

# Turning Sunlight into Electricity

## Inorganic Solar Cells and Beyond

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The intensity of solar radiation in the Earth's direction from the Sun is approximately  $1353 \text{ kW/m}^2$ , a number also called the 'solar constant'. Accordingly, it is estimated that Earth receives about 96 billion kilowatts from the Sun each second. If this colossal and unlimited energy could be more fully utilized, our dependence on fast dwindling fossil cache will be drastically reduced. Solar energy is available in various forms such as direct solar radiation, wind, wave power, rain (in the form of hydropower), photosynthesis and ocean thermal gradients. Among these, the direct conversion of sunlight into electricity is clean and attractive. This article highlights various routes to directly harness electricity from sunlight.

### Sunlight to Electricity through Inorganic Solar Cells

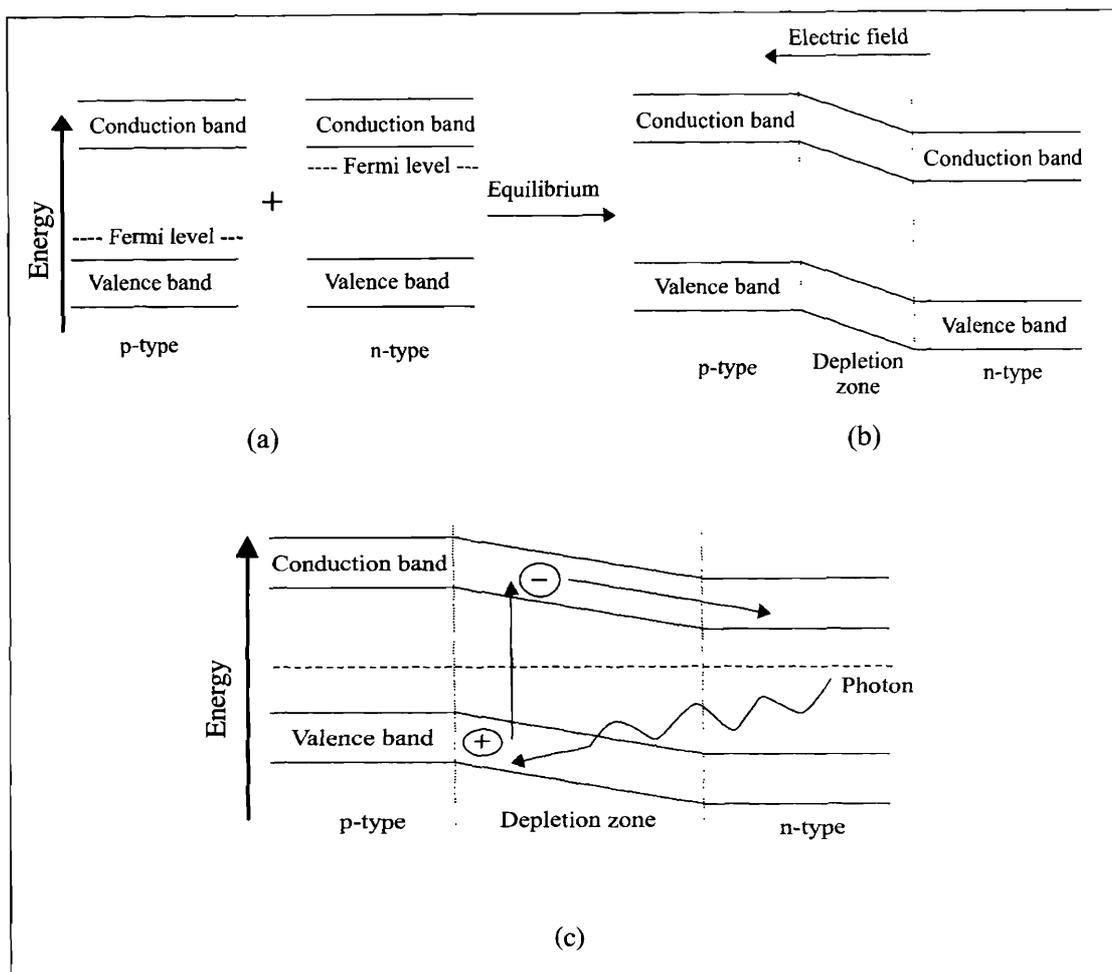
Inorganic solar cells are p-n junction devices. In the region of the crystal where n- and p-type meet, there is discontinuity in the electron concentration. Although both n- and p-type are electrically neutral, the n-type has a greater concentration of electrons than the p-type (*Figure 1a*). In order to try and equalize the electron concentration, electrons drift from n- to p-type. However, this produces a positive electric charge on the n-type and a negative electric charge on the p-type. The electric field thus set up encourages electrons to drift back to the n-type. Eventually, a state is reached in which the two forces are balanced and the electron concentration varies smoothly across the junction. This is the situation in the dark (*Figure 1b*).

The use of the p-n junction as a solar cell depends on its response to light. If the wavelength is short enough for the photon energy

#### Keywords

Sunlight, electricity, solar cells.





to be greater than the band gap energy then electrons will be promoted across the band gap to the conduction band. The promoted electron will be attracted to the positively charged n-type region. The gap in the valence band will move to the p-type region because an electron from this side would be attracted across to the n-type region to fill any electron hole there. The promoted electron and the electron hole are now separated in space and hence the conduction electron cannot simply emit light and return to the valence band. It is free, however, to travel through the n-type to an external circuit (Figure 1c). The electric current thus produced can be used to do work. Thus, the illuminated p-n junction acts as a battery.

**Figure 1. Band diagrams of (a) p- and n-type inorganic semiconductor, (b) p-n junction in dark, and (c) p-n junction on illumination.**

Individual solar cells generate only a low voltage (typically around 0.6V) and power output ( $\sim 1.5$  Peak-Watt Power ( $W_p$ )). The cells are therefore packaged together to form a 'solar module' or a 'solar panel' that provides a useful voltage and current. The efficiency of silicon solar cells for the conversion of light energy to electricity has increased steadily over the years to present values of up to 18% for amorphous silicon, and 25% for single crystal cells. At the same time, the cost of cells has fallen substantially, as a result of improved manufacturing technology and greater production throughput. In the late 1970s, module prices were US \$ 15 to 20 per  $W_p$ , whereas today they are around US \$ 5 per  $W_p$  (1US\$  $\sim$  Rs. 45). In recent years, increased attention has been paid to the development of thin amorphous cells as these hold promise to be lower cost devices though somewhat less efficient. Crystalline silicon is not the only semiconductor that can be used for photovoltaic cells. Other possible candidates include gallium arsenide (GaAs), cadmium telluride (CdTe) and copper indium diselenide ( $CuInSe_2$ ).

### Sunlight to Electricity through Organic Solar Cells

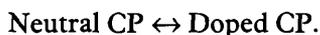
Another exciting prospect still in the research stage, but with good scope for cost reduction, is that of organic solar cells or organic photovoltaic devices [1]. Synthetic organic materials such as plastics are used literally everywhere in our daily lives. It is therefore not a big surprise that ever since the discovery of semiconducting polymers, possibilities have been foreseen for the replacement of inorganic solar cells with their organic counterparts. If these can be developed successfully, then they may revolutionize the whole field of photovoltaics to bring down the cost and open a new range of applications.

Organic materials used presently in solar cells include conducting polymers, dyes, pigments and liquid crystals. Among these, conductive polymers are perhaps the best known for their photophysical properties. In 1977, Heeger, MacDiarmid and Shirakawa showed that conjugated polymers [2] could be made electrically conductive by suitable doping. The discovery and



the subsequent development of conducting polymers<sup>1</sup> led to Nobel Prize in Chemistry to these authors in 2000 [3].

Conjugated polymers are organic molecules with repeating structural units attached to each other by alternating single ( $\sigma$ ) and double ( $\pi$ ) bonds<sup>2</sup>. In this alternating chain of single and double bonds, the molecular  $p_z$ -orbitals constituting the  $\pi$ -bonds are actually overlapped and spread over the entire molecule, and the electrons in this molecular orbital are respectively delocalized (free to move) along the entire molecular chain. A many-fold increase in the conductivity of the polymer is achieved by oxidizing it to produce p-doped materials or reducing it to produce n-doped materials. For example, as-synthesised polyacetylene (PA) is a neutral semiconductor with its electronic conductivity less than silicon. Electronic conductivity of the conjugated polymer is promoted through its doping that changes the oxidation state of the conjugated polymer without affecting its structure. Doping of the conjugated polymer (CP) is a redox process involving the creation of charged species as shown below.



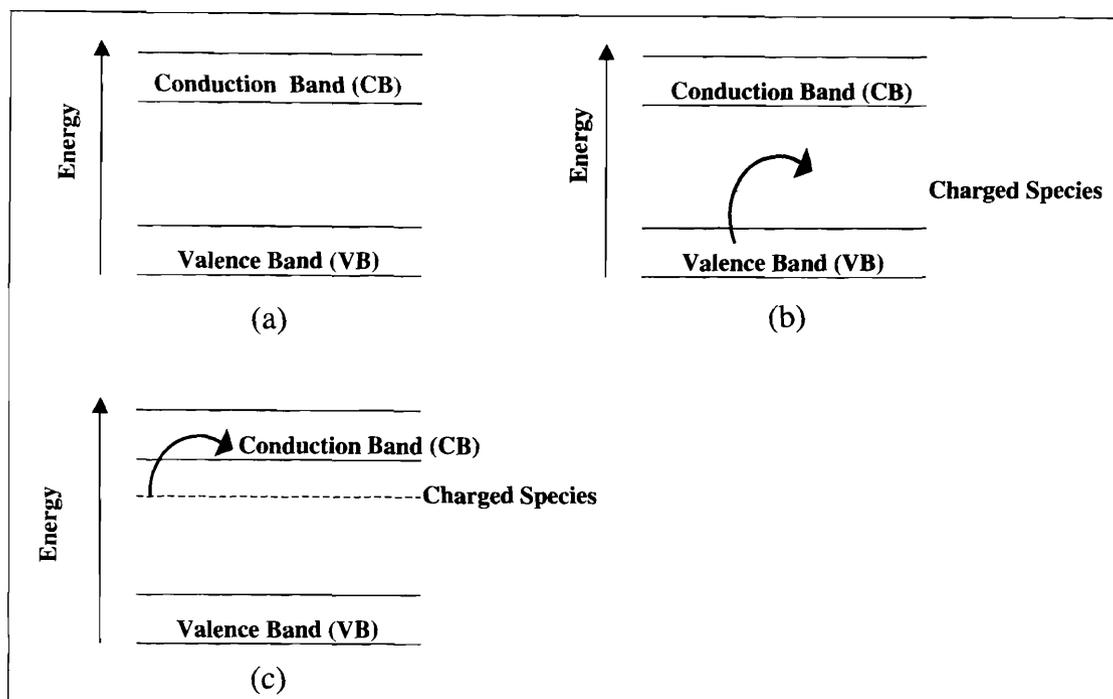
In the doping process, electrons are removed from the top of the valence band (p-type doping) or added to the bottom of the conduction band (n-type doping) as shown in *Figure 2*. Upon p-doping, electrons are removed from the conjugated polymer leaving electron holes in the  $\pi$ -electron orbitals. These electron holes can be filled by  $\pi$ -electrons hopping from the nearby molecules making the conjugated polymer electronically conducting.

If the conjugated polymer has two energetically equivalent (Kekule) structures, as in polyacetylene,  $(-\text{CH})_x$ , a surface defect called 'soliton' is formed that moves in a solitary wave, a non-linear process involving non-dispersive transport of energy in a dispersive medium. By contrast, if the conjugated molecule does not have two energetically equivalent structures, it results in a motionless charged state called 'polaron', i.e. an electron in a

See the article by T P Radhakrishnan, Renaissance of the Plastic Age, *Resonance*, Vol. 6, No. 2, 2001.

<sup>2</sup> A Sigma ( $\sigma$ ) bond is a bond formed by the overlap of two hybrid orbitals through areas of maximum electron density. A Pi ( $\pi$ ) bond is a bond formed by the overlap of two un-hybridized, parallel p-orbitals through areas of low electron density. The primary bond used to connect two atoms to each other is the  $\sigma$ -bond. Any additional bonds between two atoms will be  $\pi$ -bonds. The  $\sigma$ -bond is the stronger of the two types because of its effective use of areas of maximum electron density. The  $\pi$ -bonds are weaker and more vulnerable to chemical attacks. This is primarily because  $\pi$ -bonds locate maximum electron density between the bonding nuclei but off to the sides a little bit. A single bond is always a  $\sigma$ -bond. A double bond is a  $\sigma$ -bond and a  $\pi$ -bond. A triple bond is a  $\sigma$ -bond and two  $\pi$ -bonds.





**Figure 2.** Band diagrams for (a) neutral, (b) *p*-doped, and (c) *n*-doped conjugated polymer.

polarised lattice, brought about by the distortion of the lattice with concomitant lowering in the lattice energy. The polaron has a spin = 1/2 and the combination of two polarons results in a spinless bipolaron, which is thermodynamically more stable.

The photovoltaic properties of crystalline inorganic semiconductor solar cells can be described by energy bands. The situation in polymeric organic solar cells is however complex due to the absence of a 3-dimensional crystal lattice, different intramolecular and intermolecular interactions, local structural disorders, amorphous and crystalline regions and chemical impurities. But, the basic steps of photovoltaic conversion, namely light absorption, charge separation, and charge transport and collection, need to be fulfilled in the organic photovoltaic materials as well.

In conjugated polymers, the delocalised  $p_z$ -orbitals constituting the  $\pi$ -bond actually produce two orbitals, namely a lower bonding ( $\pi$ ) orbital and an upper antibonding ( $\pi^*$ ) orbital. The difference between the energy states corresponds to the energy



gap of the semiconducting polymer material, which is smaller for the longer conjugation length of the molecule. The absorption of light with energy equal to or above the energy gap generates an electron in the  $\pi^*$ -level and an electron hole in the  $\pi$ -level. Unlike inorganic semiconductors, where photo-generated electrons and electron holes are free in the conduction and valence band, respectively, the generated electrons and electron holes in the conducting polymer are loosely bound together by coulombic forces. The electron-electron hole pair is called 'exciton' and moves within the material as one entity. The operation of a polymeric solar cell requires splitting of the excitons prior to their recombination. The excitons can be dissociated by charge transfer at interfaces such as the interface between a metal and the polymer material or interface between molecules of different electron donating and accepting properties. The electron is accepted by a material (electron acceptor) with large electron affinity and the electron hole by a material (electron donor) with lower ionization potential. The excitons can also be dissociated simply in an electric field strong enough to overcome the coulomb attraction between the electron and the electron hole in the exciton.

In a donor-acceptor molecular junction, the charge separation process can be further increased to an excitonic step, where some sort of charge transfer exciton is formed with an electron in the acceptor side and an electron hole in the donor side of the junction, and to an electronic step, where the electron and electron hole are separated by thermal dissociation or ionisation in an electric field. In most of the organic solar cells, the separated electrons and electron holes are transported to the opposite electrodes in an internal electric field created by asymmetry of the electrodes due to different work functions or in-built potentials. In order to reduce recombination, the electrons and electron holes are preferentially transported in different materials or phases. For example, in the case of a donor-acceptor device, an acceptor material with good electron conductivity and a donor material with good electron hole conductivity is ideal. Good



non-blocking contacts between the molecular materials and the electrodes of the cell are essential for efficient charge collection. Interestingly, operational lives for organic solar cells exceeding 10000 h have already been achieved.

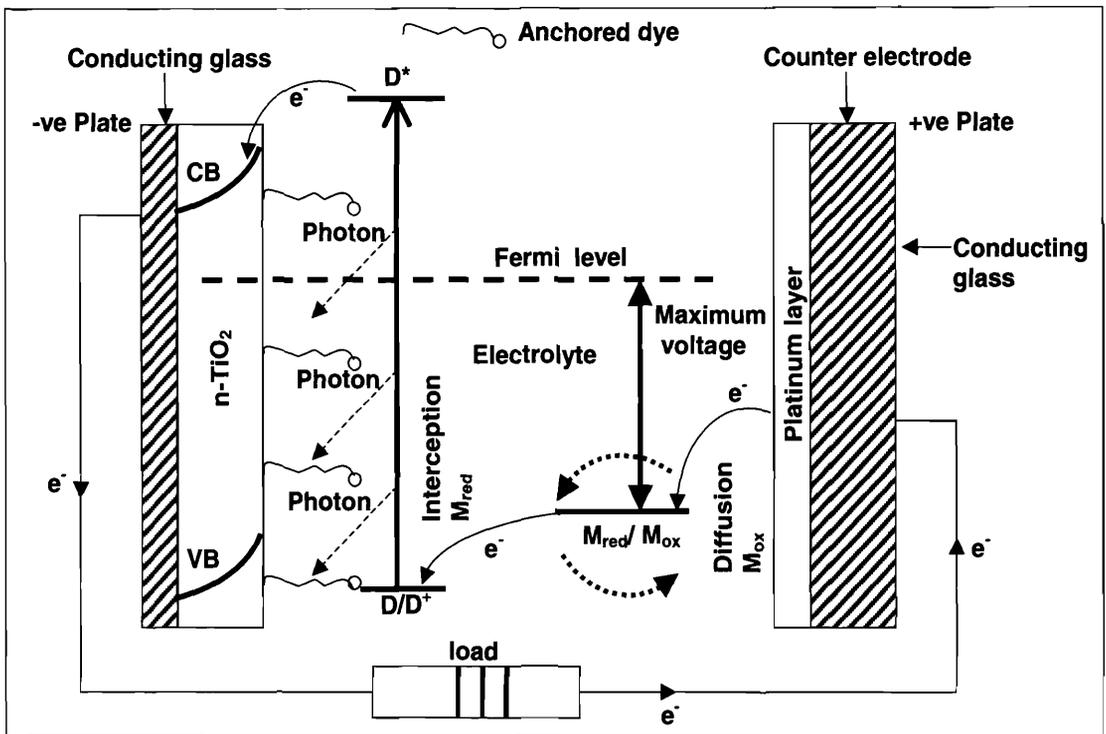
### Sunlight to Electricity through Dye-Sensitized Solar Cells

Yet another variant of photovoltaic technology is the so-called 'dye-sensitized solar cell' [4]. Titania itself is a semiconductor with a relatively high band gap of  $\sim 3.2\text{eV}$  and therefore absorbs light energy in the ultraviolet rather in the visible part of the spectrum. By virtue of its low cost, however, titania is most attractive as a photovoltaic material and therefore considerable work has been undertaken to shift its spectral response into the visible region. Although this has not been achieved, research has now shown that it is possible to circumvent the band gap problem by means of a subterfuge. This involves separating the optical absorption and charge-generating functions. A dye, which is capable of being photoexcited, is adsorbed onto the surface of the titania and acts as an electron-transfer sensitizer. The coated titania serves as the negative electrode in a photochemical cell. The operating principle of such a cell is shown in *Figure 3*. The dye (D), after having been excited ( $D^*$ ) by a photon of light, transfers an electron to the conduction band of the titania ('injection process'), and itself becomes  $D^+$  in the process. The cell electrolyte contains a 'redox mediator', i.e. a substance that can be oxidized and reduced electrochemically. Positive charge is transformed from the dye to the mediator ( $M_{\text{red}}$ ) and the dye is returned to the reduced state ('interception process'). The oxidized mediator ( $M_{\text{ox}}$ ) diffuses to the positive counter electrode, where it is reduced again by the electrons traveling around the external circuit. The theoretical maximum voltage that such a cell can deliver is the difference between the redox potential of the mediator and the Fermi level<sup>3</sup> of the semiconductor (*Figure 3*).

<sup>3</sup> Fermi level is the thermodynamic electrochemical potential or the energy in a solid, below which it is more likely that the electronic states are occupied with electrons and above which it is more likely that the electronic states are not occupied; because it is defined statistically, there may or may not be an energy level at this energy.

In practice, the titania electrode is present as a thin film of tiny





crystals that have diameters of just a few nanometers and are sintered together. This film is deposited on a transparent, conducting glass substrate (generally coated with tin oxide) that acts as a current collector. The titania is ultra porous and has a very high surface area, which assists the uptake of dye from solution. The dye-coated electrode is then assembled into a cell with a counter electrode, also made from conducting glass and the intervening space is filled with electrolyte and the mediator, typically iodide-triiodide couple:  $I^- / I_3^-$ . Various physico-chemical processes occurring during the illumination of a DSSC with light are shown in Box 1. A small amount of platinum is deposited on the counter electrode to catalyze reduction of the mediator. Such cells have demonstrated efficiencies of 10% in the laboratory and 5% in the field.

Undoubtedly, compared to inorganic solar cells, the dye-sensitized titania cells have lower efficiency under conditions of strong solar radiation, but exhibit far superior performance at

*Figure 3. Operating principle of a dye-sensitized solar cell.*

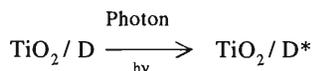


## Suggested Reading

- [1] R M Dell and D A J Rand, *Clean Energy*, Series Editor, J H Clark, The Royal Society of Chemistry, 2004.
- [2] *Hand Book of Conducting Polymers*, Vols. I & II, Ed. T A Skotheim, Marcel Dekker, New York, 1986.
- [3] *The Hindu Speaks on Scientific Facts*, Vol. II, Editor-in-chief, N Ram, Kasturi & Sons Ltd., p.207, 2004.
- [4] J Halme, *Master's Thesis*, Helsinki Institute of Technology, Helsinki, 2002.

## Box 1. Physico-chemical Processes Occuring on Illumination of a DSSC with Light.

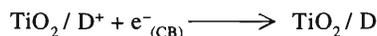
(a) Dye excitation



(b) Charge injection into semiconductor



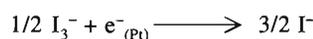
(c) Back reaction of injected electron with dye cation



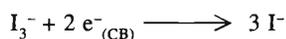
(d) Reduction of oxidized sensitizer by the electron donor of the electrolyte



(e) Regeneration of charge mediator



(f) Reaction of the injected electron with electron acceptor in the electrolyte



The efficiency of the DSSC is dictated by spectral response of sensitized titania brought about by the aforesaid physico-chemical processes.

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low illumination levels. This technology is in infancy but holds great promise for cost-effective clean energy in future.

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