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Getting Power from Plastic – Solar Power Generation Using Blends of Organic Polymers and Nanostructures

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Abstract

The worldwide demand for energy is increasing each year causing a related increase in the amount of carbon dioxide produced to generate the energy. Photovoltaic devices offer carbon dioxide free power generation, although carbon dioxide is produced as a by product of their fabrication. Currently silicon based technology is most efficient and widely used form of solar power, but this can be expensive and energy intensive to produce as high temperatures and pressure are required to produce the high quality silicon necessary for power generation. We have investigated the possibility of using blends of inorganic nanostructures in a photoconductive polymer matrix to produce photovoltaic power. Although organic solar cells are not able to match silicon in efficiency at present they are easier to process and can be fabricated on flexible substrates which allow them to be used in a wider range of locations than silicon. Our experiments have demonstrated that by adding silver or barium titanate nanoparticles to polymers such as dihexyl sexithiophene (DH6T) and poly-3 (hexylthiophene) (P3HT) we can increase the photoconductivity of these materials by at least an order of magnitude and use these materials to easily fabricate photovoltaic cells by means of simple processes such as spin coating and sublimation.

Introduction

Currently photovoltaic power production represents less than 1% of the renewable energy production, although it is the fastest growing area of renewable energy, growing between 15 and 20% in the period of time from 1992 to 1998 (Goetzberger and Hebling, 2000) and continues to show signs of a year on year increase. Photovoltaic devices can be broadly divided into two categories, conventional semiconductor devices (CSC) and excitonic semiconductor devices (XSC), where CSC type devices are fabricated from silicon and related materials and XSC devices describes photovoltaic devices fabricated using polymers

and other organic materials in their active layer (Persson and Inganas, 2005). CSC devices, as the name implies, function in the same way as other semiconductor devices, in this case an incoming photon of the appropriate wavelength will excite the material causing an electron to be promoted to the conduction band and a hole left behind in the valence band (Nelson, 2003). In an XSC device the process is more involved and is further complicated by the use of different terminology as the descriptive terms were developed by organics chemists in this case. In XSC devices the valence band is known as the Lowest Occupied Molecular Orbital (LUMO) and the conduction band is known as the Highest Unoccupied Molecular Orbital (HOMO) as organic chemistry tends to describe effects in terms of molecular orbitals rather than energy levels, but the meanings are interchangeable. In this case an incoming photon will cause an excitation of the active layer, but rather than promoting an electron to the HOMO from the LUMO will create an electron-hole pair bound by coulomb forces, this state is known as an exciton, a full description of the process involved in converting an exciton into useable electrical energy is given along with a brief overview of the major types of solar cells is given in the sections below.

The comparative increases in efficiencies of the various types of solar cells to date are shown in Figure 3 below (Kazmerski, 2010).

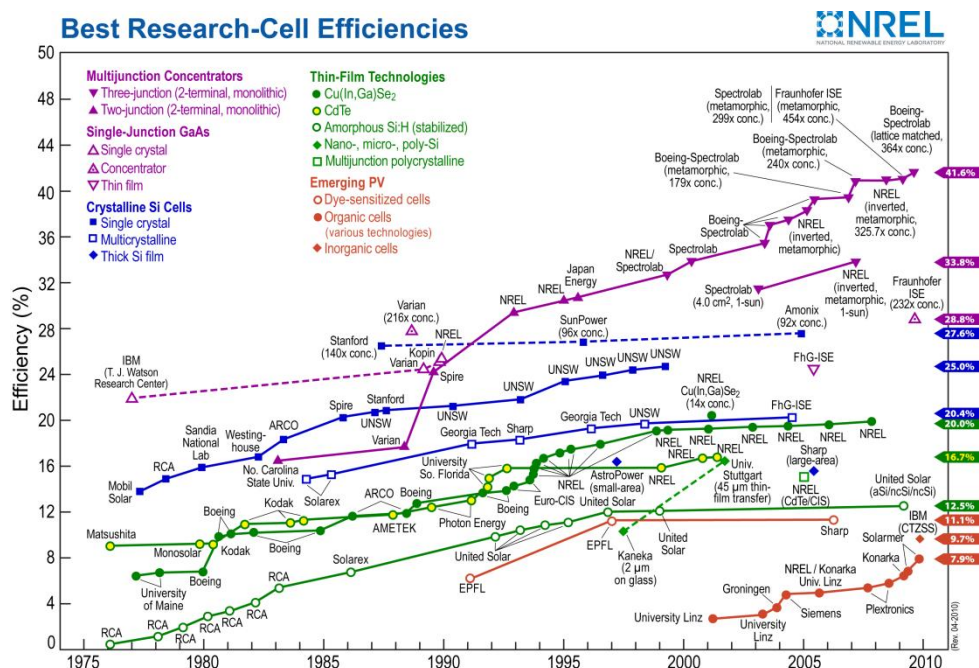


Figure 1 – Solar Cell Efficiencies.

Solar Cells – An Overview

First Generation Silicon Cells

The earliest (first generation as defined by Bagnall and Boreland (2008)) solar cells were bulk silicon cells comprising a single layer of mono-crystalline silicon grown using the Chochralski method and cut into thin wafers using a diamond saw. This was an expensive

process and due to the fact that initially up to 50% of the high grade silicon required for solar cell use was wasted in the cutting process, later developments enabled these losses to be reduced by roughly 30% with the use of the multi-wire saw (Goeztberger and Hebling, 2000). As the Chochralski method involves the creation of a single crystal rod, the subsequent slices are approximately circular and therefore area is wasted when constructing a bank of cells due to the difference in area between the circular crystal and the square cell.

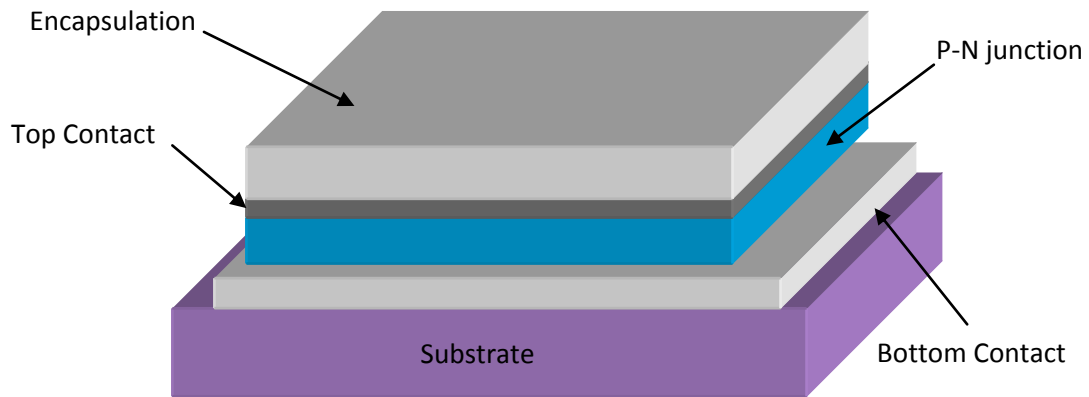


Figure 2– Typical silicon solar cell structure.

CSC solar cells are essentially p-n junctions formed from p and n doped material (usually silicon, but others are used), although in practice it is rare for two separate pieces of silicon to be used, standard practice being to dope either a p or n type wafer to form a p-n junction or a p-i-n junction, where the i stands for intrinsic, i.e. undoped material. These types of solar cell are still the most widely used and relatively efficient as the majority of solar cells are still of this type and they regularly achieve mass produced efficiencies in excess of 20% (Bagnall and Boreland, 2008).

An alternative to the Chochralski method is a process called block casting which results in a multi-crystalline structure (mc-Si) and is cheaper and can be formed into regular shaped sections prior to cutting, the structure is still similar to that described above for bulk silicon devices (Hepp and Bailey, 2005).

Another material used in bulk solar cells is amorphous silicon (a-Si), which has a glass like material structure, insofar as it has no regular crystalline structure. The use of a-Si is growing in popularity as a material for making solar cells; these are widely fabricated using rf plasma enhanced chemical vapour deposition (PECVD). The efficiency of amorphous silicon (~16% (Kazmerski, 2010)) does not currently have the potential to better that of single or multi crystalline silicon due to the presence of numerous traps and impurities such as hydrogen produced in the fabrication process (Hepp and Bailey, 2005) .

Second Generation Solar Cells

Second generation solar cells, as defined by Bagnall and Boreland (2008), comprise thin film alternatives to bulk crystalline silicon cells, the aim being to produce similar efficiencies

while dramatically reducing the amount of material used, and hence reduce the overall the cost of this type of cell. Silicon remains the most common material used in these devices, particularly a-Si and polycrystalline silicon (p-Si). However, other materials are increasing being used such as CuIn(Ga)Se₂ (CIGS), CdTe/CdS (CdTe) (Bagnall and Boreland, 2008). In general these materials are deposited onto cheap substrates by PECVD or similar alternative methods such as hot wire chemical vapour deposition (HWCVD), but low temperature alternatives are being investigated. These devices generally have efficiencies of around 20% (Kazmerski, 2010).

Third Generation Solar Cells

Third generation solar cells comprise multi-layer cells which are built up of layers of materials with different band gaps to enable the widest part of the spectrum of incoming photons to be captured and converted into energy. The material that has been used most often in these types of devices is gallium arsenide (GaAs); this has been developed by the US military since the mid 1950s, but has increased in use since the invention of the metal organic chemical vapour deposition method (MOCVD). These types of device generally have efficiencies in the range of 30-40% (Kazmerski, 2010).

Organic Solar Cells

Organic solar cells and variations thereof represent an exciting alternative to the materials and methods described above as they offer a potentially cheap and abundant supply of solar cells due to the relative ease and generally low temperatures involved in the fabrication process. They also have the advantage of being more flexible than CSC materials and can therefore be fabricated on flexible substrates which can be used in places where inflexible materials would be inappropriate such as clothing or areas subject to movement. There are two main types of organic solar cells currently being researched; dye sensitised cells and heterojunction devices.

The dye sensitised cell, also known as the Gratzel cell after its inventor, was first reported in 1991 and has since achieved efficiencies of around 11% (Gratzel, 2006), This used a liquid organic dye at surface of an inorganic wide band semi-conductor for absorption of light and photon injection into conduction band. Gratzel improved interfacial area between donor and acceptor using ruthenium dye sensitised nanoporous TiO₂ (band gap 3.2eV). The liquid electrolyte was not ideal and work has been done to replace this with a solid hole transporting material which it is reported combines light absorption and charge (hole) transport in a single material (Gratzel, 2006).

Heterojunction organic solar cells are the focus of our research, and are an extension of the original attempts to duplicate the PV properties of silicon solar cells. The first organic solar cells mimicked the structure of CSC cells, in that they were bilayer devices comprising of an electron donor material and an electron acceptor. Due to the limitations of exciton mobility, which will be discussed below, these devices were not successful and bulk heterojunction

devices were developed. These early devices consisted of a blend of donor and acceptor polymers and over the past few years have developed to include blends of polymers (as electron donor) and nanoparticles as electron acceptors, the most commonly used blend being a combination of poly-3 (hexylthiophene) P3HT and Phenyl-C61-butyric acid methyl ester (PCBM) a type of carbon known as a fullerene with a polymer ligand to aid solubility. Recent innovations have lead to efficiencies in this type of device of up to 10%. The general structure of bulk heterojunction solar cells is shown in figure 2 below.

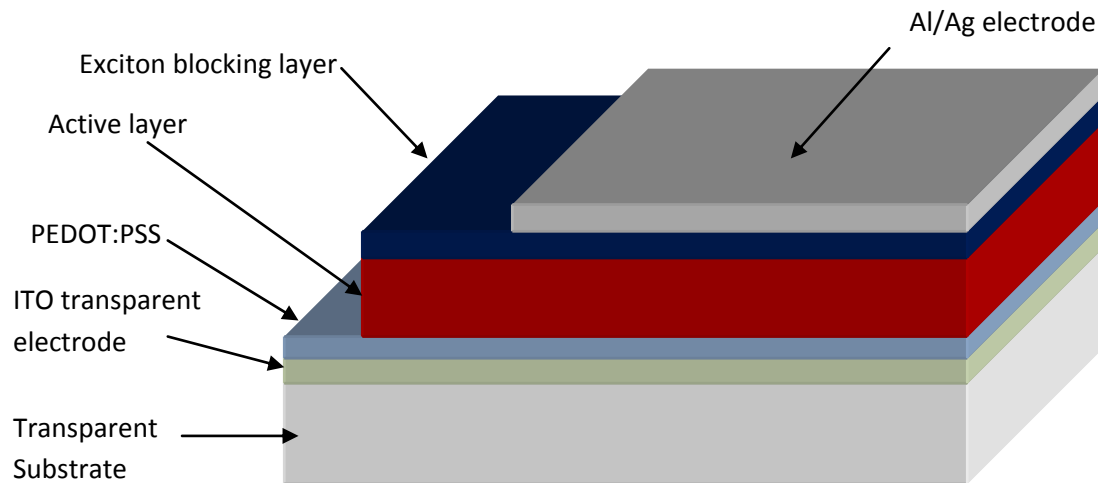


Figure 3– Typical organic heterojunction solar cell structure.

The transparent electrode (Indium-Tin-Oxide (ITO)) is required to allow incident photons to pass through into the active layer; it is also required to be electrically conductive to complete the circuit. PEDOT:PSS is a conductive polymer, this layer improves the electrical connection between the active layer and the ITO layer. The active layer can comprise a variety of materials and structures, but in essence its role is to capture as close to 100% of the incident photons as possible and convert them into electrical energy. The exciton blocking layer enhances efficiency by preventing excitons migrating to the top electrode before they have been split into useful charge carriers. The top electrodes are generally silver or aluminium and are required to complete the electrical circuit.

Excitonic Behaviour

Excitons are quasi-particles that are composed of a bound state of an electron and a hole (a virtual positive particle). Electrons and holes are both Fermions, which are particles that have half integer spin and obey Fermi-Dirac statistics, but as the exciton is made up of two Fermions, which can have either the same or opposite spins the sum of the spins add up to either zero or an integer value and therefore they behave as Bosons and obey Bose-Einstein statistics.

Excitons exist as two main types; Frenkel excitons which are tightly bound and generally have a radius equivalent to roughly one lattice spacing and Mott-Wannier excitons which are loosely bound and can extend over many lattice spacings (Gregg, 2005); Which of the two

types is present in a given material depends upon the permittivity of the material, in general low permittivity materials (those with a permittivity less than silicon dioxide $\sim 3.7-3.9$) form Frenkel excitons and high permittivity materials form Mott-Wannier excitons. The majority of polymeric materials used in solar cells have relatively low permittivities and therefore form Frenkel excitons.

Persson and Inganäs (2005) have suggested a seven step model for the generation of power by organic solar cells; the seven processes are as follows:

1. Incoupling of the photon – The material should be as transparent as possible to light and reflection and other losses should be minimised either by antireflective coatings or by the composition of the material itself.
2. Photon absorption – Optical absorption is related the distribution of the modulus of the optical electrical field $|E|^2$, which is dependent upon the local dielectric function and the geometry of the device.
3. Exciton formation – The excitation of an organic solid produces an exciton, usually the type of excitons produced in organic polymers are Frenkel excitons.
4. Exciton Migration – Exciton migration is described in terms of the Diffusion Length (LD) and is generally of the order of a few tens of nanometres in organic materials although some experiments by Kurrle and Pflaum (2008) using the polymer diindenoperylene (DIP) have demonstrated diffusion lengths of up to $\sim 100\text{nm}$ and exciton lifetimes of $\sim 10\text{ns}$. Excitons have a finite lifetime, and can decay by a variety of mechanisms, some of which are beneficial such as dissociation into electrons and holes and some of which are not such as radiative decay which results in the creation of a photon which is re-emitted and lost, thermal and vibronic decays also result in a loss.
5. Exciton Dissociation – Dissociation generally requires an external influence such as an interface between materials in order to occur. In general an inhomogeneity is required for dissociation to occur; this is often due to a difference in the electron affinities of two materials. Once excitons have dissociated they can either become useful charge carriers or they can occasionally recombine to form new excitons. There are two types of recombination, geminate, where the electron and hole from the original exciton recombine and non-geminate biomolecular recombination where electrons and holes form different dissociated excitons recombine.
6. Charge Transport – Once the excitons have dissociated into electrons and holes, the charge carriers must be free to migrate to the electrodes. Electrons and holes have different mobilities within materials and can become trapped or recombine if the distance to the electrode is too great.
7. Charge collection at the electrodes – Whether charges can be collected at the electrode are a function of the surface of the electrode and the interface between the electrode and the polymer. Collected charges are then free to pass into the electrical circuit.

Work done by EMTERC

We are working on producing hybrid organic/inorganic solar cells, which have active layers containing organic polymers blended with inorganic materials as these hold the promise of higher efficiency.

As described above, excitons will only dissociate into free charge carriers at or very near the interface between different polymers or between polymer and incorporated nanostructures. This is due to the existence of a potential barrier between the two materials caused by the difference in work functions of the materials. The conditions required for charge separation are that the binding energy of the exciton is less than the potential barrier height of the interface, e.g. that the difference in energy of the highest occupied molecular orbital of the polymer (HOMO) and the work function of the nanostructure is greater than the coulomb forces of the exciton. The volume over which charge separation can occur is known as the dissociation region. By increasing the relative permittivity of the photoconductive material we believe that it is possible to increase the diameter and hence the volume of the dissociation region. If this can be increase to the point where all the dissociation regions around each nanostructure overlap then the maximum amount of excitons can be converted into charge carriers. The relative permittivity of the material (ϵ) determines its ability to permit an electric field. It is linked to the Debye Length (L_D) by the following equation (Gregg, 2005):

$$L_D = \left[\left(\frac{\epsilon \epsilon_0 k T}{q^2 N} \right) \right]^{1/2} \quad (1)$$

Where ϵ is the relative permittivity, ϵ_0 is the permittivity of free space, k is Boltzmann's constant, T is the temperature, q is the charge of the particle (typically the elementary charge of the electron) and N is the carrier concentration.

The Debye Length is a measure of the distance over which mobile charge carriers' screen out electric fields. As the Debye Length around the nanostructures increases then the exciton dissociation region around each nanostructure also increases proportionately. Given the short diffusion length of excitons in polymers, in order for efficient charge capture to occur the nanostructures should be homogeneously distributed with a separation of the same order as the diffusion length. By increasing the permittivity, and hence the Debye Length, the distance between nanostructures can be increased as the dissociation region expands. The typical size of these nanostructures varies up to ~100nm, with the ideal size being the same order as the distance between the nanoparticles. By correctly choosing suitable materials to ensure the energy barrier is greater than the binding energy of the exciton and by tuning the Debye length it should be possible to maximise the amount of free charge carriers created. This could be done by ensuring that all of the dissociation regions around each nanoparticle overlap and therefore the whole blend becomes a superposition of these regions. Thus regardless of the short lifetime, and hence diffusion length, of excitons increasing the relative permittivity will increase the likelihood of dissociation into free charge carriers.

We have made steps in this direction by incorporating barium titanate (BT) particles with an octyl phosphonic acid (OPA) ligand (Kim et al, 2007) into a matrix with various blends of polymers such as P3HT and DH6T and other nanoparticles such as PCBM and silver. We have demonstrated that BT/OPA increases the relative permittivity of insulating polymers (Black et al, 2010) in a patented blend of polymers and nanoparticles (Paul and Black, 2010). Further blending of BT/OPA with photoconductive polymers such as P3HT has demonstrated a marked increase in the photoconductivity of the blend compared to the unmodified polymer. Work is now progressing to incorporate these materials into the active layer of hybrid solar cells with the aim of increasing the efficiency of these cells by increasing the exciton diffusion length and hence the number of excitons converted into charge carriers.

Discussion and Conclusions

While organic photovoltaic devices currently are of lower efficiency than silicon and other CSC materials, the ease of processing combined with the fact that they can be fabricated on flexible substrates means that they are likely to have a wide range of uses in the future. While it is likely that future main solar power will remain in the area of CSC devices, future personal power generation e.g. phone/MP3 player charging could be done by XSC devices incorporated into clothing. Also in areas prone to tectonic activity the flexibility of XSC devices could allow solar power to be used without expensive shock absorbing mechanisms. It is anticipated that by incorporating BT/OPA into a P3HT polymer matrix as the active layer of a solar cell similar to that shown in Figure 3, the efficiency of these cells can be improved as a result of increasing the Debye Length and hence the exciton diffusion length of these materials.

We look forward to being able to report success in this endeavour in the not too distant future.

References

- BAGNALL, D. M. & BORELAND, M. (2008) Photovoltaic technologies. *Energy Policy*, 36, 4390-4396.
- BLACK, D., PAUL, S. & SALAORU, I. (2010) Ferro-electric Nanoparticles in Polyvinyl Acetate (PVAc) Matrix - A Method to Enhance the Dielectric Constant of Polymers. *Journal of Nanoscience and Nanotechnology*, 2, 1-5.
- GOETZBERGER, A. & HEBLING, C. (2000) Photovoltaic materials, past, present, future. *Solar Energy Materials and Solar Cells*, 62, 1-19.
- GRÄTZEL, M. (2006) Photovoltaic performance and long-term stability of dye-sensitized mesoscopic solar cells. *Comptes Rendus Chimie*, 9, 578-583.
- GREGG, B. A. (2005) Coulomb Forces in Excitonic Solar Cells. IN SUN, S. S. & SARICIFTCI, N. S. (Eds.) *Organic Photovoltaics: Mechanisms, Materials and Devices*. 1st ed. Boca Raton, Taylor and Francis.
- HEPP A. F. AND S. G. BAILEY, (2005), *Inorganic Photovoltaic Materials and Devices: Past, Present and Future*, IN SUN, S. S. & SARICIFTCI, N. S. (Eds.) *Organic Photovoltaics: Mechanisms, Materials and Devices*. 1st ed. Boca Raton, Taylor and Francis.
- HOPPE, H. & SARICIFTCI, N. S. (2004) Organic Solar Cells: An overview. *J. Mater. Res.*, 19, 1924-1944.
- KAZMERSKI, L., National Renewable Energy Laboratory (NREL)
<http://en.wikipedia.org/wiki/File:PVeff%28rev100414%29.png> accessed 29th April 2010.
- KIM, P., JONES, S. C., HOTCHKISS, P. J., HADDOCK, J. N., KIPPELEN, B., MARDER, S. R. & PERRY, J. W. (2007) Phosphonic acid-modified barium titanate polymer nanocomposites with high permittivity and dielectric strength. *Advanced Materials*, 19, 1001-1005.
- KURRLE, D. & PFLAUM, J. (2008) Exciton diffusion length in the organic semiconductor diindenoperylene. *Applied Physics Letters*, 92, 133306-1.
- NELSON, J. (2003) *The Physics of Solar Cells*, Imperial College Press.
- PAUL, S. & BLACK, D. (2009) Organic Photoconductive Material. UK.
- PERSSON, N.-K. & INGANAS, O. (2005) Simulations of Optical Processes in Organic Photovoltaic Devices. IN SUN, S. S. & SARICIFTCI, N. S. (Eds.) *Organic Photovoltaics: Mechanisms, Materials and Devices*. 1st ed. Boca Raton, Taylor and Francis.