



Numbury Surendra Babu / Elixir Materials Science 108 (2017) 47818-47824 Available online at www.elixirpublishers.com (Elixir International Journal)

Materials Science



Elixir Materials Science 108 (2017) 47818-47824

A Review of Third Generation Solar Cells: Polymer Solar Cells

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ABSTRACT

ARTICLE INFO

Article history: Received: 20 June 2017; Received in revised form: 20 July 2107; Accepted: 26 July 2017;

Keywords

Renewable energy, Polymer solar cells. The development of polymer solar cells has improved power-conversion efficiencies from 3% to almost 9% in recent progress. Based on semiconducting polymers, these solar cells are fabricated from solution-processing techniques and have unique prospects for achieving low-cost solar energy harvesting, owing to their material and manufacturing advantages. The potential applications of polymer solar cells are broad, ranging from flexible solar modules and semitransparent solar cells in windows to building applications and even photon recycling in liquid-crystal displays. The various device structures used in organic polymer solar cells are reviewed. The operating principles behind these devices are explained in order to provide the reasoning behind the different structures and bilaver and bulk heterojunction devices discussed.

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Introduction

Renewable energy is essential for the current and future societies as currently, the global energy production depends heavily on the fossil fuels which are limited. Some agencies estimate the diminishing of oil and natural gas reserves by 2042 whereas coal reserves are estimated to last until 2112 [1,2]. Compared to last four decades, the global energy consumption has increased significantly and is expected to double by 2050 hence the need for renewable energy is obvious. In this context solar energy has become one of the most attractive alternative energy options due to the seemingly infinite energy provided by the sun of approximately 120,000TW which reaches earth's surface [3] where only a fraction of this power needs to be captured to satisfy the 2050 power need as explained by Hug, H. et al.,[4]. Even though a small fraction of solar energy has to be captured to satisfy the need, there would be no worry about the energy supply line. Therefore if the 19^{th} century was the age of coal and the 20^{th} of oil, the 21^{st} will be the age of the sun.

Renewable energy sources such as solar energy are considered as a feasible alternative because "More energy from sunlight strikes Earth in 1 hour than all of the energy consumed by humans in an entire year." [5]. Facilitating means to harvest a fraction of the solar energy reaching the Earth may solve many problems associated with both the energy and global environment [6]. Therefore, intensive research activities have resulted in attention-grabbing to the different classes of photovoltaic solar cells.

Solar Photovoltaic cells

The term "photovoltaic" comes from the Greek (*phos*) meaning "light", and from "volt", the unit of electro-motive force, the volt, which in turn comes from the last name of the Italian physicist Alessandro Volta, inventor of the battery (electrochemical cell). Therefore, the word expresses in itself already that a photovoltaic device is able to convert light into electricity. The physical phenomenon responsible for converting light to electricity-the photovoltaic effect-was first observed in 1839 by a French physicist, Edmund Becquerel.

the 1870s. In the 1880s, selenium photovoltaic cells were built that exhibited 1%-2% efficiency in converting light to electricity. In 1931, the German Scientist, Bruno Lange, rediscovered the selenium-based solar cell. In 1954, Calvin Fuller and Gerald Pearson, of Bell Labs, discovered that the efficiency of silicon rectifiers (which convert AC to DC) changed depending on their purity as well as the lighting They soon discovered that the rectifiers conditions. converted 4% of the incoming sunlight into electrical energy. Along with Darryl Chapin, a colleague, Calvin Fuller and Gerald Pearson started a team to work on what they named the Bell Silicon Solar Battery. In 1958, six small silicon solar panels, providing 100 mW of power were included on the satellite Vanguard I. Since then, the global photovoltaic production has gone from 100 mW to over 200 MW in 1999.

The PV effect was first studied in solids, such as selenium, in

Today, photovoltaic systems are capable of transforming one kilowatt of solar energy falling on one square meter into about a hundred watts' of electricity. One hundred watts can power most household appliances: a television, a stereo, an electric typewriter, or a lamp. In fact, standard solar cells covering the sun-facing roof space of a typical home can provide about 8500 kilo watt hours of electricity annually, which is about the average household's yearly electric consumption. By comparison, a modern, 200-ton electric-arc steel furnace, demanding 50,000 kilowatts of electricity, would require about a square kilometer of land for a PV power supply. Certain factors make capturing solar energy difficult.

Besides the sun's low illuminating power per square meter, sunlight is intermittent, affected by time of day, climate, pollution, and season. Power sources based on photovoltaics require either back-up from other sources or storage for times when the sun is obscured. In addition, the cost of a photovoltaic system is far from negligible, up to now this cost is still about 5 times higher than the cost of electricity provided by conventional technologies. Thus, solar energy for photovoltaic conversion into electricity is

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abundant, inexhaustible, and clean; yet, it also requires special techniques to gather enough of it effectively.

An enormous amount of research and development has been expended in improving the ever-useful transistor, and there has been a constant spin-off of valuable information in relation to solar cells. The situation has reversed recently: Much of the research being done in PV is affecting transistor technology.

Working of solar cell

The solar cell works in following steps: 1. Photons in sunlight hit the solar panel and are absorbed by semiconducting materials, such as silicon. Photons with energy equal to the band gap energy are absorbed to create free electrons. Photons with less energy than the band gap energy pass through the material.

- 2. Formation of electron-hole pair (exaction)
- 3. Exciton diffusion to Junction.

4. Charge separation- Electrons (negatively charged) are knocked loose from their atoms, causing an electric potential difference. Current starts flowing through the material to cancel the potential and this electricity are captured i.e. Electrons that are created on the n-type side may travel through the wire, power the load, and continue through the wire until they reach the p-type semiconductor-metal contact. Here, they recombine with a hole that was either created as an electron-hole pair on the p-type side of the solar cell. Due to the special composition of solar cells, the electrons are only allowed to move in a single direction.

5. An array of solar cells converts solar energy into a usable amount of direct current (DC) electricity.

Generations of solar cell



*Hybrid - inorganic crystals within a polymer matrix

The harvesting of solar energy has been introduced to different technologies classified into three generations [7]. The first and second solar energy generation reported to base respectively on crystalline silicon and emerging thin-film technologies, Silicon solar cells, in particular, are attractive relative to other 'green' solutions for manifold reasons, paramount amongst them being relative efficiency and ease of implementation. At present, the active materials used in the fabrication of solar cells are mainly inorganic materials, such as silicon (Si), gallium-arsenide (GaAs), cadmium-telluride (CdTe), and cadmium-indium-selenide (CIS). The power conversion efficiency for these solar cells varies from 8 to 29%. With regard to the technology used, these solar cells can be divided into two classes. The crystalline solar cells or silicon solar cells are made of either (mono- or poly-) crystalline silicon or GaAs. About 85% of the PV market is shared by these crystalline solar cells. Amorphous silicon, CdTe, and CI(G)S are more recent thin-film technologies.

Silicon solar cells technology has been proved to be efficient in solar energy harvesting reaching up to 22% conversion efficiency [8,9]. However high purity required in silicon solar cells made the cells more expensive.

There is however a significant problem apparent in any large scale implementation of solar technology is expense. Relative to conventional power generation processes, such as coal or nuclear power stations, silicon solar power generation is exorbitantly expensive. This exceptional expense per Watt hour arises largely out of the material and processing costs associated with creating the solar cell itself and has unfortunately served to price silicon solar cells out of the highly competitive energy market.

To overcome the expenses of silicon solar cells, the technology has been shifted to less expensive thin-film solar cells as the third generation solar energy mostly through dye sensitized solar cells (DSSCs) and Polymer solar cells. Currently, the third generation of solar cells based on nanostructured semiconductors, organic-inorganic and polymer semi conductors based was developed to achieve high efficiency with more economical cost i.e dye-sensitized solar cells (DSSCs) [10]. DSSCs have received considerable attention for transferring clean solar energy into electricity over the past decade [11, 12]. In the DSCs system, light is absorbed by the dye anchored on the TiO₂ surface and then electrons from the excited dye injected into the conduction band (CB) of the TiO₂, generating electric current, while the ground state of the dye is regenerated by the electrolyte to give efficient charge separation. It is thus that the dye in DSCs is essential for efficient light harvesting and electron generation/transfer.

Up to now, there have been two kinds of dyes, namely metal-organic complexes and metal-free organic dyes, which have been widely investigated as sensitizers of DSSCs. The noble metal ruthenium polypyridyl complexes such as N3 and black dye developed by Gra⁻tzel and co-workers [13, 14] have proved to be the best dyes with overall energy conversion efficiency (η) greater than 10% under AM 1.5 irradiation. Similar to the synthesis of N749, N719 is designed on the basis of N3 and N749 known as the "black dye" with the efficiency of 11.1% . Recently Grätzel group reported a DSC using ruthenium dye (Z991) which achieved a conversion efficiency of 12.3%.

However, and despite all of this effort, after 25 years of continuous research, the theoretical limits of 25% is still faraway [15]. But other issues in considering Ru based dyes are their cost as Ru is a rare metal with a high price and its toxic nature.

Polymer solar cells

A polymer solar cell is defined by applying semiconducting conjugated polymers [16–18] as active components in the photocurrent generation and power conversion process within thin film photovoltaic devices that convert solar light into electrical energy. In the year 2000, Heeger, MacDiarmid, and Shirakawa received the Nobel Prize in Chemistry for the "discovery and development of conducting polymers", representing a new class of materials.

Conjugated polymers are excellent candidates for use in low-cost electronics and photovoltaics (PV) [19]. These polymers generally exhibit an alternating single bond–double bond structure (conjugation) based on sp2-hybridized carbon atoms. This leads to a highly delocalized π -electron system with large electronic polarizability. This enables both absorption within the visible light region, due to π - π * transitions between the bonding and anti bonding pz orbitals, and electrical charge transport-two requirements that need to be met by semiconductors for power generation in solar cells. Using conjugated polymers to fabricate optoelectronic devices such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic solar cells (OSCs) is attractive because of their unique process ability from solution [20]. Conjugated polymers, functionalized by solubilizing side-chain derivations, can be readily dissolved in common organic solvents-or even water-and thus can be used as "ink" for all kinds of deposition processes forming thin and homogeneous films. This property is especially interesting when combined with classical printing techniques, as it enables both spatially localized deposition (e.g., by inkjet or offset printing) and large area roll-to-roll manufacturing, allowing highthroughput production easily surmounting those achieved by classical semiconductor batch processing.

Polymer-based solar cells have reached power conversion efficiencies of 5% in recent reports [21-23]. Deposition of organics by screen printing, doctor balding, inkjet printing, and spray deposition is possible because these materials can be made soluble. These techniques are required for the high-throughput roll-to-roll processing that will drive the cost of polymer-based PV down to a point where it can compete with current grid electricity. Additionally, these deposition techniques all take place at low temperature, which allows devices to be fabricated on plastic substrates for flexible devices. In addition to the inherent economics of high-throughput manufacturing, light weight and flexibility are qualities claimed to offer a reduction in the price of PV panels by reducing installation costs. Flexible PV also opens up niche markets like portable power generation and aesthetic PV in building design.

Working Principles of Polymer Solar Cells

Incident light that is absorbed within the photoactive layer of a polymer solar cell leads first to the creation of a bound electron-hole pair—the "exciton". These excitons diffuse during their lifetime with diffusion lengths generally limited to about 5–20nm in organic materials [24–28].

This consideration is important to the design of active layer architectures. If an exciton does not eventually separate into its component electron and hole, it eventually recombines by emitting a photon or decaying via the normalization (non radiative recombination). Hence, an exciton dissociation mechanism is required to separate the excitons which have binding energies ranging between 0.1 and 1eV [29–33].In single layer organic solar cells this may be achieved by the strong electric field present within the depletion region of a Schottky contact. Exciton dissociation in current polymer solar cells relies on gradients of the potential across a donor (D)/acceptor (A) interface, which results in the photo induced charge transfer between these materials [34].

On photon absorption, an electron is excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). This electron-hole pair then relaxes with a binding energy between 0.1–1.4 eV, and is known as an exciton [35–37]. This is in contrast to inorganic materials, where the exciton binding energy is only a few mille electron volts. The binding energy is larger in organic semiconductors because electron and hole wavefunctions are localized and the dielectric constants are low ($\epsilon \sim 3-4$), enhancing the Coulomb attraction between the

electron and hole. The bound excitons must migrate to an interface where there is a sufficient chemical potential energy drop to drive dissociation into an electron-hole pair that spans the interface across the donor (material with low electron affinity) and acceptor (material with high electron affinity) The charged pair formed after exciton dissociation, a geminate pair, is often still coulombically bound and must be dissociated by an internal field [38–41].



Figure 1a. An organic semiconductor in the dark, with a band gap of energy E_g . (b) Incident light of energy greater than the energy gap excites an electron from the HOMO state to the LUMO state. (c) The photon energy greater than the gap energy is 'lost' by thermal relaxation to the LUMO level

After dissociation, each charge carrier must be transported through the device to the appropriate contact while avoiding traps and recombination. These charges are transported primarily by drift caused by the built-in field, though diffusion can play a large role. The current that reaches the contacts with no applied field is known as the short circuit current, Jsc, and the maximum potential generated by the device is known as the open-circuit voltage, Voc. Of course, for the current to do work, it must be generated with some potential. The ratio between the maximum power generated and the product of J_{sc} and Voc is known as the fill factor and is related to the quality of the device. The efficiency of the planar heterojunction device is limited by the exciton diffusion length. This is the distance over which excitons travel before undergoing recombination and is ~3-10 nm in most organic semiconductors [42-44]. Excitons formed at a location further from the heterojunction than the exciton diffusion length have a lower probability of being harvested. The active volume of this type of solar cell is thus limited to a very thin region close to the interface, which is not enough to absorb most of the solar radiation flux. In order to overcome this limitation, researchers have moved to nanostructuring the materials such that the domain size is on the order of twice the diffusion length.



Figure 2. Working principle of a polymer solar cell.

A good charge collection is important for the overall efficiency of a PSC. This means that the generated charges need to be transported to the electrodes without recombination. In order to achieve this, the active layer needs to offer continuous pathways for charge extraction. The challenge of generating both large interfacial area and continuous pathways to the electrodes simultaneously explains why it is important to be able to control the morphology of the active layer in order to produce PSCs with high efficiency.

Device Architectures

The common materials used in state-of-the-art polymerbased PV cells shown in figure 4. These and other conjugated molecules are electronically active because of their highly polarizable π -systems, which are hybridized orbitals based on the constituent p atomic orbitals. The π - π * optical transitions are strong (absorption coefficients greater than ~105 cm⁻¹), typically fall in the visible, and can be tuned synthetically through molecular design. Charge carrier mobilities are usually in the range of 10^{-7} - 10^{-3} cm²/V.s, when measured under conditions relevant to solar cell operation.



Fig. 3 Common materials used in polymer photovoltaics. From left to right, PCBM: (6,6)-phenyl-C61-butyric acid methyl ester; MDMO-PPV: poly(2methoxy-5-(3',7'dimethyloctyloxy)-1,4-phenylene-vinylene); RR-P3HT: regioregular poly(3-hexylthiophene).

A polymer solar cell comprise of a thin film of the photoactive material sandwiched between two electrodes of different work functions. One of the electrodes is a transparent conductor from where light is permitted to the photoactive layer. In all these architectures, many steps are involved between photon absorption and electricity generation, all of which must be efficient to make an efficient device.



Fig 4. Polymer solar cell Architecture

The earliest type of PSC was based on a single layer of polyacetylene and showed a very low efficiency. The performance was later improved by the use of a bilayer structure. Today, the most common device structure is the bulk heterojunction (BHJ), in which the donor and acceptor components are intimately mixed in one layer (Figure 4). This results in a large interfacial area between the donor and acceptor material which is beneficial for the formation of the charge-transfer state (CT-state) and charge separation. Lab-scale devices are usually prepared on glass substrates coated with indium tin oxide (ITO) as the anode. On top of the ITO, a thin layer of Poly (3,4ethylene dioxy thio phene)-poly(styrene sulfonate)) (PEDOT:PSS) is spin coated. This will lower the work function of the ITO and make the surface smoother. The active layer with the polymer: fullerene blend is deposited on top of these layers, usually by spin coating. The cathode is then evaporated on top of the active layer. The cathode usually consists of an interlayer of e.g. lithium fluoride followed by an aluminum layer. A schematic picture of two architectures is found in Figure 6.



Figure 5. Schematics of different solar cell architectures; (a) single layer (b) bilayer and (c) BHJ

PSCs are often divided into two types; conventional and inverted device architecture. In inverted polymer solar cells (iPSCs), ITO acts as the cathode instead of anode as in the conventional device architecture. The conventional (standard) architecture is the most common device structure for high performing PSCs. Unfortunately, the standard solar cells exhibit short operational life time caused by the oxygen- and water-sensitive cathode materials. The inverted device structure was developed to overcome this problem and has been shown to have a superior stability compared to standard solar cells. On the contrary, inverted devices often show lower efficiency than conventional PSCs due to a too high work-function of the ITO cathode. To improve the electron collection efficiency (charge selectivity) at the cathode, and thereby the overall power conversion efficiency, significant effort has been made to modify the interface between the cathode and the organic photo-active layer. Since inverted devices do not require a transparent bottom electrode other materials than ITO can be used as electrode material. This is an advantage of inverted devices since ITO contains indium, which is both rare and expensive. The use of more abundant electrode materials would therefore reduce the price of PSCs.



Fig 6.Chematic image of two different device architectures. Standard geometry (left) and inverted geometry (right)

Bilayer heterojunctions

The first 2-component organic photovoltaic cells were reported during the 1980s. The devices consisted of thin films of 2 different materials in a bilayer configuration (Figure 7) and showed that at the interface between 2 materials with different electron affinities charge transfer is energetically favorable. This discovery led to the development of bilayer heterojunction polymer solar cells consisting of distinct electron donor and acceptor layers. However, these early devices were still limited in efficiency to approximately 1%.



The synthesis of semiconducting organic polymers in the late 1970s led to the development of a variety of new flexible electronic devices, including photovoltaics. Building on the idea of 2-component bilayer solar cells described above, the use of soluble semiconducting polymers to fabricate solar cells began in the early 1990s Sariciftci et al. built a device using poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] [MEH-PPV] and C_{60} . They began by spin-coating the MEH-PPV onto a glass substrate coated with ITO. The fullerenes were then evaporated on top of the MEH-PPV to form a p-n heterojunction. Although these devices had low power conversion efficiencies (only 0.02%) when illuminated with a laser at 514.5 nm, they were the first to use C_{60} , which has become the most commonly used acceptor material. The low efficiencies in these devices demonstrated the weakness of the bilayer design. The interface between the donor polymer (MEH-PPV) and the accepter material (C_{60}) is relatively flat and therefore the interfacial surface area is quite low. This leads to a narrow-width diffusion region along the interface. Only the light absorbed within the diffusion region will generate an exciton that has an opportunity to separate before recombining and therefore the charge generation in these devices is quite low.

Bulk heterojunction polymer solar cells

The bilayer heterojunction is limited by a small interfacial surface area and therefore, in 1995, 2 groups [45, 46] introduced interpenetrating networks of donors and acceptors in what has come to be known as a bulk (or dispersed) heterojunction. In these devices, the electron acceptors (e.g., C_{60}) are blended into the electron donor (e.g., the polymer) to form a composite (Figure 8).



Figure 8. Bulk heterojunction solar cell with high interfacial surface area.

The bulk heterojunction (BHJ) solar cell is a thirdgeneration solar cell that in its simplest configuration is comprised of two kinds of material, where one functions as an electron donor and the other functions as an electron acceptor. The working mechanism can be summarized as follows: excitons created by incident photons will form in the donor material and migrate toward the interface between the donor and acceptor material. The acceptor material, having a higher electron affinity with respect to the donor material, will accept the electron from the donor, causing exciton dissociation at the interface. The dissociation of the photo generated exciton (usually a Frenkel exciton in polymers and small molecules) is itself typically a two-step process consisting of the formation of a charge transfer exciton followed by further dissociation into mobile electron-and hole-polarons [47,48]. The subsequently separated hole polarons and electron polarons will travel through the donor and acceptor materials, respectively, towards their individual electrodes-anode for the holes and cathode for the electrons. The two materials can be simply put into contact (a so-called bilayer heterojunction solar cell) or synthesized as a blend. In a bilayer heterojunction solar cell, geminate recombination due to the small exciton diffusion length in organic semiconductors (typically <15 nm) is a major loss mechanism [49]. In this context, the advantage of a blend (as in a bulk heterojunction) is a larger interface area and an inter penetrating donor-acceptor morphology to minimize the distance that excitons must travel to reach an interface for dissociation. The bulk heterojunction blend also needs to have percolation pathways for both electrons and holes to avoid efficiency losses due to poor charge collection, as will be explained later. The dominant configuration in the field of bulk heterojunction solar cells has consisted of a π -conjugated semiconducting polymer (termed just "polymer" in much of the remainder of this report) as the donor and the small molecule methanofullerene as the acceptor, where efficiencies have reached 11.7% for single junction lab-scale solar cells and 7%-9% for modules [50,51]. The principal disadvantages of the methanofullerene-conjugated polymer bulk heterojunction are the low ambient stability of the blend [52, 53], the very low contribution of the fullerene to charge generation, the high exciton binding energy in the polymerpotentially resulting in open circuit photovoltage losses [54] and the low charge carrier mobilities in both the fullerene (~1 $cm^2 \cdot V^{-1} \cdot s^{-1})$ and $cm^2 \cdot V^{-1} \cdot s^{-1})$ [55]. and the polymer (typically $10^{-4} - 10^{-1}$

Overall Energy Conversion

In the vast majority of photovoltaic bulk heterojunctions, a conjugated polymer is a donor (p-type component) due to the scarcity of n-type polymer acceptors with good stability, suitable energy levels and acceptable electron mobilities. Small molecule methanofullerenes PC61BM and PC71BM are most commonly used as the acceptor components in allorganic binary blends. A key difference between a methanofullerene-polymer blend bulk heterojunction solar cell and a semiconductor nanocrystal-polymer blend bulk heterojunction hybrid solar cell is that the polymer is not solely responsible for most of the light absorption since the quantum dots are strong absorbers as well [56]. In contrast, methanofullerenes have a very weak visible light absorption due to the low oscillator strength of electronic transition from the ground state to their first excited state, which is a triplet state . A more subtle difference relates to mutual solubility of the blend components; it has been established that the significant solubility of PCBM in the polymer phase greatly facilitates carrier transport following charge separation .

As shown in Figure 1, the donor has a higher lowest unoccupied molecular orbital (LUMO) than the conduction band minimum of the acceptor quantum dot, followed on the right side of the figure by a cathode made of a metal whose Fermi level is slightly lower or roughly proximate with the conduction band of the quantum dot. Thus, the electron flows from the donor towards the cathode. The valence band maximum of the acceptor is the lowest energy level; the next lowest is the donor's highest occupied molecular orbital(HOMO).On the left side of the energy diagram in Figure 2, a material that has a Fermi level roughly proximate or slightly higher than the HOMO of the donor material is chosen as the anode. As displayed in the diagram, such a cascaded energy level arrangement will direct the flow of charge through the cell in a manner conducive to charge collection at the electrodes, in turn enabling electricity generation in the external circuit.

IV-characteristics

The performance of a PSC is usually evaluated by illumination of the device with a solar simulator. For northern European latitudes an air-mass (AM) 1.5G spectrum is used, corresponding to a solar inclination angle of 48.2° . The commonly used lamp intensity is called 1 sun (1000 W m⁻²) and corresponds to the sunlight intensity on a bright day (no cloud coverage) at zero altitude on Earth. When illuminated, a PSC will generate a photocurrent. The devices are then evaluated using the IV-curve produced by normalizing the generated photocurrent (I) in regard to device area and plotting it against the voltage (V) (Figure 9).



Figure 9. Current density-voltage characteristics for a solar cell.

Four important parameters extracted from the IV-curve are the short-circuit current density (JSC), which is the photocurrent divided by the area under short-circuit conditions, i.e. when no voltage is applied. The open-circuit voltage (VOC) is achieved at zero photocurrent. The VOC of a device is dependent on the difference between the HOMO of the polymer and the LUMO of the acceptor and can be correlated to the energy of the CT-state. The maximum power point (MPP) or solar cell efficiency (η) is the point where the power is the highest. The fill factor (FF) describes the shape of the IV-curve and is given by the ratio between the MPP and the product of JSC and VOC.

Conclusion

Organic solar cells show good promises in the development of low cost photovoltaic alternatives. A structured and systematic research is required in the field to successfully utilize the foreseen advantages of organic solar cells. Since all the deign architecture and materials developments revolve around our level of understanding of the basic mechanism it accounts chief importance in all researches going on in the field of organic photovoltaics.

The efficiency of polymer-based organic solar cells has risen significantly over the past 10 years from approximately 3% to nearly 11%. While much of this increase can be attributed to the development of new polymers with increased quantum efficiency, the optimization of device structures has also played an important role.

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47824