polymer solar cell

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Contents

Introduction

A **polymer solar cell** is a type of flexible solar cell made with polymers, large molecules with repeating structural units, that produce electricity from sunlight by the photovoltaic effect. Polymer solar cells include organic solar cells (also called "plastic solar cells"). They are one type of thin film solar cell, others include the more stable amorphous silicon solar cell.

Most commercial solar cells are made from a refined, highly purified silicon crystal, similar to the material used in the manufacture of integrated circuits and computer chips (wafer silicon). The high cost of these silicon solar cells and their complex production process generated interest in alternative technologies.

Compared to silicon-based devices, polymer solar cells are lightweight (which is important for small autonomous sensors), potentially disposable and inexpensive to fabricate (sometimes using printed electronics), flexible, customizable on the molecular level and potentially have less adverse environmental impact. Polymer solar cells also have the potential to exhibit transparency, suggesting applications in windows, walls, flexible electronics, etc. An example device is shown in Fig. 1. The disadvantages of polymer solar cells are also serious: they offer about 1/3 of the efficiency of hard materials, and experience substantial photochemical degradation.

Polymer solar cells inefficiency and stability problems, combined with their promise of low costs[1] and increased efficiency made them a popular field in solar cell research. As of 2015, polymer solar cells were able to achieve over 10% efficiency via a tandem structure.

Device physics

Polymer solar cells usually consist of an electron- or hole-blocking layer on top of an indium tin oxide (ITO) conductive glass followed by electron donor and an electron acceptor (in the case of bulk heterojunction solar cells), a hole or electron blocking layer, and metal electrode on top. The nature and order of the blocking layers – as well as the nature of the metal electrode – depends on whether the cell follows a regular or an inverted device architecture. In an inverted cell, the electric charges exit the device in the opposite direction as in a normal device because the positive and negative electrodes are reversed. Inverted cells can utilize cathodes out of a more suitable material; inverted OPVs enjoy longer lifetimes than regularly structured OPVs, but they typically don't reach efficiencies as high as regular OPVs.
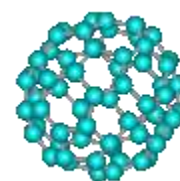
In bulk heterojunction polymer solar cells, light generates excitons. Subsequent charge separation in the interface between an electron donor and acceptor blend within the device's

active layer. These charges then transport to the device's electrodes where the charges flow outside the cell, perform work and then re-enter the device on the opposite side. The cell's efficiency is limited by several factors, especially non-geminate recombination. Hole mobility leads to faster conduction across the active layer.

Organic photovoltaics are made of electron donor and electron acceptor materials rather than semiconductor p-n junctions. The molecules forming the electron donor region of organic PV cells, where exciton electron-hole pairs are generated, are generally conjugated polymers possessing delocalized π electrons that result from carbon p orbital hybridization. These π electrons can be excited by light in or near the visible part of the spectrum from the molecule's highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), denoted by a π -π* transition. The energy bandgap between these orbitals determines which wavelength(s) of light can be absorbed.

Unlike in an inorganic crystalline PV cell material, with its band structure and delocalized electrons, excitons in organic photovoltaics are strongly bound with an energy between 0.1 and 1.4 eV. This strong binding occurs because electronic wave functions in organic molecules are more localized, and electrostatic attraction can thus keep the electron and hole together as an exciton. The electron and hole can be dissociated by providing an interface across which the chemical potential of electrons decreases. The material that absorbs the photon is the donor, and the material acquiring the electron is called the acceptor. In Fig. 2, the polymer chain is the donor and the fullerene is the acceptor. Even after dissociation, the electron and hole may still be joined as a "geminate pair", and an electric field is then required to separate them. The electron and hole must be collected at contacts. If charge carrier mobility is insufficient, the carriers will not reach the contacts, and instead recombine at trap sites or remain in the device as undesirable space charges that oppose the flow of new carriers. The latter problem can occur if electron and hole mobilities are not matched. In that case, space-charge limited photocurrent (SCLP) hampers device performance.

Organic photovoltaics can be fabricated with an active polymer and a fullerene-based electron acceptor. Illumination of this system by visible light leads to electron transfer from the polymer to a fullerene molecule. As a result, the formation of a photoinduced quasiparticle, or polaron (P^+), occurs on the polymer chain and the fullerene becomes a radical anion (C^-_{60}). Polarons are highly mobile and can diffuse away.

Architectures

The simplest organic PV device features a planar heterojunction A film of active polymer (donor) and a film of electron acceptor is sandwiched between contacts. Excitons created in the donor region may diffuse to the junction and separate, with the hole remaining behind and the electron passing into the acceptor. Because charge carriers have diffusion lengths of just 3–10 nm in typical organic semiconductors, planar cells must be thin, but the thin cells absorb light less well. Bulk heterojunctions (BHJs) address this shortcoming. In a BHJ, a blend of electron donor and acceptor materials is cast as a mixture, which then phase-separates. Regions of each material in the device are separated by only several nanometers, a distance suited for carrier diffusion. BHJs require sensitive control over materials morphology on the nanoscale. Important variables include materials, solvents and the donor-acceptor weight ratio.

The next logical step beyond BHJs are ordered nanomaterials for solar cells, or ordered heterojunctions (OHJs). OHJs minimize the variability associated with BHJs. OHJs are generally hybrids of ordered inorganic materials and organic active regions. For example, a photovoltaic polymer can be deposited into pores in a ceramic such as TiO_2. Since holes still must diffuse the length of the pore through the polymer to a contact, OHJs suffer similar thickness limitations. Mitigating the hole mobility bottleneck is key to further enhancing device performance of OHJ's.

Active layer deposition and annealing process

Since its active layer largely determines device efficiency, this component's morphology received much attention.

If one material is more soluble in the solvent than the other, it will deposit first on top of the substrate, causing a concentration gradient through the film. This has been demonstrated for poly-3-hexyl thiophene (P3HT), phenyl-C_{61}-butyric acid methyl ester (PCBM) devices where the PCBM tends to accumulate towards the device's bottom uponspin coating from ODCB solutions. This effect is seen because the more soluble component tends to migrate towards the "solvent rich" phase during the coating procedure, accumulating the more soluble component towards the film's bottom, where the solvent remains longer. The thickness of the generated film affects the phases segregation because the dynamics of crystallization and precipitation are different for more concentrated solutions or faster evaporation rates (needed to build thicker devices). CrystallineP3HT enrichment closer to the hole-collecting electrode can only be achieved for relatively thin (100 nm) P3HT/PCBM layers.

4

The gradients in the initial morphology are then mainly generated by the solvent evaporation rate and the differences in solubility between the donor and acceptor inside the blend. This dependence on solubility has been clearly demonstrated using fullerene derivatives and P3HT. When using solvents which evaporate at a slower rate (aschlorobenzene (CB) or dichlorobenzene (DCB)) you can get larger degrees of vertical separation or aggregation while solvents that evaporate quicker produce a much less effective vertical separation. Larger solubility gradients should lead to more effective vertical separation while smaller gradients should lead to more homogeneous films. These two effects were verified on P3HT:PCBM solar cells.

The solvent evaporation speed as well as posterior solvent vapor or thermal annealing procedures were also studied. Blends such as P3HT:PCBM seem to benefit from thermal annealing procedures, while others, such as PTB7:PCBM, seem to show no benefit. In P3HT the benefit seems to come from an increase of crystallinity of the P3HT phase which is generated through an expulsion of PCBM molecules from within these domains. This has been demonstrated through studies of PCBM miscibility in P3HT as well as domain composition changes as a function of annealing times.

The above hypothesis based on miscibility does not fully explain the efficiency of the devices as solely pure amorphous phases of either donor or acceptor materials never exist within bulk heterojunction devices. A 2010 paper suggested that current models that assume pure phases and discrete interfaces might fail given the absence of pure amorphous regions. Since current models assume phase separation at interfaces without any consideration for phase purity, the models might need to be changed.

The thermal annealing procedure varies depending on precisely when it is applied. Since vertical species migration is partly determined by the surface tension between the active layer and either air or another layer, annealing before or after the deposition of additional layers (most often the metal cathode) affects the result. In the case of P3HT:PCBM solar cells vertical migration is improved when cells are annealed after the deposition of the metal cathode.

Donor or acceptor accumulation next to the adjacent layers might be beneficial as these accumulations can lead to hole or electron blocking effects which might benefit device performance. In 2009 the difference in vertical distribution on P3HT:PCBM solar cells was shown to cause problems with electron mobility which ends up with the yielding of very poor device efficiencies. Simple changes to device architecture – spin coating a thin layer of PCBM on top of the P3HT – greatly enhance cell reproducibility, by providing reproducible vertical separation between device components. Since higher contact between the PCBM and the cathode is required for better efficiencies, this largely increases device reproducibility.

5

According to neutron scattering analysis, P3HT:PCBM blends have been described as "rivers" (P3HT regions) interrupted by "streams" (PCBM regions).

Solvent effects

Conditions for spin coating and evaporation affect device efficiency. Solvent and additives influence donor-acceptor morphology. Additives slow down evaporation, leading to more crystalline polymers and thus improved hole conductivities and efficiencies. Typical additives include 1,8-octanedithiol, ortho-dichlorobenzene, 1,8-diiodooctane (DIO), and nitrobenzene. The DIO effect was attributed to the selective solubilization of PCBM components, modifies fundamentally the average hopping distance of electrons, and thus improves electron mobility. Additives can also lead to big increases in efficiency for polymers. For HXS-1/PCBM solar cells, the effect was correlated with charge generation, transport and shelf-stability. Other polymers such as PTTBO also benefit significantly from DIO, achieving PCE values of more than 5% from around 3.7% without the additive.

Polymer Solar Cells fabricated from chloronaphthalene (CN) as a co-solvent enjoy a higher efficiency than those fabricated from the more conventional pure chlorobenzene solution. This is because the donor-acceptor morphology changes, which reduces the phase separation between donor polymer and fullerene. As a result, this translates into high hole mobilities. Without co-solvents, large domains of fullerene form, decreasing photovoltaic performance of the cell due to polymer aggregation in solution. This morphology originates from the liquid-liquid phase separation during drying; solve evaporation causes the mixture to enter into the spinodal region, in which there are significant thermal fluctuations. Large domains prevent electrons from being collected efficiently (decreasing PCE).

Small differences in polymer structure can also lead to significant changes in crystal packing that inevitably affect device morphology. PCPDTBT differs from PSBTBT caused by the difference in bridging atom between the two polymers (C vs. Si), which implies that better morphologies are achievable with PCPDTBT:PCBM solar cells containing additives as opposed to the Si system which achieves good morphologies without help from additional substances

Self-assembled cells

Supramolecular chemistry was investigated, using donor and acceptor molecules that assemble upon spin casting and heating. Most supramolecular assemblies employ small

6

molecules. Donor and acceptor domains in a tubular structure appear ideal for organic solar cells.

Diblock polymers containing fullerene yield stable organic solar cells upon thermal annealing.Solar cells with pre-designed morphologies resulted when appropriate supramolecular interactions are introduced.

Progress on BCPs containing polythiophene derivatives yield solar cells that assemble into well defined networks. This system exhibits a PCE of 2.04%. Hydrogen bondingguides the morphology.

Device efficiency based on co-polymer approaches have yet to cross the 2% barrier, whereas bulk-heterojunction devices exhibit efficiencies >7% in single junction configurations.

Fullerene-grafted rod-coil block copolymers have been used to study domain organization.[41]

Supramolecular approaches to organic solar cells provide understanding about the macromolecular forces that drive domain separation

Infrared polymer cells

Infrared cells preferentially absorb light in the infrared range rather than visible wavelengths. As of 2012, such cells can be made nearly 70% transparent to visible light. The cells allegedly can be made in high volume at low cost using solution processing. Infrared polymer cells can be used as add-on components of portable electronics, smart windows, and building-integrated photovoltaics.The cells employ silver nanowire/titanium dioxide composite films as the top electrode, replacing conventional opaque metal electrodes. With this combination, 4% power-conversion efficiency was achieved.

Near-infrared Polymer solar cells based on a copolymer of naphthodithiophene diimide and bithiophene (PNDTI-BT-DT) are also being fabricated in combination with PTB7 as an electron donor. Both PNDTI-BT-DT and PTB7 formed a crystalline structure in the blend films similar to in the pristine films, leading to the efficient charge generation contributed from both polymers.

Power Conversion Efficiency

One of the major issues surrounding polymer solar cells is the low Power Conversion Efficiency (PCE) of fabricated cells. In order to be considered commercial viable, PSCs must be able to achieve at least 10–15% efficiency—this is already much lower than inorganic

PVs. However, due to the low cost of polymer solar cells, a 10–15% efficiency is commercially viable.

PCE (η) is proportional to the product of the short-circuit current (J_{SC}), the open circuit voltage (V_{OC}), and the fill factor (FF).

$$\eta = \frac{V_{OC} \times J_{SC} \times FF}{P_{in}}$$

Where P_{in} is the incident solar power. Recent advances in polymer solar cell performance have resulted from compressing the bandgap to enhance short-circuit current while lowering the Highest Occupied Molecular Orbital (HOMO) to increase open-circuit voltage. However, PSCs still suffer from low fill factors (typically below 70%). However, as of 2013, researchers have been able to fabricate PSCs with fill factors of over 75%. Scientists have been able to accomplish via an inverted BHJ and by using nonconventional donor / acceptor combinations.

Commercialization

Polymer solar cells have yet to commercially compete with silicon solar cells and other thin-film cells. The present efficiency of polymer solar cells lies near 10%, well below silicon cells. Polymer solar cells also suffer from environmental degradation, lacking effective protective coatings.
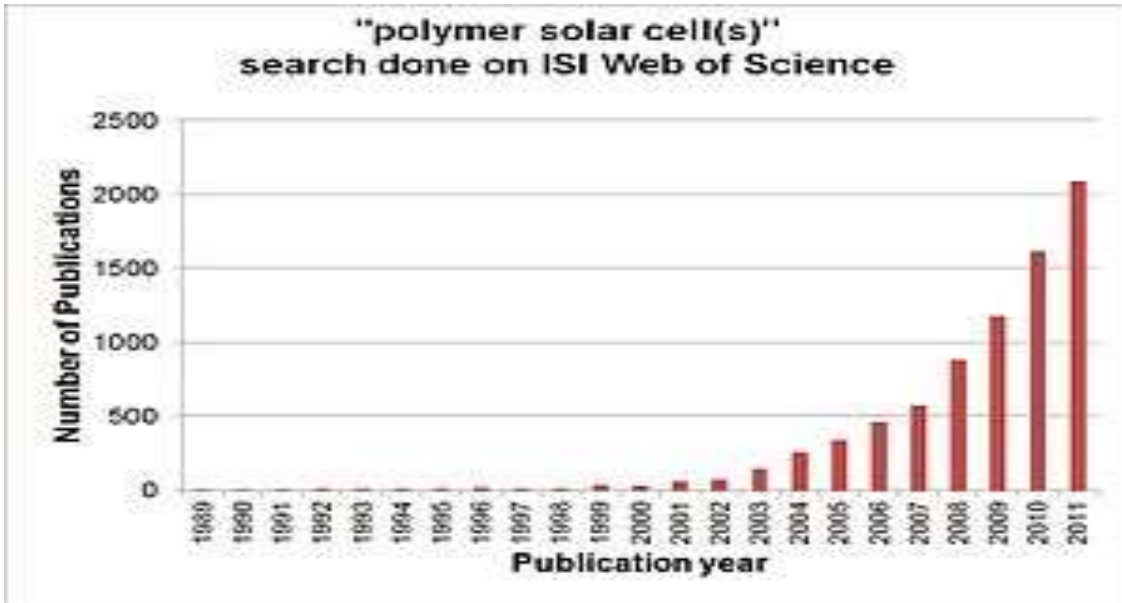
Further improvements in performance are needed to promote charge carrier diffusion; transport must be enhanced through control of order and morphology; and interface engineering must be applied to the problem of charge transfer across interfaces.

Research is being conducted into using tandem architecture in order to increase efficiency of polymer solar cells. Similar to inorganic tandem architecture, organic tandem architecture is expected to increase efficiency. Compared with a single-junction device using low-bandgap materials, the tandem structure can reduce heat loss during photon-to-electron conversion.

Polymer solar cells are not widely produced commercially. Starting in 2008, Konarka Technologies started production of polymer-fullerene solar cells. The initial modules were 3–5% efficient, and only last for a few years. Konarka has since filed for bankruptcy, as those polymer solar cells were unable to penetrate the PV market.

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However, efforts are being made to upscale manufacturing of polymer solar cells, in order to decrease costs and also advocate for a practical approach for PSC production. Such efforts include full roll-to-roll solution processing. However, roll-to-roll solution processing is ill-suited for on-grid electricity production due to the short lifetime of polymer solar cells. Therefore, commercial applications for polymer solar cells still include primarily consumer electronics and home appliances.

Modeling organic solar cells

As discussed above, organic semiconductors, are highly disorder materials with no long range order. This means that the conduction band and valance band edges are not well defined. Furthermore, this physical and energetic disorder generates trap states in which photogenerated electrons and holes can become trapped and then eventually recombine.

Key to accurately describing organic solar cells in a device model is to include carrier trapping and recombination via trap states. A commonly used approach is to use an effective medium model, where by standard drift diffusion equations are used to describe transport across the device. Then, an exponential tail of trap states is introduced which decays into the band gap from the mobility edges. To describe capture/escape from these trap states the Shockley–Read–Hall (SRH) can be used. The Shockley-Read-Hall mechanism has been shown able to reproduce polymer:fullerene device behavior in both time domain and steady state

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