Recent advancement in polymer solar cells

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March 26th, 2017

Introduction

The energy crisis today arises from the fact that world's supply for the fossil fuels are diminishing, although the demand is still rising. While they do occur naturally, it takes hundreds of thousands of years to replenish the stores. Because of that, much of the scientist's research is devoted to find renewable energy sources to satiate our energy demand.

The sun is the most powerful energy source for our planet. Even the other energy sources like wind, fossil fuel and hydro, they all have their origins in sunlight. Sunlight energy hits the surface of the earth at a rate of 120 petawatts, this shows us that the solar energy received from the sun in one day can afford the entire world's energy demand for more than 20 years. This can explain why solar cells industry is one of the most important solutions for the energy problems in the world[1].

Environmental and economic Aspects of Solar Cells

No energy source is such renewable, rich and green as solar energy. Operating solar cells as a source of energy does not result in emitting carbon dioxide or any other harmful gases, like the case in burning fossil fuels or coal industry. The photovoltaic panels use semiconductors, mostly silicon, which is an abundant element and environmentally safe, but highly expensive, causing use of solar panels to be much less than expected. whereas using organic solar cells (OSC) is much more cost affordable. Hence, research in organic solar cells either using small molecules or polymers is gaining a lot of interest.

Theory of solar cells

Solar PVs are useful in converting sunlight to electricity in presence of a suitable semiconductor e.g. silicon. The process of conversion can be divided into two steps. First step is to generate free electrons on the semiconductor surface and the second step is controlling movement of these random free electrons to generate electricity. The key concept of free electrons generation is photoelectric effect; it can further be explained by band theory. A silicon array consists of valence bands, filled with covalently bonded electrons and conduction bands, which are empty in ground state. When high energy photons from sunlight falls on the silicon surface, they excite electrons from valence bands to the conduction bands and these electrons start moving freely. The second step is to control the movement of these electrons. In solar cells, two different types of Si are attached together, n-type, which generates spare electrons and p-type, with missing electrons (hole), once excited. Hence, excess electrons from n-type diffuse to the p-type, generating DC current.

Use of organic photovoltaics instead of inorganic semiconductors, have gained interest recently. As explained in figure 1, organoelectronic materials generally have an extended conjugation. Electrons of this conjugated hydrocarbon system are delocalized and they form highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals, with energy gap from 1 to 4 eV.[2] Photons with energy higher than this gap, can excite electrons from HOMO (comparable to the valence band) to LUMO (comparable to the conduction band) to generate excited state, known as exciton. In exciton, electron hole pairs are closely attached together by electrostatic interaction, can be separated into positive and negative charges in presence of a heterojunction, created by the LUMO energy difference of two dissimilar materials, donors and acceptors. The system is configured with electrodes to generate electricity.
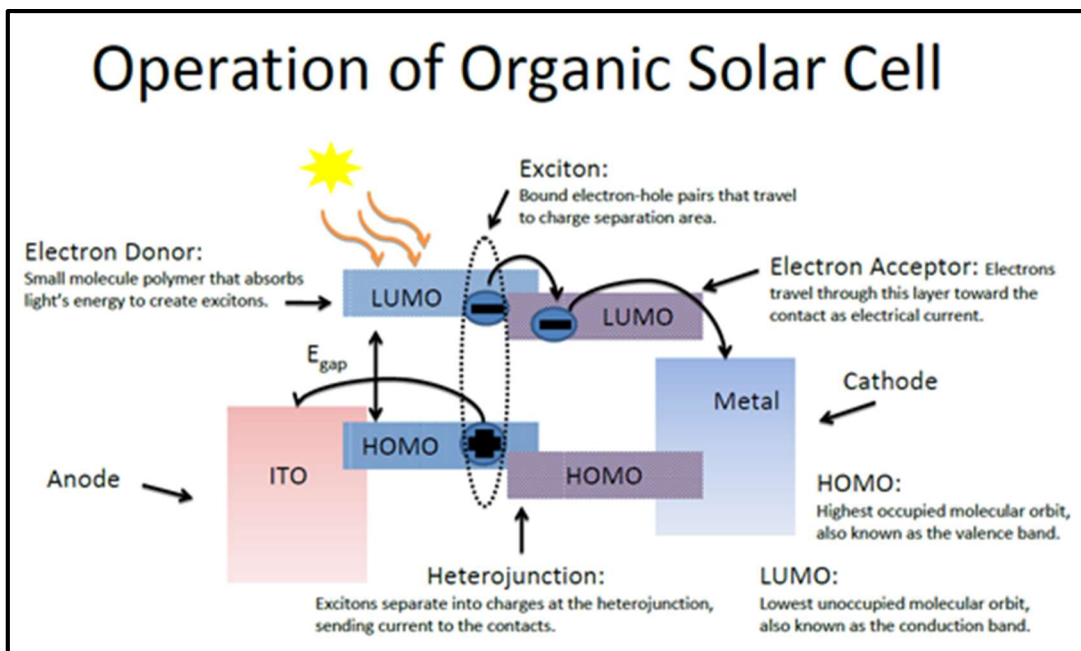
Fig1: Operation of organic solar cells

Development of bulk heterojunction (BHJ)

Early organophotovoltaics (OPV) were prepared by Tang et al. in 1986 and by Heeger and Wudl group in 1992 with efficiency 0.04-1%.[3] In both cases, researchers used bilayer heterojunction (fig 2) using different layers for donor and acceptor organic molecules. But, major issue with this type of heterojunction was limited exciton diffusion length at the interface, which is in the order of 10 nm. But, a polymer layer needs to 100 nm thick to absorb enough light. With higher thickness, only a small fraction of exciton can reach the interface.[4]

To overcome this drawback, concept of bulk heterojunction (BHJ) was introduced, where donor and acceptor materials are mixed together to form a bicontinous interpenetrating network with higher interface (fig 2) and thus increasing exciton diffusion length.
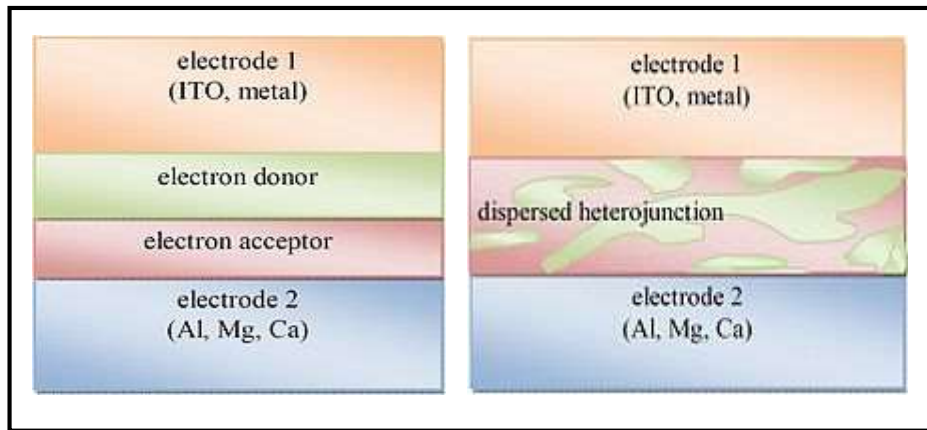
Fig 2: bilayer and bulk heterojunction

In polymer solar cells (PSC), the mechanism of BHJ, can be divided into 4 steps. First step is generation of excitons, second is exciton diffusion at the donor-acceptor interface, third is to form free charge carriers and last is charge transport and collection of electricity. Several works have been carried out in this field. In next few pages, we would like to discuss different approaches made to improve these steps to increase PSC efficiency and overall performance.

Design rules for light harvesting and exciton formation in PSC

Few criteria need to be maintained to get efficient light harvesting and exciton formation. The most important criterion is the absorption spectrum of polymer overlapping with the solar spectrum.

Secondly, HOMO- LUMO band gap is crucial for an efficient PSC. As low band gap broadens the absorption spectrum of polymers near solar spectrum, and hence increases absorbance of photons but also decreases the circuit voltage. Theoretical optimal band gap was calculated to be 1.3 electron volt.[5]

Another important factor is energy matching of the donor polymers with the electron acceptors. In most PSCs, fullerene based compounds are used as electron acceptors, where LUMO energy gap should not be much higher to generate excitons.

Donor-Acceptor copolymers (D-A)

D-A copolymers are relevant in this field, as they follow all the above criteria for efficient BHJ based PSC. Generally, donors are electron rich moieties and acceptors are electron deficient ones and the energy gap can be tuned by the substituent effects on both donor and acceptors separately. Figure 3, shows several donor and acceptor examples for these PSC. Designing these types in PSC is crucial, as effect of polymer backbone, side chain, substituents play important roles in monomer designing.
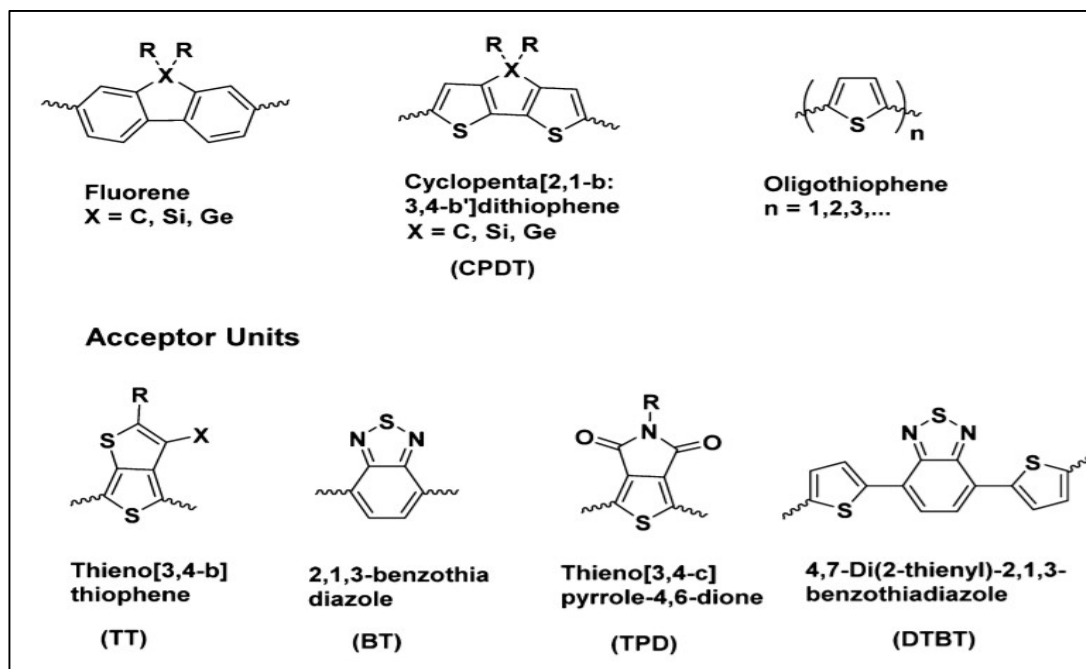

Fig 3: Different donor and acceptor polymers

Playing with the structure of the copolymer is the right way to achieve better suitability for solar cells applications. Although most of the above-mentioned copolymers have the required low band gap values, but changing their chemistry was very effective in increasing their efficiency in HJB based solar cells. For instance, in Wang's group, they synthesized and studied the structural changes effect on three low band-gap diketopyrrolopyrrole based polymers DPP with varying donor groups of furan, thiophene and phenyl. The compounds where then copolymerized with diphenylethene. Experimental work was carried out to study the effect of different donor groups and co-monomers on the band gap values, and on the charge

carrier mobility. These copolymers exhibited high π-π stacking and excellent hole-mobilities, where the charge mobility reached 2.36 cm^2 V^{-1} S^{-1}.[6]

Morphology Control in the Bulk Heterojunction Active Layer

Modifications in the structure of the active layer in BHJ based solar cells, aim at increasing the efficiency of the OPV, though all active layers have the same general BHJ structure, applying some morphological modifications may result in some changes to efficiency. When the small donor polymer molecule is successfully synthesized, it needs to be incorporated along with an acceptor molecules such as PCBM in the active layer, where applying changes especially to domain size and degree of interpenetration between domains will alter the performance of the organic solar cells.

The active layer needs to be penetrated by the exciton to migrate to the donor-acceptor interface. This penetration is largely dependable on the morphology of the interpenetrating network of the active layer. Taking in to consideration, the short life time of the exciton, the diffusion length of the active layer is found to be10 nm.

Having the right morphology enables the exciton to migrate to the donor-acceptor interface to undergo charge separation which is then transported away.

However, if the size of the domains is too small, this will increase the chances for bimolecular recombination between charge carriers. Thus, the domain size of both donor and acceptor should be finely adjusted to the correct sizes; It needs to be small enough to optimize exciton migration to the interface and at the same time, to be large enough to efficiently generate current. The research done in this field showed the ideal domain size for electron-donating conjugated polymers and an electron-accepting material to be 10-20 nm[7].

Controlling the morphology of the active layer is hence crucial to achieve higher PCE, and its importance in comparable to the necessity of developing low-band gap polymers to optimize the optoelectronic properties of the OPV[8,9].

Controlling the bulk morphology can be achieved through applying different chemical and physical processes, and here, we will explain two of these methods which are 1) solvent additives and 2) thermal annealing.

Solvent Additives

Changing the chemical composition through adding some chemical compound to the solvent was proven to be helpful in achieving the required morphology. Solvent additives method is applied during the spin casting of polymer: PCBM solutions to increase the PCE.

Here is one example that explains the effects of solvent additives on the morphology of the active layer of the OPV, and the subsequent effect on the PCE.

Solvent additives were first used in the PCPDTBT:PCBM system. Addition of a small amount of 1,8-octanedithiol (ODT), resulted in PCE increase from 2.8% to 5.5% . This increased efficiency was explained, based on TEM and AFM results. It was found that alkanedithiol selectively dissolves PCBM in the host solvent such as CB[10].

The additive, which is the ODT in this case is known to have a high boiling point, and evaporates slower than CB, so, the PCBM molecules will stay in CB longer than the donor polymer during the spin-casting process, Fig.4. Having longer time in the CB, will allow better crystallinity of the donor polymer and as well as enhanced control over phase separations in the blend[11].

PCPDTBT/PCBM   PCPDTBT/PCBM with additive

b)

PCPDTBT C$_{71}$-PCBM R: SH, Cl, Br, I, CN, CO$_2$CH$_3$
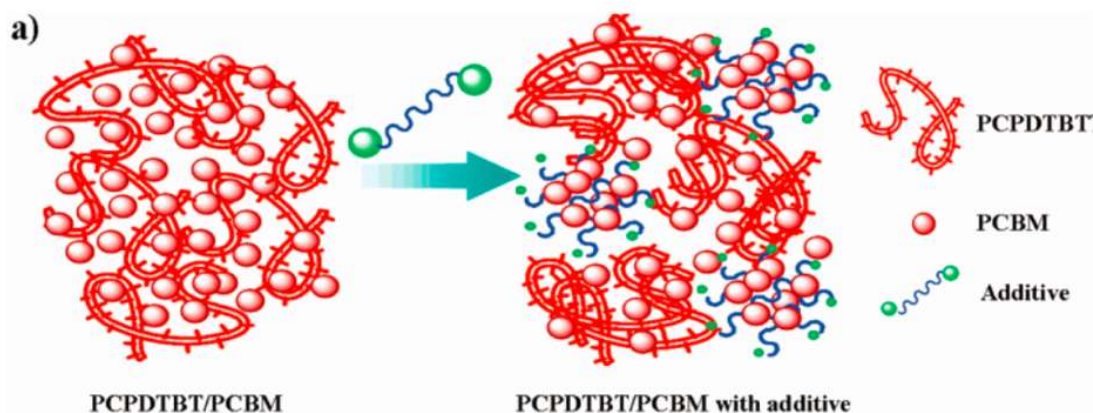
Additive
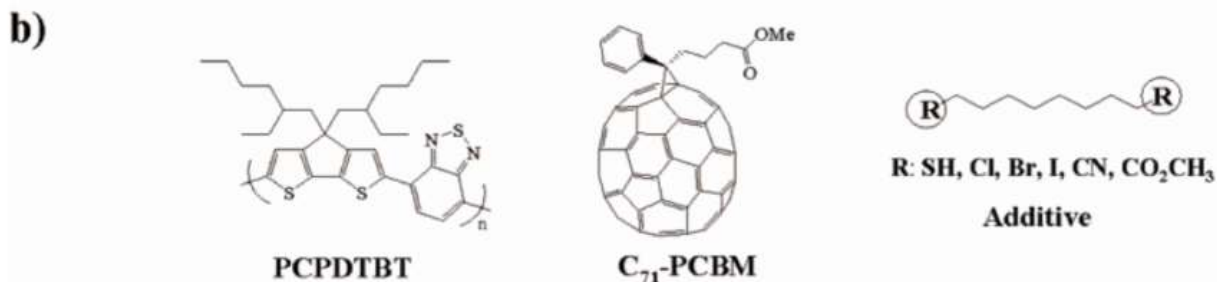
Fig.4: a)Schematic depiction of the role of the processing additive in the self-assembly of bulk heterojunction blend materials. (b) Structures of PCPDTBT, PC71BM, and additives.

Thermal Annealing:

Thermal annealing is another method to achieve powerful morphological control. It is a well-known method widely used in materials sciences research and industry, and involves heat treatment of the material that caused alteration of the physical and chemical properties of a material to increase its ductility and permeability, and harnesses its hardness, making it more workable.

This method involves the primarily heating of the material to a point that is above its recrystallization temperature, maintaining a suitable temperature, and then final cooling.

In semiconductors industry, silicon wafers are annealed, so that doping of other elements such as boron, phosphorus or arsenic, can be achieved and those elements can then diffuse into substitutional positions in the crystal lattice. This diffusion results in drastic changes in the electrical properties of the semiconducting material[12].

Thermal annealing was proven to be a successful method to control the morphology of certain types of active layer materials.

Here is one example where thermal annealing caused morphological changes that resulted in enhanced efficiency. The Friend group observed the effect of thermal annealing on P3HT blended with N,N-bis(1-ethylpropyl)-3,4,9,10-perylenebis(tetracarboxyl diimide) (EP-PTC). Annealing was carried out for 1 hour at 80 °C. The increase in efficiency was attributed to the enhanced crystallinity of P3HT from thermal annealing. The improved crystallinity resulted in better charge-transport properties in the blend[13].

Another example from Yang's lab, which did extensive efforts to optimize thermal annealing conditions in order to improve the morphology and performance of P3HT:PCBM devices, where it was observed that thermal annealing, caused self-organization which resulted in red shifting of the absorption of the device due to the enhanced interchain interaction from the highly ordered, crystalline structure[14].

Also, Erb et al. studied the effect of annealing on the structural and optical properties of P3HT:PCBM films using an X-ray diffraction technique. They found that thermal annealing caused reorientation of the P3HT main chains to a parallel way and the side chains perpendicular to the substrate in the polymer crystallites[15].
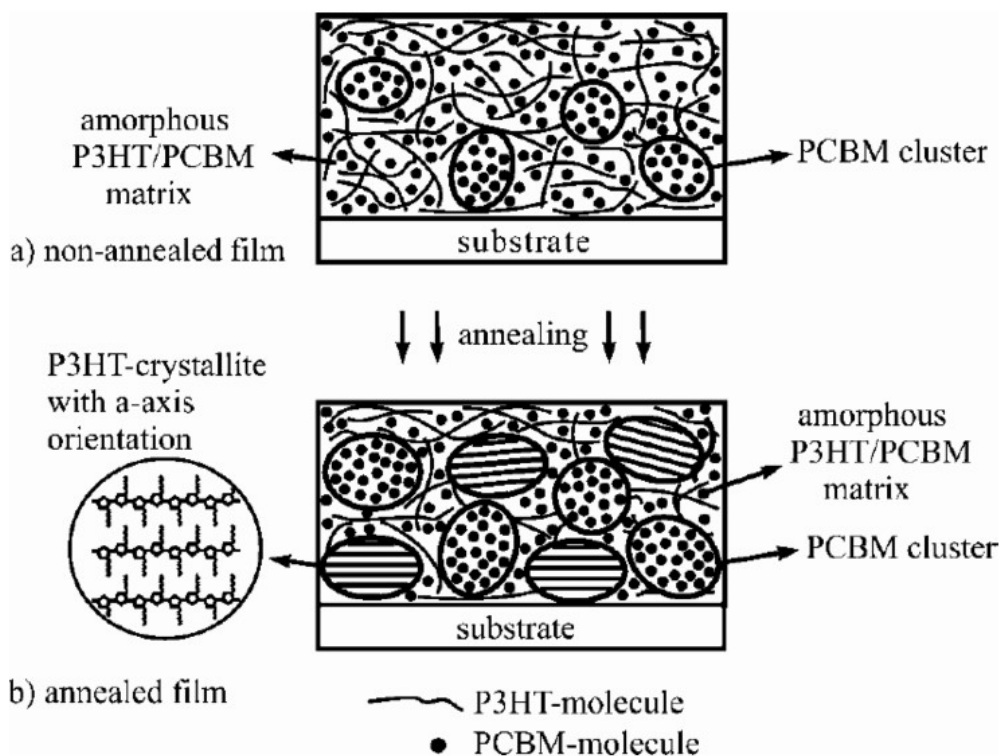

Fig 5: Schematic diagram of thermal annealing

Summary

In this report, we have explained the scope of polymer based OPV compared to traditional inorganic semiconductor based solar cells. Bulk heterojunction has shown immense opportunity in this field. As, this is still growing, much work has been done and still ongoing to improve the efficiency of OPV, we have summarized

different approaches such has general polymer design rules, D-A copolymers, morphology control of the active layer.

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