dye should be found that can absorb light in spectral range of 650–940 nm [17].

3.2. Metal Complexes Dyes. Metal complexes based dyes such as ruthenium (Ru) complexes are the best-recorded dye in photovoltaic properties. The first use of Ru complexes with carboxylated bipyridine ligands was in 1979 [18]. In 1985, Desilvestro and colleagues used a similar dye with three carboxylated bipyridine ligands and successfully obtained dye-sensitized solar cell with an IPCE of 44% [19]. As shown in Figure 8(a), N3 dye formed when thiocyanate, SCN, was

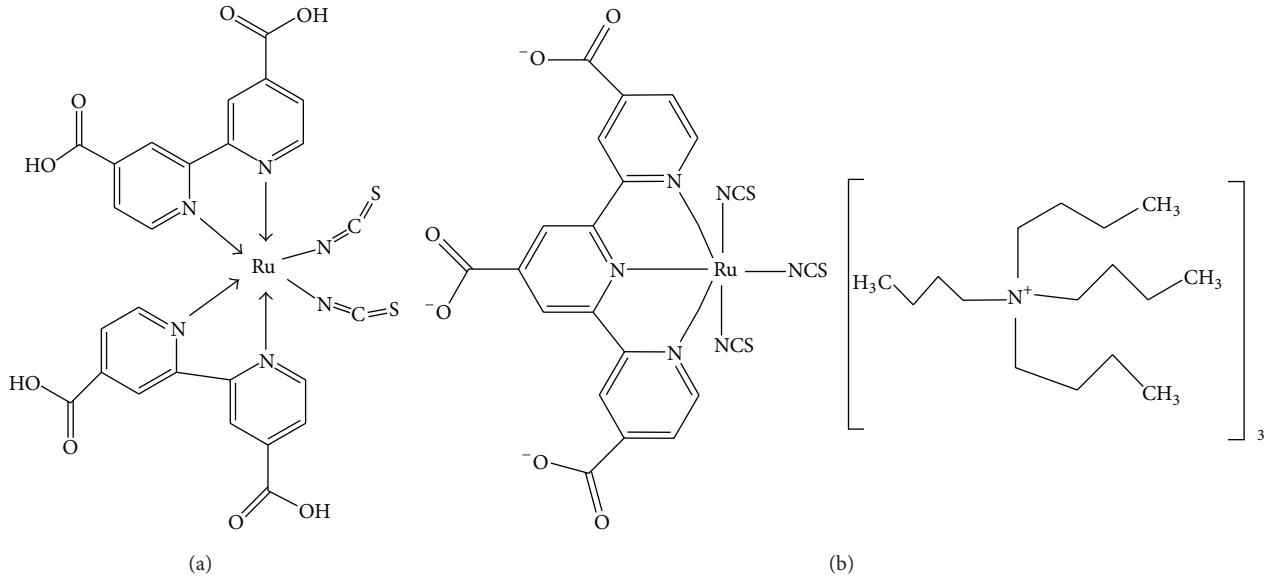

Figure 8: The molecular structure of (a) N3 dye [68] and (b) black dye [69].

inserted in Ru complexes: *cis*-$(SCN)_2$bis(2,2′-bipyridyl-4,4′-dicarboxylate) ruthenium (II). This dye was found to exhibit broad visible light absorption spectrum and IPCE spectrum extending to 800 nm, long excited state lifetime ~20 ns, and good adsorption on the semiconductor surface due to binding with four carboxyl groups leading to 10% of efficiency [20]. Usually, N3 was used to design other Ru-based photosensitizers and used as a reference dye for dye solar cell (DSCs) [21].

One of the ways to improve the efficiency of DSCs is to change the ligands of Ru complexes and optimize the photosensitizers. As already known, extending the spectral response region of the sensitizers to be near-IR region will improve the efficiency of the cell. Thus, Nazeeruddin et al. [22] designed the "black dye" also known as N749. Figure 8(b) illustrates its molecular structure. This type of dye has three thiocyanato ligands and one terpyridine ligand substituted with three carboxyl groups at Ru. IPCE spectrum was extended to 920 nm (the near-IR region) and 10.4% conversion efficiency obtained with J_{sc} of 20 mA/cm^2, V_{oc} of 0.72 V, and FF of 0.7, respectively [23].

3.3. Organic Dyes. For the past few years, work has been carried out to develop metal-free organic dyes as an alternative to the Ru complexes. The reasons are that the molecular structures of organic dyes are in diverse form and can be easily designed and synthesized. The interesting property of organic dyes is higher molar extinction coefficient compared to Ru complexes, making them attractive for thin film and solid-state DSCs applications. The advantage of higher extinction coefficient is that the organic dyes do not need thick mesoporous films as with Ru for complete light harvesting [24]. In addition, this type of metal-free organic dyes produces less environmental effects and cost saving [21]. Several researchers synthesized a dye named C220 in 2011. In their research, they compared C220 (Figure 9(a)) to a standard based dye Z907 (Figure 9(b)) and found the maximum absorption coefficient of C220 was five times higher than that of Z907, which means C220 absorbs a wider range of light than Z907. The highest efficiency reported by their group based on dye C220 solid-state dye-sensitized solar cell was 6.8% at AM 1.5 G solar irradiation (100 mW/cm^2). C220 dye achieved nearly 100% electron injection efficiency and has better light harvesting properties than the standard Ru-based dye [25].

Another dye such as Eosin-Y could be a good match to absorb solar spectrum within 350–940 nm wavelength because, in an aqueous solution, the molecules of Eosin-Y exist in a monomer form with peak absorption at 515 nm. Additionally, there was a separation by molecular absorption spectrum of Eosin-Y in the hybrid film and the peak was separated into two bands at 494 nm and 525 nm [26]. In contrast with other dyes, Eosin-Y gives good solubility in water and is a lot cheaper than ruthenium bipyridyl complex dyes [27]. Eosin-Y also can easily be absorbed into the ZnO surface to form a unique pore structure such as a wall or a sponge depending on the Zn in the electrolyte. Maximum electron injection has reached up to 47% for films of ZnO/Eosin-Y obtained by Yoshida et al. [28].

3.4. Charge Transfer at Donor-Acceptor Interface. In conversion of photon to electron to generate current, the first step is the absorption of light by the electron donor material to generate exciton. The binding energy of exciton called Frenkel exciton is very strong due to the Coulomb interaction. The exciton binding should be overcome to generate a photocurrent. The solutions to surmount this binding energy will be to use high thermal energy k_BT, high intrinsic electric field, and dissociation potential at the metal contacts. However, the above solutions yield poor efficiency as the temperature is not

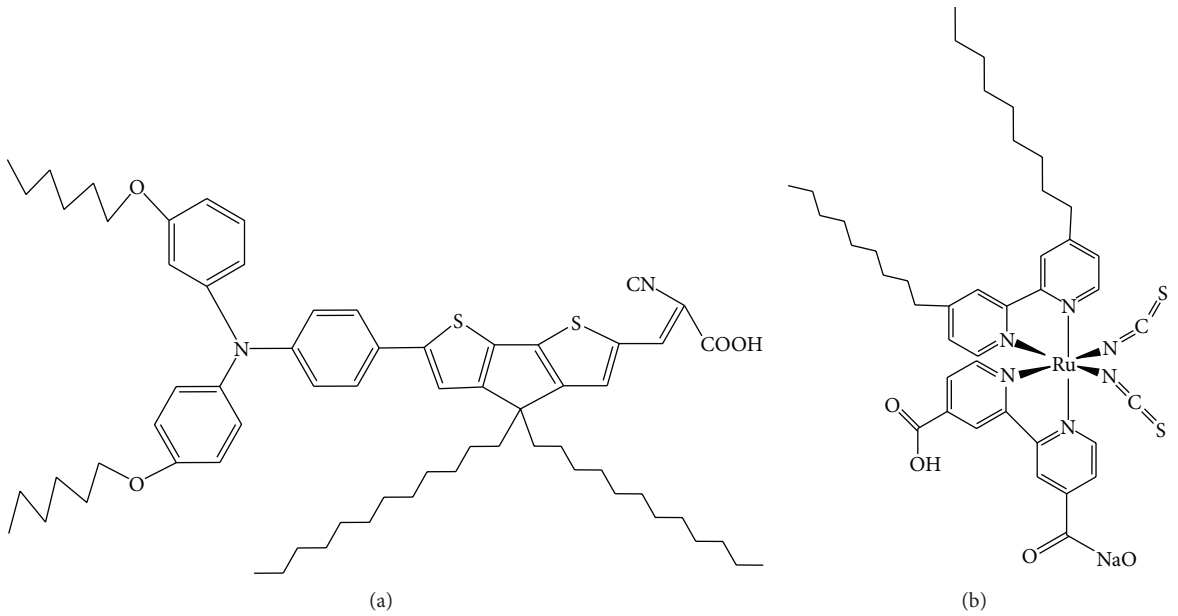

FIGURE 9: The structure of (a) C220 and (b) Z907 dyes [70].

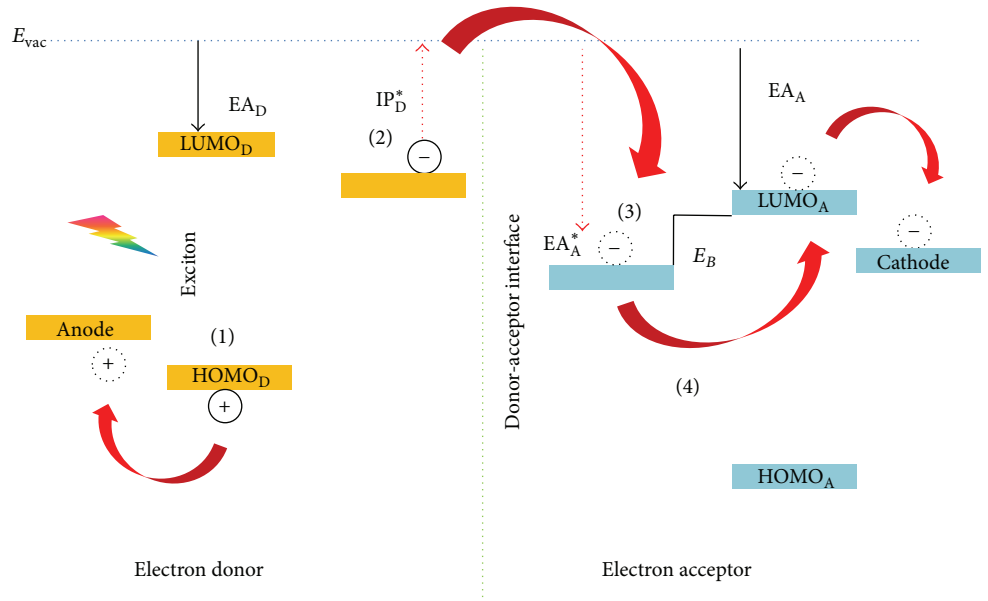

FIGURE 10: Schematic diagram illustrating exciton dissociation at donor-acceptor interface.

high enough to split them in ambient condition and normally the sample is too thick compared to exciton diffusion length. After light absorption, Frenkel exciton diffuses from donor to the acceptor material at this interface to dissociate them into an electron-hole pair. The charge transfer process is depicted in Figure 10 whereas the typical structure of the device [29] is shown earlier in Figure 2. The sequence of numbering in Figure 10 is as follows: (1) $HOMO_D$ and $LUMO_D$ of donor molecule, (2) excited donor molecule gain ionization potential energy IP_D^*, ready to be transferred to $LUMO_A$, (3) electron transferred in a picosecond timescale by gaining an electron affinity, EA_A^*, and (4) additional binding energy, E_B, between the electron on the acceptor and the hole that the ionized donor needed to surmount in order to hinder recombination so that more holes and electrons can reach the anode and cathode, respectively.

4. Prerequisites for Efficient Photovoltaic Performance

To fabricate polymer solar cells, one should pay particular attention to their optical properties, morphology, stability,

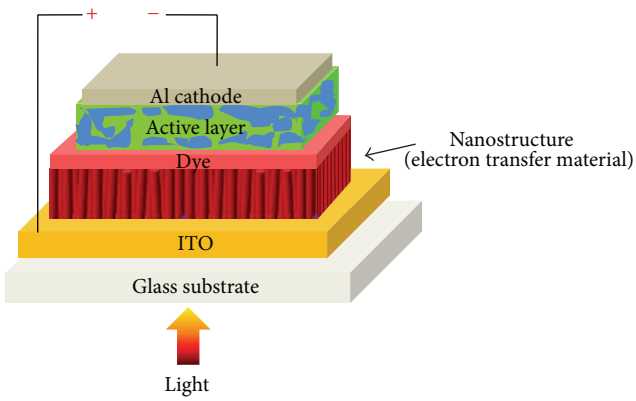

Figure 11: Hybrid nanostructure OPV.

and other criteria to ensure high photon-to-electron conversion efficiencies. Fundamental requirements for efficient charge transfer in polymer photovoltaics are [30] as follows.

(1) Domain size of the donor and acceptor must be <10 nm to hinder excitons recombination.

(2) Sufficient electrochemical potential should be applied to dissociate excitons at donor-acceptor interface (<0.3 eV).

(3) The carrier transport rate must be fast enough (10^{-4} cm^2/Vs or higher) compared to back-transfer rate. Ordered nanostructures would help to speed up the splitting of geminate pairs.

(4) The mobility of charge carriers must be high as they transported through the device before undergoing recombination. The higher the mobility, the lower is the dark current. For devices with thicknesses of 200–500 nm, mobility of 10^{-4}–10^{2} cm/Vs is probably optimal.

4.1. Strategies to Improve OPV Cell Performance. The advances in the development of OPVs can be attributed to four fronts: (i) a better understanding of the mechanism of photon-to-electron conversion; (ii) new materials with tailored energy levels and solubility; (iii) new processing approaches to induce optimal microstructures in the active layer; and (iv) new device architectures with novel interfacial layers [31].

The working principle of the device has been discussed and this includes light absorption, exciton dissociation, charge transport, and charge collection. In order to maximize the performance of an OPV cell, the nanostructures OPV cell was designed to reduce the charge recombination and maintain exciton dissociation [32, 33]. This so-called hybrid solar cell uses blends of inorganic nanocrystals with semiconducting polymers as a photovoltaic layer (Figure 11).

For the past few years, the device consisting of nanobased materials ranging between different shapes such as nanowires, nanobelts, nanorods, and even nanosprings has received much attention. The benefit of using nanostructures is to provide a large surface area per unit volume for efficient light absorption. Previous studies have shown that applying nanostructures in device structure can improve electron mobility as well as device efficiency due to wide absorption of light and unwanted holes leakage into cathode. The solubility of n-type and p-type materials is a crucial parameter of hybrid solar cells. Some of the semiconducting polymer blends with CdSe [34–36], $CuInS_2$, [37], CdS [38], and PbS [39] nanocrystals have been demonstrated. The advantages of nanostructures follow [40].

(1) Inorganic semiconductor nanostructures can have high absorption coefficients and photoconductivity.

(2) The n- or p-type doping level of the nanocrystalline materials can easily be varied so that charge transfer in composites of n- or p-type organic semiconductor materials with corresponding inorganic counterparts can be studied.

(3) If the inorganic nanoparticles are smaller than the excitons size (typically ~10 nm) their electronic structure changes. This is because the electronic and optical properties of that nanoparticle depend not only on the material of which they are composed of but also on their size [34, 41–44].

The height of nanostructures has to be tuned to absorb sufficient photons without losing charges by recombination. For instance, 200 nm thick P3HT absorbs over 90% of incident light at the maximum absorption peak wavelength. Therefore, it means that the pattern height should be about 200 nm thick. If it is thicker than 200 nm, the film absorbs almost 100% of incident photons, but some of the photons may recombine due to longer distance travel. Higher series resistance and lower shunt resistance occur in thicker film. On the contrary, in thinner film <200 nm, the film absorbs less than 90% of photon charges. In this case, lower resistance and higher shunt resistance are beneficial. Other than that, a 10 nm to 40 nm period pattern is sufficient to dissociate excitons efficiently since their diffusion length is between 5 nm and 20 nm [6]. Huynh et al. [36] had demonstrated the cell made of CdSe nanocrystals with P3HT and exhibited 0.57 V of V_{oc}. A device based on blends of TiO_2 with MDMO-PPV exhibited an I_{sc} of 0.6 mA/cm^2, V_{oc} of 0.52 V, FF of 0.42, and external quantum efficiency of up to 11% [45].

Similar to TiO_2 (anatase), ZnO has the same bandgap and the conduction band edge but has higher electron mobility than TiO_2. In recent years, the use of ZnO in DSCs has increased dramatically in terms of number of publications beating TiO_2. One of the reasons is mainly that ZnO is easily synthesized in the wurtzite crystalline structure. Much research had been conducted by using different morphology of ZnO such as nanoparticles, nanowires, nanorods, nanotubes, nanoflowers, nanosheets, and branched nanostructures via a wide range of techniques [21]. For example, Olson and colleagues [46] fabricated the device consisting of P3HT : PCBM blended into ZnO nanofibres and produced an efficiency of 2.03%. Takanezawa et al. [47] had shown that ZnO nanorods lead to the improvement of electron transport in bulk-heterojunction solar cells.

4.2. Historical Studies of Hybrid Solar Cells. In the last decade, there are many studies carried out on hybrid photovoltaic devices based on bulk-heterojunction system consisting of a conjugate mixture of p-type polymer and inorganic semiconductor such as n-type CdSe and ZnO. For example, the bulk-heterojunction solar cell type efficiencies of 1.6% and 0.9% were produced using a mixture of ZnO nanoparticles/MDMO-PPV and blend nanoparticles ZnO/P3HT [48, 49]. The combination of Eosin-Y with nanoporous film achieved about 2.0%–2.4% efficiency by Hosono et al. [50] and Lee et al. [51]. Based on the experiment in 2012 done by some researchers in Belgium, reported values of V_{oc}, FF, J_{sc}, and efficiency of PCPDTBT : PCBM are 0.67 V, 38%, 5.63 mA/cm^2, and 1.4%, respectively [52]. The inverted type of the same photoactive layer achieved about 91% of J_{sc} and 0.58 V of V_{oc} [53]. Theoretically, PCPDTBT can absorb more photons at longer wavelength, which can achieve maximum J_{sc} up to a maximum 32 mA/cm^2. This promising donor material can increase the PCE of the devices [54]. Nanorods based on CdSe : PCPDTBT obtained 0.63 mV of V_{oc}, 4.05 mA/cm^2 of J_{sc}, 0.39 of FF, and 1.12% of PCE [54].

The other parameter attributable to the performance of the device is EQE, which is the ratio of the charge carriers collected to the number of incident photons. About 28% of EQE of PCPDTBT : PCBM was recorded versus a silicon reference, using a custom-built setup comprising a lock-in amplifier and monochromatic beam of a quartz tungsten halogen lamp [55]. Additionally, bulk-heterojunction of 1 : 1 PCPDTBT : PCBM was reported to yield ~0.04% of quantum yield (QY) compared to pristine PCPDTBT which is ~6% by using LDS 821 dye [56]. So far, development of PCPDTBT polymers with narrow bandgaps represents a great advancement in the field.

The current developments of conjugated polymer/nanocrystal nanocomposites for bulk heterojunction-type photovoltaics incorporating Cd- and Pb-based nanocrystals or quantum dots were reviewed by Su et al. [57]. The mechanisms through which conjugated polymers can sensitize semiconductor nanocrystals (TiO_2, ZnO) to ensure efficient charge separation, as well as how they can support immobilized nanocrystals for use in photocatalysis, were addressed. 2,5-di(thiophen-2-yl)thieno[3,2-b]thiophene and thieno[3,4-c]pyrrole-4,6-dione units have been investigated [58] in blend films of CdSe tetrapods and the donor/acceptor conjugated polymer PDTTTPD. The AM 1.5 power conversion efficiency (PCE) of a photovoltaic device containing a PDTTTPD/CdSe tetrapod blend (1 : 9, w/w) that had experienced thermal annealing (130°C, 20 min) was three times greater than that of the corresponding device incorporating the as-prepared PDTTTPD/CdSe tetrapod blend (2.9% versus 1.0%). Synchrotron X-ray reflectivity revealed that annealing (i.e., removal of pyridine ligands from the surfaces of the CdSe tetrapods) caused the thickness of the PDTTTPD/CdSe tetrapod blend film to decrease (and its average density to increase) relative to that of the as-prepared blend film. Transmission electron microscopy and atomic force microscopy revealed that thermal annealing enhanced the degree of aggregation of the CdSe tetrapods and induced denser morphologies, leading to substantially increased charge transport, which enhanced the PCE of the device.

5. Future Suggestion

Since photovoltaic technology has become an alternative to nonrenewable energy source, a number of organics photovoltaic materials have been designed, synthesized, and applied in many solar cell applications. Tailoring the active layer materials by considering the band gap, mobility, solubility, morphology, molecular energy level, photon absorption, and so on is the key to boosting the efficiency. Future study and development to optimize and balance all of these parameters are required for higher solar cell performance. In principle, organic based solar cell not only can improve power conversion efficiency, but also can produce an affordable cost per generated power when commercialized. The common reason for low efficiency of OPV device is due to the mismatch between absorption spectra of conjugated polymers and the solar irradiance spectrum. The low bandgap polymer is an approach to enhance light harvesting; however, to choose a polymer that can have broad overlap with the solar emission spectrum is not an easy task. A group of polymers from 2,1,3-benzothiadiazole (BT) has been extensively studied as an active layer material that showed outstanding photovoltaic performance. PCPDTBT : PCBM blend extends it spectral sensitivity to 900 nm (infrared region) [11]. However, polymer with DPP derivatives exhibits good charge carrier mobility both for electrons and holes. Additionally, one of the promising strategies to realize absorption enhancement was based on dye-sensitized. Organic dyes as Eosin-Y are considered a cheaper sensitizer than the commonly used ruthenium bipyridyl complexes. However, serious precaution has to be taken since the direct release of waste water containing Eosin-Y will cause environmental problem due to its toxicity [59]. By creating ordered nanostructures, faster electron transport can improve current density as well as other parameters. In fact, over 10% efficiency has been achieved using TiO_2 nanocrystalline films sensitized by Ru-based dyes [60–62].

6. Conclusions

To conclude, this paper reviews types of device structures and materials for efficient photons absorption and charge collection in solar cells. The device performance can be enhanced by matching energy level of each material. Researchers carry out extensive efforts and studies in order to create promising low bandgap polymers, dyes, and semiconducting materials in order to increase the power conversion efficiency. This step is very important and is seen as a stepping-stone for large scale productions.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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