

# Solar Energy Harvesting Through Photovoltaics and Photocatalysis

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## Introduction

The rise in global population is driving the demand for energy every day. However, the depleting fossil fuel reserves and greenhouse emissions have thrown the challenge of finding alternative energy sources that are both clean and renewable. The solar energy, with a power output of  $3 \times 10^{24}$  J/year has the capability of fulfilling the Earth's energy demand. However, the sunlight needs to be properly harvested in order to generate alternative energy sources. This article presents a brief overview of the solar photovoltaic (PV) (sunlight to electricity) and solar photocatalysis (sunlight to chemical/fuel) materials and current technologies. [1] Under the PV domain, only basic categories of solar cells have been discussed. The advanced categories such as tandem, multijunction or hybrid configurations have not been mentioned. Similarly, a brief discussion on photocatalysis centres around the basic principles and various materials under study. The details of reactor designs, product profiles and efficiency values have not been discussed. Such details can be found in the cited papers and references therein.

## Solar Photovoltaic Technologies

The photovoltaic effect was discovered by Henry Becquerel in 1839. However, it took more than 100 years to develop first solar cell with Silicon having 6% efficiency [2]. Since the initial years of development, till today, silicon solar cells remain the backbone of PV technology. The development of microelectronics industry also contributed a lot into the progress of Si based solar cells since its discovery. The rapid development over the past fifty years has also been made possible by increasing awareness about global warming and depleting fossil fuel reserves, which has triggered large scale research on PV technologies. As a result of which, the contribution of PV to gross electricity production has grown from 0.01 % in 1990 to about 1.7% in the recent times. Globally, 300 GW of total installation has been targeted for the year 2017. [3] At the fundamental scale, the solar cell materials should satisfy two conditions: (i) Efficient light absorption and charge carrier generation (ii) separation of charges to minimise recombination. All materials development revolves around the challenge of finding the suitable materials and their combinations that can satisfy the above two requirements. Fig. 1 shows the basic classification of solar PV devices.

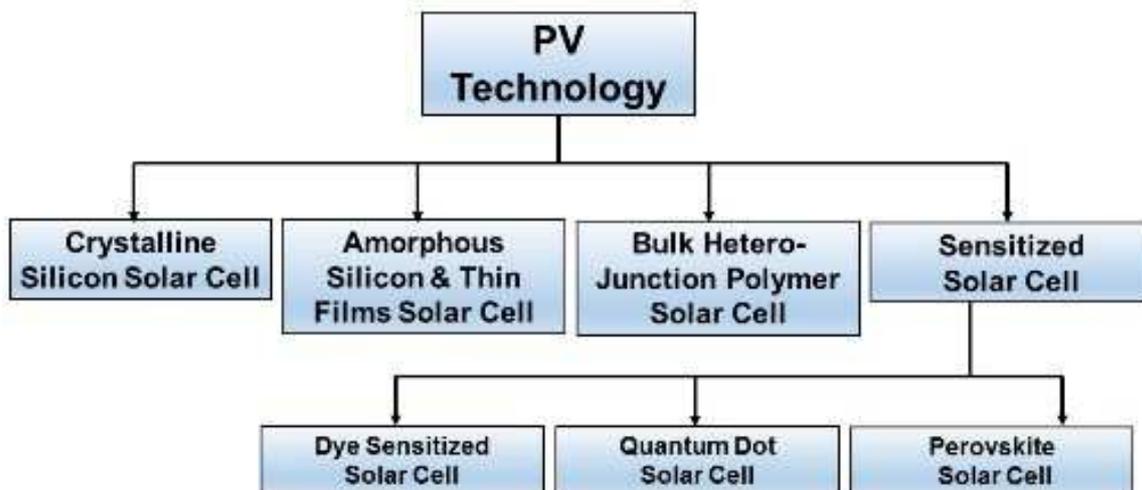
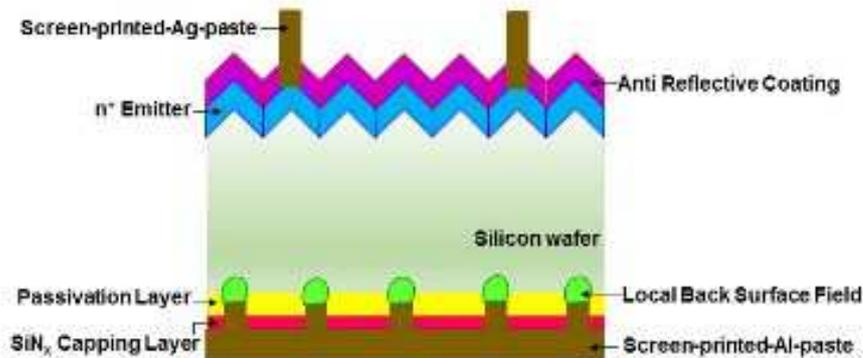


Fig. 1 Broad classification of existing solar cell (PV) technologies

### Crystalline Silicon solar cells

Since the first silicon *p-n* junction solar cell was demonstrated by the Bell Laboratories in 1954, over 60 years of research in both academics and industrial research labs has resulted reaching efficiencies of more than 25 % in the recent times. The crystalline silicon has been the primary material for solar cells, however, amorphous and polycrystalline silicon have also been used extensively. Solar cells based on single crystal Si wafers have undergone much improvement in the recent times due to light trapping by texturing, nano-structuring, passivating layers, efficient charge collecting contacts and annealing technologies. At present, there are few different approaches to fabricate high efficiency solar cells, which are discussed below.

**PERC solar cells:** The Passivated Emitter Rear Cell was proposed by Marteen Green of the University of New South Wales, Australia, through which they had obtained an efficiency of 22.8 %. [4] One of the main features is the engineering of the back contact by passivation for minimizing recombination, which is great drawback for conventional crystalline silicon collar cells. Further, it is designed in a way that the optical losses arising from the Aluminium back contacts were also reduced. Additionally, the front side of the cell can also be modified using the existing PV technologies resulting in a higher efficiency. The rear side is coated with  $\text{Al}_2\text{O}_3/\text{SiN}$  layer, which helps to passivate the dangling bonds and reduce recombination. Fig. 2 shows a schematic representation of a PERC solar cell.



**Fig. 2 Schematic representation of an PERC (Passivated Emitter - Rear Contact) solar cell**  
Adapted from <https://www.pv-tech.org/technical-papers/the-road-to-industrializing-perc-solar-cells>

**Tunnel Oxide Passivated Contact (TOPCon) solar cells :** The PERC solar cells described above suffer from relatively complicated fabrication protocol. This has been simplified using an ultrathin  $\text{SiO}_2$  layer (1 – 2 nm), followed by a layer of doped silicon. The presence of the extremely thin oxide layer ensures uniformity while the charges can flow through tunnelling process. This was developed by Fraunhofer ICE and resulted in an improved efficiency compared to that of PERC cells. The full metallization at the back contact simplified the fabrication process and also the passivation led to minimization of the recombination. [5]

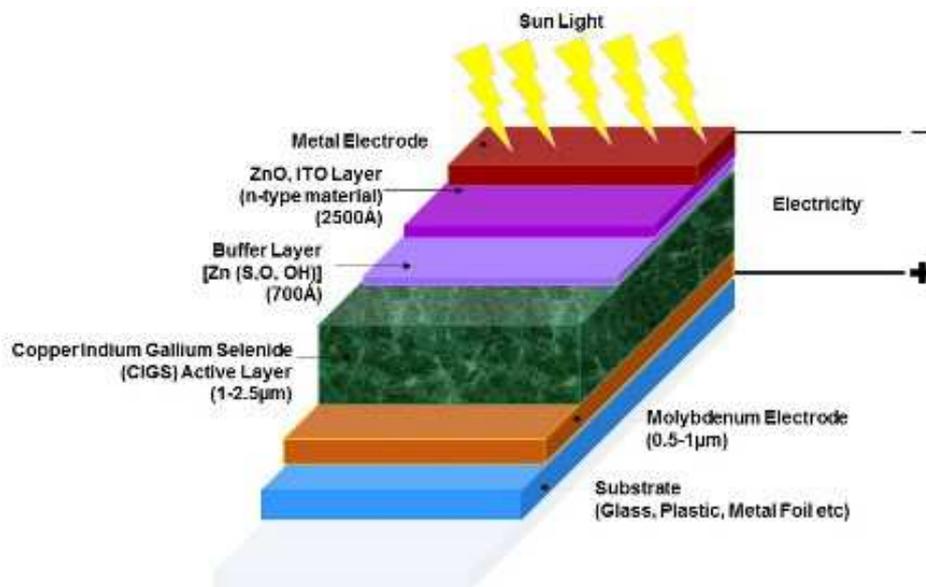
**HIT solar cells:** Heterojunction with Intrinsic Thin (HIT) layer type configurations are based on the silicon heterojunction design, but a very thin intrinsic amorphous Si (a-Si) layer helps in charge separation. Further, a hydrogenated a-Si layer ensures the passivation by reducing the interfacial charge density. [6].

#### **Thin Film Solar Cells:**

Although crystalline silicon solar cells, fabricated on single crystal Si wafers, have dominated both the research and commercial worlds, the inherent limitations such as higher recombination, thermal degradation and indirect band gap of Si had motivated research on alternative compound semiconductors such as CdTe for solar cell applications. Further, it was realised that, these materials have high visible light absorption and hence a thin coating/layer was sufficient to achieve PV effect, leading to substantial savings in terms of materials cost.

**Amorphous Silicon (a-Si) solar cells:** In this context, amorphous silicon solar cells, fabricated on a layer of silicon grown by CVD process, was in fact the first type of thin film solar cells. The a-Si layers show direct band gap and therefore higher absorption of light even in a smaller quantity of material. However, though the toxicity is far less compared to the Cd or Te based materials, the a-Si technology employed expensive, explosive and highly toxic gaseous precursors such as silane and phosphene. Further, the dangling bonds leads to higher recombination which resulted in hydrogen passivation approach (a-Si: H). The discovery of a-Si and a-Si: H happened in late 1970s and early 1980s and it was predicted that the technology had the potential to achieve about 15 % efficiency. Using textured surfaces for light trapping and multijunction design, a stabilised efficiency of 13.6 % has recently been achieved.

**CIGS and CZTS Solar cells:** The  $\text{Cu}(\text{In,Ga})\text{Se}_2$  and  $\text{Cu}(\text{Zn,Sn})\text{S}_2$  are the quaternary compound semiconductor material which have been extensively investigated for solar cell applications. Due to suitable band gap to absorb large part of the solar radiation and ease of chemical synthesis, these materials have been the dominant players in thin film solar cell technology. Although its challenging to maintain the composition/stoichiometry; however, one main advantage is that the band gap can be tuned to a desired value by changing the relative composition of the constituents. Depending on the type of conductivity of the prepared materials (*n* or *p* type), another *p* or *n* type material is usually employed to design the solar cell device in a *p-n* junction configuration. Fig. 3 presents a schematic representation of a CIGS thin film solar cell.



**Fig. 3 Representative description of a  $\text{Cu}(\text{In,Ga})\text{Se}_2$  thin film solar cell**  
 Adapted from <https://www.nrel.gov/pv/copper-indium-gallium-diselenide-solar-cells.html>

**CdTe solar cells:** CdTe is a compound semiconductor with a direct band gap and one of the first 'non-silicon' material to be explored for solar cell designs. In spite of toxicity and environmental concerns, a lot of research has been carried out in fabrication of CdTe thin films and solar cell devices. One of the advantages has been that simple chemical processing can be done using aqueous precursors to obtain CdTe thin films. However, high vacuum and high temperature deposition processes for Cd and Te has been widely employed for the fabrication of high quality CdTe thin films. Usually a  $p-n$  junction is formed with an  $n$ -type material such as CdS to achieve a solar cell design. The developments in the field of thin film solar cells have been nicely reviewed in the references [7, 8].

**Dye Sensitized solar cell:**

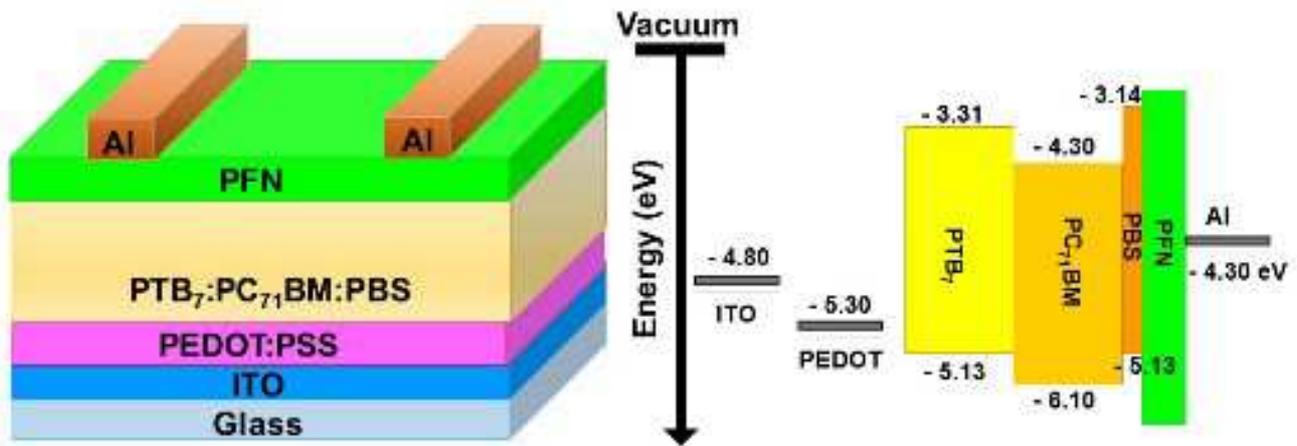
In 1991, O'Regan and Michael Gratzel proposed a revolutionary new concept in solar cells called Dye Sensitised Solar cells (DSSC), which paved the way to fabricate relatively low-cost PV devices.[9] The basic components of DSSC are conductive glasses (as electrodes),  $\text{TiO}_2$  or similar chemically stable  $n$ -type conductor, an electrolyte redox reaction (and hole conduction) and a dye for absorbing the solar radiation. [1]

**Transparent conducting electrodes:** The purpose of the TC electrodes is to collect and transport electrons generated by light irradiation to and from the outer circuit of the device. Since sunlight has to enter through the electrodes, the basic design involves a glass substrate coated with F doped  $\text{SnO}_2$  (FTO) layer. On the other hand, very thin and semi-transparent coatings of highly conductive metals such as Platinum or Gold are also employed on the glass substrates. The FTO coated glass substrates are widely commercially available and serve as the backbone of DSSCs.

**Nanostructured semiconductors:**  $\text{TiO}_2$  (Titanium dioxide) was the first and foremost material to be used in the DSSC design. In particular, materials in nanostructured form is highly desirable, which possesses higher surface to volume ratio for anchoring the dye (or sensitizer) molecules. The chemical stability of the metal-oxide based semiconductors is one of the most important characteristics for the fabrication of DSSCs.

**Light absorbing dye:** The light absorbing dyes lie at the centre of DSSC concept. Gratzel's group invested a class of Ruthenium based dyes for use in DSSCs. One of them is  $\text{C}_{58}\text{H}_{86}\text{N}_8\text{O}_8\text{RuS}_2$ , popularly known as N-719 dye. These class of materials have high absorption capability particularly in the visible region of the solar spectra; however, almost 30 years of research have produced many highly functional dyes with suitably engineered HOMO and LUMO levels as well as with tailored energy gaps for achieving desired absorption of light.

**Redox electrolytes:** The redox electrolyte is another integral component of DSSC, which work in conjunction with the dye. When the dye absorbs light and the photogenerated electrons are transferred to the conduction band of the semiconductor, the holes are taken away by the electrolyte and undergoes a simultaneous oxidation and reduction processes. This also helps to regenerate the dye. A detail description of the operation of DSSCs can be found in references. Efficient operation of a DSSC requires that the electrolyte should be stable in contact with the dye, should not absorb light by itself and must have long red-ox cycle life. A typical example of a common electrolyte is a mixture of iodine/tri-iodide solution, which cycles between  $\text{I}/\text{I}^{3-}$  states to take care of the photogenerated holes and keep the dye protected from degradation. Although, liquid based electrolytes have been used extensively in the initial stages of the development of DSSCs, potential problems with leakage and stability resulted in the invention of solid and quasi-solid-state electrolytes. A schematic description of a DSSC is presented in Fig. 4.



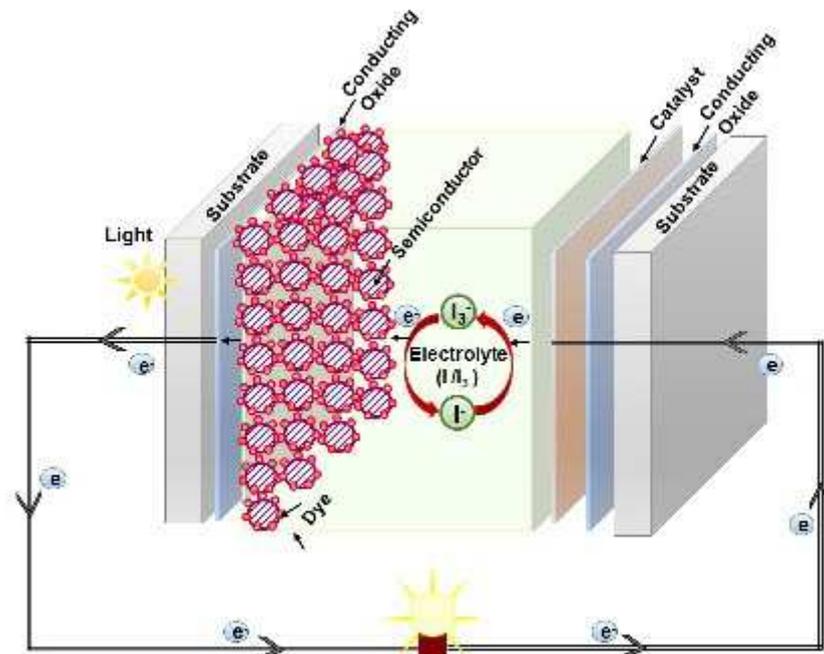
**Fig. 4 Schematic representation (left) and energy level diagram (right) of a polymer based Bulk Heterojunction (BHJ) solar cell**

#### **Polymer Solar cells:**

The polymer solar cells owe their existence to the discovery of conducting and light absorbing polymers by Alan Heeger and group. [10] In generic terms, however, polymer can find application in any part of the solar cell, as flexible substrate, hole or electron conducting layers and light absorbing active medium. The central concept of polymer solar cells is the bulk heterojunction (BHJ) formed between interpenetrating layers of an electron donor and an acceptor, one or both of which can be polymers. In case of polymeric BHJ, the transfer of photogenerated electrons takes place in an ultrafast manner giving rise to charge separation upon irradiation of light. In contrast with inorganic materials, the polymeric materials have Highest Occupied Molecular Orbitals (HOMO), which is equivalent to valence band maxima and Lowest Unoccupied Molecular Orbitals (LUMO), equivalent to the conduction band minima. The light absorption takes place according to the difference between these two energy levels. One of the most promising ways to achieve higher efficiency in polymer solar cells is to have a BHJ formed between an electron donor and an electron acceptor. [6,6]-phenyl C<sub>61</sub>-butyric acid methylester (PCBM) is a fullerene derivative, which forms an efficient BHJ with poly(3-hexylthiophene) (P3HT). The P3HT(donor)-PCBM (acceptor) combination has yielded polymer solar cells with efficiencies higher than 5%. Use of conductive polymers as hole conduction layer is also adopted for solar cells. poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is such a conjugated polymer, which is coated onto FTO or ITO coated glass as a hole extraction layer before depositing the active layer. [11] A representative diagram of a polymer solar cell is shown in Fig. 5.

#### **Quantum Dot Solar cells**

The concept of QD solar cells is similar to that of DSSCs, where the quantum dots of suitable light absorption characteristics are used for the functionalization of the active layer (for eg. TiO<sub>2</sub>). The QDs of suitable band gaps not only modify the overall absorption features of the solar cells but also helps to separate the electron-hole pairs generated by light. In general, for active layers with higher band gap, QDs of lower band gap are chosen so that higher amount of visible light is absorbed. Chalcogenide based semiconductors have been widely used for QD fabrication because of size and composition dependent optical absorption behaviour. Normally, the dimensions of QDs are controlled within a few nm to few 10s of nm to achieve effective quantum confinement and modification of optical properties with respect to their bulk counterparts. Both binary semiconductor systems (CdS, CdTe, CdSe, ZnS etc) and ternary semiconductors such as CuInS<sub>2</sub> have been employed. In order to sensitize the host material (such as TiO<sub>2</sub>), a number of different strategies have been implemented. These include functionalization (attachment of the QD to the surface of the bigger TiO<sub>2</sub> particles), alloying or composite formation, core-shell structuring and doping into the host material. The choice of the sensitization protocol depends on the availability of the suitable process and precursor materials as well the targeted level of sensitization required. The QDs are fabricated in-situ by simple chemical techniques such as chemical bath deposition and successive ionic layer adsorption and reaction (SILAR). In these techniques, the QD particles are directly grown onto the host materials leading to better interfacial property and resultant charge transfer mechanism. However, in some cases, the host material may not withstand chemical processing for the growth of QDs and hence the QDs are grown ex-situ and then deposited onto the host material by dip or spin coating techniques. In spite of great advancement in the fabrication of quantum dots with superior light absorption capabilities, the photovoltaic device performance has not improved much beyond 10 % efficiency. Much of the limitation of QD sensitized solar cells can be attributed to the lack of stability of the QD systems and hence the devices need to be operated in suitable redox couple electrolytes (hole scavenging medium), which ensures chemical stability of the materials. The innovation in solid state hole transporting materials may lead to better flexibility in the deployment and operation of QD sensitized solar cells.[12]



**Fig. 5 Schematic representation of a Dye Sensitised Solar Cell**  
 (adapted from Parisi *et al.* Renewable and Sustainable Energy Reviews. 39. 2014)

### Metal Halide Perovskite based solar cells

Metal halide based perovskites (for eg. Methylammonium lead trihalide,  $\text{CH}_3\text{NH}_3\text{PbX}_3$ ) have attracted a lot of attention in the recent times as a solar cell light absorbing materials since its discovery in 2009 with an initial efficiency of 3.8 %.[13] A hybrid material consisting of both organic and inorganic components, such perovskites show exceptionally high light absorption and hence even a 500 nm film (layer) is sufficient to absorb a significant part of the visible spectrum. Further, the material can be solution processed / screen printed on different types of substrates (including the flexible materials), which, therefore has potential of wide-scale deployment and lowering of fabrication costs. In about 10 years since the first report, the perovskite based solar cells have reached about 25 % efficiency and has emerged as one of the leading solar cell technologies. Initial research and development work centred around Lead based perovskites; however, concerns about toxicity soon led to search of lead-free perovskites. One of the promising alternatives is Tin (Sn) in terms of power conversion efficiencies and a lot of research has been carried out in the recent times to achieve stability of the devices. It has been shown that the lone pair  $s^2$  electrons of divalent metal ions and the symmetry of structure lead to high optical absorption in such perovskites. Further, the dispersion of the valence band caused by the interaction of  $s^2$  orbitals of metal ions and p orbitals of the halogen ions results in a small effective mass of the holes, which also contributes towards the photovoltaic activity. Alternatively, Sn based perovskites show high carrier mobility and long diffusion lengths, which are essential for solar cell applications. Furthermore, the optical band gap of Sn based perovskites is smaller than that of Pb based counterparts, leading to the absorption of wider part of the solar spectrum. [14]

### Solar Energy Harvesting through Photocatalysis

Although solar photovoltaic (PV) technology is the most efficient way to harness solar energy, but photocatalysis offers an alternative pathway to utilize solar power for driving chemical reactions. At the fundamental scale, in a manner similar to solar cells, a photoactive material absorbs sunlight and produces electron hole pairs. In this case, however, both electrons and holes are utilised to carry out oxidation and reduction processes to achieve certain chemical reactions. Fig. 6 depicts the schematic representation of a photocatalysis process. When a semiconductor of suitable band gap (band gap energy equivalent to the energy of the incoming light) is irradiated with light, electrons from the valence band are excited to the conduction band, leaving vacancies (or positively charged holes,  $h^+$ ) at the VB. As the Figure Y shows, an example of photocatalytic water decomposition, the *holes* can initiate a chemical reaction (oxidation) by ionising water and the ionized radical can take *electrons* (reduction) from the conduction band of the photocatalyst to form hydrogen. The research in photocatalysis practically originated with the 1972 report from Fujishima and Honda on photoelectrochemical decomposition of water to produce hydrogen. [15] In these initial stages, however, the photocatalyst material was used as an electrode and the water splitting was caused by sunlight with assistance from applied bias (which helped to separate the electron-hole pairs by providing additional energy). The concept of solar energy driven water splitting was then extended to water purification (such as photocatalytic dye degradation and pollutant removal) and  $\text{CO}_2$  reduction (conversion of  $\text{CO}_2$  into carbon containing fuel/useful materials).[16,17]

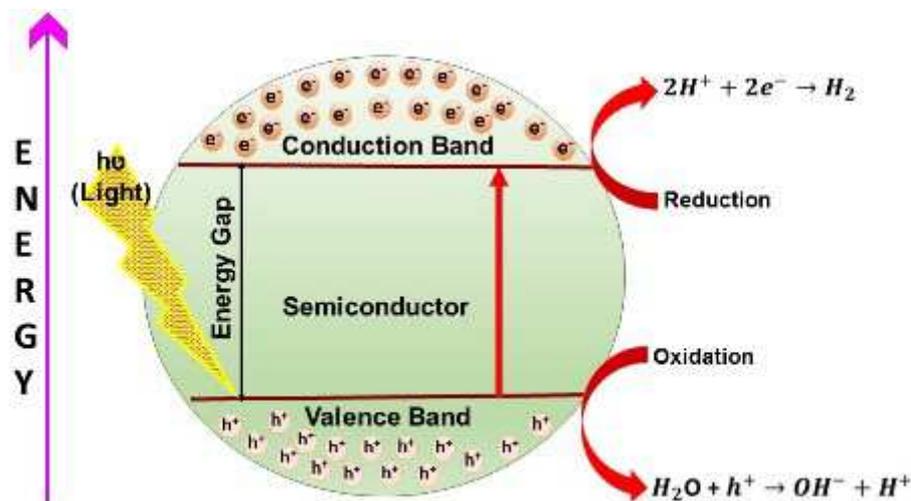


Fig. 6 Diagram showing basic principle of photocatalysis (semiconductor in circular shape only for representation)

The central concept of a photocatalysis process is a semiconductor material with suitable band gap to efficiently absorb the solar radiation. However, the band-gap energy alone is insufficient to drive efficient photocatalysis process. The electrons and holes should have sufficient energy required for carrying out the desired chemical reaction. This implies, in addition to a suitable band gap energy, the positions of the valence and conduction band edges also have high importance. There are various semiconducting materials that have been explored for photocatalysis. As discussed under the thin film solar cells subtopic, the compound semiconductor materials such as CdTe, CdS, ZnS, CdSe have direct band gap suitable for visible light absorption and the band edges are also suitable for photocatalytic water decomposition. However, lack of stability in aqueous ambience is a serious drawback of these types of materials. The metal oxides, such as SnO<sub>2</sub>, ZnO, TiO<sub>2</sub>, SrTiO<sub>3</sub> are highly stable but possess larger band gap (> 3 eV), which results in the absorption of only UV part of the solar spectra (< 5 % of sunlight). On the other hand, there are a few stable oxide materials such as hematite (Fe<sub>2</sub>O<sub>3</sub>), BiFeO<sub>3</sub>, BiVO<sub>4</sub>, which show excellent visible light absorption because of lower band gaps (2 – 3 eV); however, the conduction or valence band positions are not always suitable for a desired chemical reaction. Extensive research is currently underway on improving the photocatalyst materials to achieve better stability, and to tailor the band gap for suitable energy and position of the band edges. Such approaches include doping, composite formation, functionalization, Z-scheme process etc. Details of these can be found in the listed references.

**Conclusions:** More than half a century of research in solar PV technologies, in particular on Silicon solar cells, has resulted in fully commercialised products. However, drawbacks and limitations of Silicon has also provided motivation to explore other types of solar cell devices. In one of such latest developments, organic halide based perovskites have shown high potential in solar cell efficiencies, reaching more than in less than 10 years since discovery. On the Silicon front, multijunction, tandem and hybrid technologies are gaining momentum to achieve higher efficiencies. On the other hand, photocatalysis has largely remained at the research level because of inherent thermodynamic limitations. However, new materials combinations, configurations and reactor design along with higher temperature operation may yield higher efficiency.

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### About the author



Somnath C Roy completed his BSc and MSc degrees in Physics from the Banaras Hindu University, Varanasi in 1997 and 1999, followed by PhD from IIT Delhi in 2005. After a brief stint as a Lecturer in the Amity University Noida, he joined the prestigious Materials Research Institute at the Pennsylvania State University, USA in 2006 as a Post-doctoral researcher. In 2010, he moved to IIT Madras as an Assistant Professor in the department of Physics, and became an Associate Professor in 2015. During the past 9 years at IIT Madras, he has been involved in the growth and study of 1D nanostructures for solar energy and gas sensing applications and has guided two PhD theses. At present, Dr. Roy's group, called the Environmental Nanotechnology Lab, is comprising of 8 PhD students, 2 post docs and a number of UG and PG project students. Several funding agencies such as DST, DRDO, Nissan, CSIR and ONGC have generously funded his research. Dr. Roy has taught both UG and PG level courses at IIT Madras. With a total of 40 publications till date, his current *h*-index is 15. Recently, he has been selected for the Bhaskara Advanced Solar Energy (BASE) Fellowship and also the Shastri Indo Canadian Institute's (SICI) Faculty Travel and Internationalization (FTI) award grant.

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## The Architecture of Open Source Applications

Carpentry is an exacting craft, and people can spend their entire lives learning how to do it well. But carpentry is not architecture: if we step back from pitch boards and miter joints, buildings as a whole must be designed, and doing that is as much an art as it is a craft or science.

Programming is also an exacting craft, and people can spend their entire lives learning how to do it well. But programming is not software architecture. Many programmers spend years thinking about (or wrestling with) larger design issues: Should this application be extensible? If so, should that be done by providing a scripting interface, through some sort of plugin mechanism, or in some other way entirely? What should be done by the client, what should be left to the server, and is "client-server" even a useful way to think about this application? These are not programming questions, any more than where to put the stairs is a question of carpentry.

Building architecture and software architecture have a lot in common, but there is one crucial difference. While architects study thousands of buildings in their training and during their careers, most software developers only ever get to know a handful of large programs well. And more often than not, those are programs they wrote themselves. They never get to see the great programs of history, or read critiques of those programs' designs written by experienced practitioners. As a result, they repeat one another's mistakes rather than building on one another's successes.

This book is our attempt to change that. Each chapter describes the architecture of an open source application: how it is structured, how its parts interact, why it's built that way, and what lessons have been learned that can be applied to other big design problems. The descriptions are written by the people who know the software best, people with years or decades of experience designing and re-designing complex applications. The applications themselves range in scale from simple drawing programs and web-based spreadsheets to compiler toolkits and multi-million line visualization packages. Some are only a few years old, while others are approaching their thirtieth anniversary. What they have in common is that their creators have thought long and hard about their design, and are willing to share those thoughts with you. We hope you enjoy what they have written.

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