

*Review Article***Materials Research and Opportunities in Solar (Photovoltaic) Cells**

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The progress of solar (photovoltaic) cells over the years is reported here. The selection and engineering of materials that have been used in the first to the fourth generation solar cells present salient features on why such newer materials were or would be introduced are discussed. Our perspectives to look beyond silicon as solar cell materials are presented. The issues of toxicity and earth-abundance of elements in forming active materials of solar cells are discussed. Measurement parameters, methods to improve performance, and mechanism of operation of different solar cells have also been discussed.

Keywords: Solar Cells; Photovoltaic Devices; New Materials for Solar Cells**Introduction: Use of Solar Energy**

It is now well-documented that several factors such as increasing energy needs, rapid decrease in energy sources from fossil fuels, and urgent requirement to protect the environment for the future generations, prompted the search for green and renewable energy sources more than ever. At the moment, almost 80% of world's energy supplies come from burning of fossil fuels. Apart from their limited reserve that would last for another couple of decades, use of these resources has been a major cause behind degradation of the environment such as global warming, acid rains, increase in carbon dioxide content in the environment, smog, etc. that affect all kinds of habitats cutting across borders and boundaries of countries and continents. Green energy resources such as solar, wind and tidal, and hydropower offer a supplement to the fossil fuels so that the usage of conventional source of energy can be restricted. All these renewable, nonconventional, and green resources of energy produce little or no pollution or greenhouse gases and also, more importantly, have unlimited resources. With the urgency to use such green energy resource, it is important that researchers tap all possible sources of

renewable energy. While each form of energy source is relevant and applicable to a geographical location or so, every quantum of such green energy will be beneficial to cater energy requirement of the future.

Among the green energy resources, sunlight is the most abundant, renewable, and readily available source. Another primary advantage of this source of energy is that it can be exploited even in remote areas, where supply of electricity is limited for various reasons. While both thermal and photonic components of solar spectrum could in principle be converted to electricity, photovoltaic (PV) solar cells were considered for immediate use since they were being successfully used in spacecraft for many years that studied terrestrial science. At present, photovoltaic solar cells are of relevance due to their rapid growth amounting to a total global capacity of 67,400 megawatts (MW) at the end of 2011 that represents 0.5% of worldwide electricity supply (<http://www.epia.org/home/>). The foremost challenge for large-scale commercial applications of photovoltaic solar cells is their high manufacturing cost. The solar panels are based on mostly monocrystalline, polycrystalline, or amorphous silicon, cadmium

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telluride, and copper indium gallium selenide/sulphide. Processing of active materials in the solar cells requires expensive instruments leading to an increase in the manufacturing cost. The fast growth of the PV market is sustainable if the manufacturing cost could be reduced to compete with the cost per watt (or \$/W) that the conventional mode of power generation offers. It is hence appropriate to look for newer materials which may lower the manufacturing cost reducing the \$/W of the solar cells. Another route to reduce the \$/W has been to improve the power conversion efficiency (PCE), i.e., the percentage of light energy getting converted to electrical energy, of a photovoltaic device with a proper choice of material(s). Different technologies have been developed to achieve a balance between the manufacturing cost of PV solar cells and their efficiency to compete with the cost of electricity from fossil fuels.

Evolution of Solar (Photovoltaic) Cells

While the principle of solar cells in the form of photovoltaic effect was discovered by French physicist Becquerel in 1839, a practical photovoltaic cell was developed in 1954 at Bell Laboratories (Chapin *et al.*, 1954). They used a diffused silicon *pn*-junction as a solar cell that yielded an efficiency of 6%. Since then, the quest for new materials that would offer an improved efficiency continued. Most of the semiconductor materials that researchers targeted had a bandgap of 1.0 eV or more, so that visible range of solar spectrum is absorbed for conversion to electricity. Shockley and Queisser established that a single-junction solar cell could reach a maximum efficiency of 30% for an optimum band gap material (Shockley and Queisser, 1961). On the basis of the materials used, mechanism involved, fabrication method, and the manufacturing cost of solar cells, researchers have categorized the generation of solar cells.

First Generation Solar Cells

The first generation solar cells are based on single crystalline and multicrystalline silicon. Crystalline silicon solar cells derived their name from the way they were made. The monocrystalline silicon solar cells are made from thin wafers that were cut from a

singular continuous crystal specially grown for this purpose. Polycrystalline silicon solar cells are made by melting the silicon material and pouring it into a mould. Since the discovery at Bell Laboratories, the crystalline silicon solar cell efficiency has reached up to 24% (Green *et al.*, 2005). The efficiency of single *pn*-junction crystalline silicon solar cells could reach up to the theoretically predicted limit of 30% (Shockley and Queisser, 1961). In India, much research has been carried out in this direction with microcrystalline and polycrystalline silicon (Ray *et al.*, 1988; Sastry *et al.*, 1985). At present, silicon solar cells cover roughly 86% of the PV market due to their relatively high conversion efficiency. The efficiency of commercial products in modules typically reach about 15-20% (<http://www.solarplaza.com/top10-crystalline-module-efficiency/>, 2012). The manufacturing techniques that are used to produce first generation solar cells are inherently expensive, resulting in years to pay back their purchasing cost.

Second Generation Solar Cells

In second generation solar cells, thin film technology has been used. These solar cells are thinner, flexible to some extent, and less expensive as compared to the first generation solar cells. The solar cells have a light-absorbing thickness of 10 μm as compared to 200-300 μm used for crystalline silicon solar cells. Semiconductor materials for the second generation solar cells ranged from amorphous and micromorphous silicon (Carlson and Wronski, 1976; Song and Anderson, 2000) to binary or quaternary semiconductors, such as cadmium telluride (CdTe) (Britt and Ferekides, 1993), gallium arsenide (GaAs) (Olson *et al.*, 1990) and copper indium gallium selenide (CIGS) (Sites and Liu, 1996). The use of direct band gap semiconductors, in contrast to indirect band gap silicon, lowered the cost of photoabsorbing materials since thinner-films of such semiconductors were enough to absorb sufficient amount of solar light for photoconversion. Thin-film solar cells based on such materials have shown signs of dominance in photovoltaic market covering 18% of the global photovoltaic market. This type of solar cells is stable and has been commercialized with a module efficiency of ~20%. Though the power conversion

efficiency of these solar cells is less than that of crystalline silicon solar cells, the second generation solar cells are expected to be cost-effective as compared to the cost of electricity generation from fossil fuels. A comprehensive review on this type of solar cells can be found in the literature (Green *et al.*, 2005). Unfortunately, there are still some unresolved issues in commercializing these solar cells in terms of production in mass quantities at a competitive price and at a reasonable efficiency level.

Third Generation Solar Cells

Organic semiconductors and conjugated polymers, with its success in light-emitting diodes and flat panel displays, are being considered as advanced materials for the third generation solar cells. Such solar cells, still at the laboratory level, are based on thin-films of the materials. With the difference in operation mechanism, organic/polymeric solar cells can be sub-classified into organic photovoltaic devices (OPV) and plastic (polymer) solar cells (Wohrle and Meissner, 1991; Peumans *et al.*, 2003; Yang *et al.*, 2005; Li *et al.*, 2005; Brabec *et al.*, 2001; Park *et al.*, 2009), photoelectrochemical solar cells (Keis *et al.*, 2002; Gratzel, 2001), and organic dye-sensitized solar cells (DSSC) (Oregon and Gratzel, 1991; Law *et al.*, 2005). Overall, the power conversion efficiency of DSSCs has reached more than 12% in the lab-scale (Yella *et al.*, 2011). Commercial applications of DSSCs may however be limited due to the liquid electrolyte used in the cells. In organic or polymeric PV devices, bulk-heterojunctions based on regioregular poly(3-hexylthiophene) (P₃HT) as a hole-transporting material and a fullerene derivative, namely phenyl-C61-butyric acid methyl ester (commonly known as PCBM), as an electron-transporting material are one of the most-studied systems (Li *et al.*, 2005; Scharber *et al.*, 2006). Recently, some low band gap polymers are being used to harvest near-IR spectrum of solar energy (Albrecht *et al.*, 2012; Peet *et al.*, 2007). In organic or polymeric solar cells, device operation involves photogeneration of excitons, exciton dissociation or charge separation, and carrier transport to the opposite electrodes. Some of the advantages of organic or polymeric PV devices are (1) films are spun from solutions, (2) fabrication of large-area

devices is possible, (3) the requirement and hence the cost of the materials is low, and (4) devices can be fabricated on flexible electrode substrates. The major disadvantage of this class of semiconductor is that the carrier mobility in these materials is often low hindering efficient flow of holes and electrons to the opposite electrode. Nonetheless, third generation solar cells are expected to enter the market soon.

Fourth Generation Solar Cells

Materials engineering being one of the fastest and rapidly growing fields of research, newer materials offer themselves as supplements or complements in device fabrication. A bright example in this direction is the inclusion of (inorganic) semiconducting quantum dots in organic/polymeric photovoltaic devices and dye-sensitized solar cells. Such devices, often termed as nanophotovoltaics, are considered to be the fourth generation solar cells and have a high prospect as a future of solar cell technology. Here, the advantages of semiconducting quantum dots have been brought to supplement performance of organic and polymeric solar cells. Some of the proven examples in this direction are quantum dot-sensitized solar cells (QDSSC) (Kamat, 2008; Nozik, 2002; Sun *et al.*, 2008), quantum dot-based thin film solar cells (Panthani *et al.*, 2008; Ip *et al.*, 2012), and hybrid bulk-heterojunction solar cells (Huynh *et al.*, 2002). Xu *et al.* have reported QDSSCs based on CdSe nanoparticles with an efficiency of 4.54% (Xu *et al.*, 2012). Sargent's research group has reported an efficiency of 7% in solar cells based on inorganic quantum dots (Ip *et al.*, 2012). Researchers across the globe are focusing on a range of materials and methods to fabricate devices in order to improve this emerging technology to achieve a proper balance between the manufacturing cost and the efficiency of solar cells.

Recently, a new type of solar cells based on organometal halide perovskite materials has attracted much attention due to high efficiency and stability. The efficiency of methylammonium lead halide perovskite sensitized solar cells reached 16.2% within a very short period of research and development (Kim *et al.*, 2012; Lee *et al.*, 2012; Burschka *et al.*, 2013;

Liu *et al.*, 2013). In Fig. 1, we have shown a bar diagram representing efficiencies of different types of solar cells. Some commonly used active materials in each type of solar cells are also mentioned. Fig. 1 shows that the efficiencies of photovoltaic devices based on the new materials are yet to match that of silicon solar cells. Researchers across the globe are still optimistic due to the rapid progress in the parameters of these higher-generation solar cells, in addition to low material production cost of such solar cells.

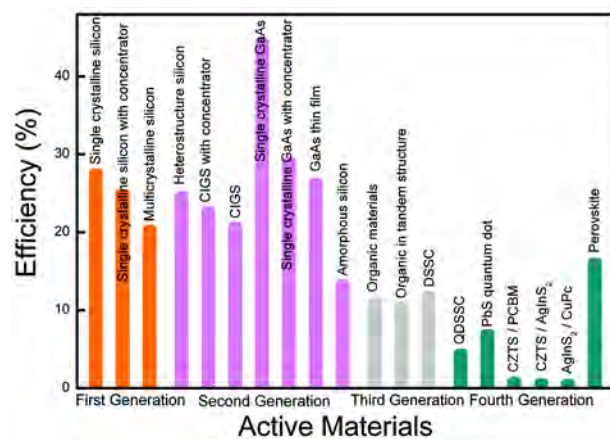


Fig. 1: Efficiency of different generations and types of solar cells along with some commonly used active materials in each type of solar cells. Data were obtained from Research Cell Efficiency Records, National Center for Photovoltaics (NCPV) at National Renewable Energy Laboratory (NREL), Golden, Colorado, USA (<http://www.nrel.gov/ncpv/>, 2014)

Parameters of Solar Cells

Open-circuit Voltage (V_{OC})

The photovoltage generated across the two terminals when the circuit remains open is known as the open-circuit voltage (V_{OC}). The difference in the quasi Fermi levels determines the V_{OC} of a solar cell. Generally, photoexcited electrons go through a thermalization process to lose their potential energy to the phonons until the electrons reach the lowest energy level of the conduction band (in case of inorganic semiconductors) or the lowest unoccupied molecular orbital (LUMO, in case of organic semiconductors). Thus, the band gap of the

semiconductor is often regarded as a measure of achievable photovoltage. A higher band gap could result in a higher photovoltage. In the same context, a higher band gap material cannot absorb sufficient light in the visible region. There should hence be an optimum band gap for an efficient performance of photovoltaic devices under a white light illumination. Shockley and Queisser calculated the optimum band gap for maximum power conversion efficiency assuming only radiative recombination under solar radiation (Shockley and Queisser, 1961). They obtained a power conversion efficiency of 30% for a semiconductor with a band gap of 1.12 eV. Interestingly, the value matches quite well with the band gap of silicon.

Short-circuit Current (J_{SC})

When the cell is short-circuited, the current which flows through the external circuit is known as the short-circuit current (I_{SC}). To achieve a high value of I_{SC} , we should have an active material of high optical absorption coefficient along with high carrier mobility. The I_{SC} of a solar cell also depends on the incident light intensity and the cell area. It is hence effective to calculate short-circuit current density (J_{SC}) under a given solar illumination to compare short-circuit current of different devices based on a range of materials.

Fill Factor (FF)

Since the I - V characteristics of a solar cell under illumination condition passes through the fourth quadrant, the power, which is a product of the voltage and the current, in this quadrant is negative implying that one would be able to draw power from the device. In Fig. 2, the current-voltage characteristics of a typical solar cell under dark and under certain illumination have been shown. In the I - V characteristics, we can obtain a point in the fourth quadrant that corresponds to maximum power achievable (P_{Max}), that is, product of the voltage and the current is highest at this point. The point is called as the maximum power point for which there are maximum voltage (V_{Max}) and maximum current (I_{Max}). The shape of the I - V curve in the fourth quadrant is very crucial to maximize the product at the maximum

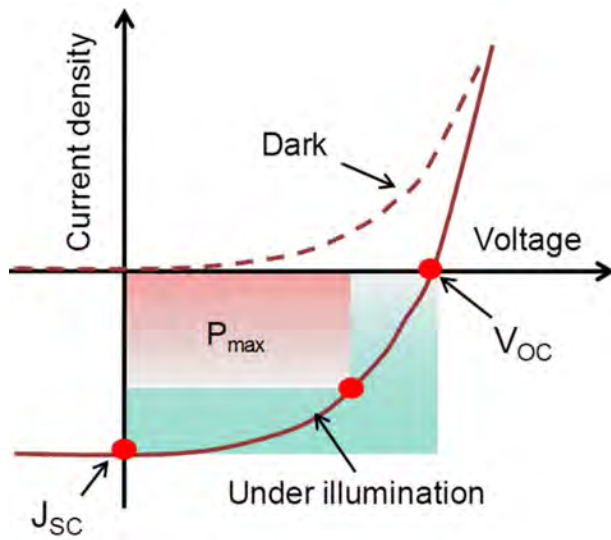


Fig. 2: Current density versus voltage (J - V) characteristics of a typical solar cell under dark (dashed line) and illumination (solid line) conditions. Parameters of solar cells such as the open-circuit voltage (V_{OC}), the short-circuit current density J_{SC} , and the maximum power point P_{Max} are shown on the J - V curve

power point. This maximum area is higher when the I - V curve resembles a rectangle with sides of V_{OC} and J_{SC} . The ratio between these two areas is known as the fill factor (FF) which represents a measure of the shape of I - V characteristics in the fourth quadrant, that is, the fill factor is defined as:

$$FF = \frac{I_{max} \times V_{max}}{I_{SC} \times V_{OC}} \quad (1)$$

Using this fill factor, power conversion efficiency (PCE) of a solar cell can be defined as :

$$\begin{aligned} PCE(\eta) &= \frac{P_{max}}{P_{in}} \times 100 = \frac{I_{max} \times V_{max}}{P_{in}} \times 100 \\ &= \frac{I_{SC} \times V_{OC} \times FF}{P_{in}} \times 100, \end{aligned} \quad (2)$$

where P_{in} is the incident light power. Since the power conversion efficiency (η) depends on the incident wavelength and intensity, η is measured under a simulated solar spectrum. In order to compare the

efficiencies of different solar cells, a standard solar irradiance is considered. The most common standard irradiance is AM1.5 (air mass 1.5 ~1 Sun) and this standard illumination ($\sim 100 \text{ mW/cm}^2$) can be achieved by most commercial solar simulators. The physical principles behind the operation of different types of solar cells are generally different. The current-voltage characteristics of well-performing cells are however similar and can be characterized and compared with each other in terms of FF , V_{OC} , and I_{SC} .

Power Conversion Efficiency

Power conversion efficiency (PCE) is the most important parameter of solar cells. It is defined as the percentage of maximum output of electrical power to the incident optical power. The generated output electrical power is the product of the generated photovoltage and the photocurrent. Therefore, in order to achieve a high PCE, one should have a high photovoltage as well as a high photocurrent under an illuminated condition.

Thin-film (Photovoltaic) Solar Cells: Device Architecture

The basic components of thin-film solar cells are an active layer and a pair of electrodes. The active layer may comprise one or several materials. The active layer absorbs sunlight; the two electrodes which have in general dissimilar work-functions collect carriers to yield photocurrent in the external circuit. The electrodes should form ohmic contacts with the active layer that is next to the electrode so that the interfaces do not impose barriers for the charge carriers to reach the electrodes. Depending on the materials used in the active layer and the electrodes, several device architectures can be formed:

- Metal₁/Semiconductor/Metal₂ (Schottky junction)
- Metal₁/ p -type semiconductor/ n -type semiconductor/metal₂-based on the same semiconductor material (Homojunction)
- Metal₁/ p -type semiconductor/ n -type semiconductor/metal₂-based on two different semiconductor materials (Heterojunction)

- Metal₁/p-type semiconductor/insulator/n-type semiconductor/metal₂ (*p-i-n* junction)
- Junction₁-Junction₂-Junction₃ (tandem solar cells)

When a *p*-type semiconductor and an *n*-type semiconductor are brought in contact, electrons from the *n*-type semiconductor diffuse to the *p*-type semiconductor due to a concentration gradient of the carriers. Similarly, holes from the *p*-type material diffuse to the *n*-type semiconductor. During diffusion process, the carriers leave behind uncompensated immobile charges at the regions from where they diffused. Electrons leave donor ions (+) at the *n*-type region and holes leave acceptor ions (-) at the *p*-type region of the *pn*-junction. These immobile charges create an electric field that forms a potential barrier which finally opposes the carriers to diffuse further. The region across the junction where the electric field appears is termed as the depletion region.

Under illumination, electron-hole pairs (excitons) form in both sides of the junction. These photo-generated electron-hole pairs if diffused to the junction become dissociated due to the electric field at the junction. (In case of a single layer structure based on a bulk semiconducting material, the excitons can be dissociated just after the photogeneration). Now, the holes flow through the *p*-type material and electrons flow through the *n*-type material to the opposite direction. These separated electrons and holes form quasi fermi levels at both sides of the junction and the difference between these two quasi fermi levels is the origin of open-circuit voltage (V_{OC}) of the solar cells. When contacts are made in the external circuit, a short-circuit current (I_{SC}) flows through the circuit without any applied voltage. In Fig. 3, a schematic representation of a *pn*-junction, depletion region, band-bending, and the origin of V_{OC} have been depicted.

The operation mechanism of organic photovoltaic devices differs from that of inorganic semiconductor solar cells. In organic PV devices, the built-in electric field due to the electrodes acts only near the interfaces. Since the active region of an organic device consists of two materials, the interface between the materials provides the required energy-offset to

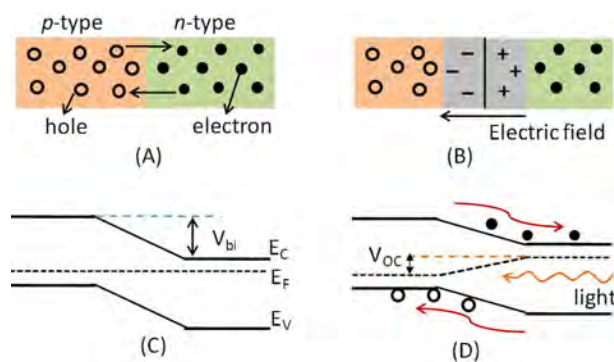


Fig. 3: Schematic representations of a *pn*-junction formation showing (A) diffusion of carriers under contact, (B) formation of a depletion region, (C) band-bending at the junction, and (D) movement of carriers under an illuminated condition and the origin of V_{OC}

dissociate excitons, that is, after photogeneration of excitons, they may diffuse to the donor-acceptor interface. If the difference in electron affinities or the difference in ionization potentials or the difference in both the levels of the donor and acceptor materials is higher than the exciton binding energy, the excitons in the organic PV devices become dissociated.

Thin-film (Photovoltaic) Solar Cells: Materials Engineering

As has been stated, device operation of organic or polymeric thin-film solar cells involves three steps, namely, (1) exciton generation due to illumination, (2) exciton dissociation or charge separation, and (3) carrier transport to the opposite electrodes. Since the three steps occur in a sequence, efforts have been made to enhance efficiency or output of each of the steps. Generation of excitons expectedly depends on matching of optical absorption spectrum of the active materials with the solar illumination. Active materials are hence chosen accordingly. Exciton dissociation or charge separation, which occurs at the interface between a donor and an acceptor layer, takes place due to the internal field that develops owing to the difference of energy levels at the interfaces. Carrier transport, the third step, is directed by the internal field generated by the difference in work-functions of the two electrodes. Apart from the electric-field, mobility of charge carriers plays a major role in determining the short-circuit current of photovoltaic

devices.

Considering the limitation of organic and polymeric materials in each of the steps of device operation, efforts have been made to incorporate quantum dots or nanostructures in photovoltaic devices. In other words, the fourth generation solar cells involving nanostructures in organic devices are meant to overcome the drawbacks of the third generation solar cells. In solar cells based on organic and inorganic semiconductors or hybrid materials, advantages of the both types of materials are clubbed together. Some of the advantages can be listed as follows:

- One of the major advantages of inorganic nanocrystals is their broad absorbance. Extinction coefficient of some nanocrystals is high ($\sim 10^4 \text{ cm}^{-1}$). Band gap of the nanocrystals can be tuned through quantum confinement to suit the need of photoabsorption in a wider spectral region.
- Wannier excitons in nanocrystals have a lower binding energy than Frenkel excitons that form inorganic molecules upon photoillumination. This is due to the fact that the electron and the hole of a Wannier exciton can reside in different molecules as opposed to Frenkel excitons, where the two carriers reside in the same molecule. Typical binding energy of excitons in inorganic quantum dots (diameter $\sim 2\text{-}4 \text{ nm}$) is in the range of 0.05 to 0.2 eV; whereas, Frenkel excitons in organic molecules have a binding energy of 0.1 to 1.0 eV.
- There is a possibility of formation of multiple excitons in nanocrystals from a single photon (Binks, 2011). The quantum mechanical origin of the process is still under debate.
- Mobility of both types of charges in inorganic nanocrystals is high.
- Most of the quantum dots are very stable under ambient condition.

Fabrication of organic solar cells with inorganic nanomaterials could leap the research on solar cells a

step forward. In general, some conjugated polymers are used as a hole-transporting material (*p*-type) and inorganic nanostructures are used as an electron-transporting material (*n*-type) or vice versa. The first hybrid solar with sufficient efficiency was reported by Huynh *et al.* (Huynh *et al.*, 2002). Since then several studies have been reported based on different inorganic nanocrystals such as CdS, CdSe, CdTe, ZnO, SnO₂, TiO₂, Si, PbS, PbSe, etc. (Cui *et al.*, 2006; Hines and Scholes, 2003; Holder *et al.*, 2008; Kuo *et al.*, 2008; Kuwabara *et al.*, 2009; Lutich *et al.*, 2009). Dayal *et al.* have reported a hybrid solar cell with an efficiency of 3.2% under AM 1.5 irradiation using a low band gap polymer and CdSe nanoparticles (Dayal *et al.*, 2009). One of the disadvantages that the inorganic nanocrystals imposes in photovoltaic devices is that the insulating capping ligands that are necessary to form dispersed solution or ink of the nanocrystals hinder inter-nanocrystal carrier transport.

International Status: Research to Technology

Country-wise, Taiwan, Germany, China, and USA are the market leaders of this technology. During 2013, with a most likely forecasting scenario, 25 different countries are projected to have >100 MW of PV demands. India seems to be catching up with a seventh rank (projected for 2013) worldwide.

The solar modules that are commercially available are generally based on crystalline Si, amorphous-Si, CdTe and CIGS materials. Some of the leading companies in this field are Yingli Green, First Solar, Suntech Power Co., SunPower, and so on. Konarka and Mitsubishi have been manufacturing solar modules based on organic photovoltaic devices. In the competing global solar markets, cost reduction and increasing cell efficiencies are the key factors to the module manufacturers to sustain their business or to drive the business to the next level.

Different companies have been trying to increase the ultimate output wattage by engineering the installation procedure of solar panels. Instead of simply collecting the solar light which is just shining the surface of a solar panel, a new technology has been developed with an addition of optical equipment such as lenses and mirrors to focus greater amounts

of solar energy onto highly efficient solar cells (concentrated solar power, CSP). Although this technique could hike the manufacturing cost slightly, the advantages of CSP over conventional solar panel setups offer a high throughput for further research and development technologies. There are also some upcoming technologies to develop new architectures for solar cell installation. The basic mechanism behind such a technology is that the solar panels keep moving with the sun to acquire extra solar light. Genie Lens Technologies has developed a new route to enhance light absorption of solar panels. A large polymeric transparent sticker is applied to the front of the panels. Microstructures on the polymer stickers are capable of bending and redirecting the sunlight which increases the power output by about 10% and more.

Manufacturers of other household products are also tapping solar energy in their product. To name a few, automobiles, roofs and facades of buildings, portable electronics, etc. will soon be decorated with solar cells not only to make the products attractive to consumers, but also contribute to renewable energy production in one's own household.

Research Directions Across the World

The basic aim behind the progressing technology is to make a balance between the manufacturing cost and the module efficiency. As we know, silicon solar cells require a surface coating that increases the cost of the modules. Tonio Buonassisi and his group at MIT developed an alternative in the form of a polymer layer on silicon solar cells that sustained more than 200 h of continuous operation without any degradation.

Stretchability, in addition to flexibility of polymers has brought a new dimension in the organic solar cell technology. Such a property of polymers would integrate them in textiles, moving parts of machinery, one-time bonding to curved surfaces such the exteriors of buildings, automobiles, and many others.

Scientists from the Swiss Federal Laboratories for Materials Science and Technology have developed thin film solar cells on flexible polymer foils with an efficiency of 20.4%. They used copper indium gallium (di)selenide (CIGS) semiconducting material for the

solar cell fabrication. It appears that CIGS has a large potential to provide cost-effective solar panels. The technology is currently awaiting scaling-up for commercial production.

These are more examples of new research directions to improve the efficiency of solar cell modules. Some of the techniques are almost ready for commercial production. In the laboratory scale, much research focuses on new materials and manufacturing processes. Recently, use of earth-abundant elements is gaining interest so that the cost of materials becomes low.

Major Contributions from Indian Researchers and Industries

Maharishi Solar Technology Pvt. Ltd., New Delhi, one of the oldest players in the market, has been manufacturing solar cells based on polycrystalline silicon material. Researchers at IIT Bombay, in National Centre for Photovoltaic Research and Education (NCPRE), have achieved 20-22% efficiency in single crystal silicon solar cells. The Solar Energy Centre (SEC), a unit of the Ministry of New and Renewable Energy, is providing technical assistance to industries for the development of solar energy products. Moser Baer, in collaboration with CSIR-NPL, New Delhi has developed CIGS-based solar cells with an efficiency of 12-15%. In the arena of dye-sensitized solar cells (DSSCs), IIT Kanpur, CSIR-IICT Hyderabad, and IIT Delhi are working to achieve 6-10% efficiency.

Thin-film (Photovoltaic) Solar Cells: Our Approach

Hybrid Core-shell Nanoparticles

Photoinduced electron transfer from a semiconducting quantum dot to another quantum dot (Tu and Kelley, 2006) or to certain organic molecules has been reported to be ultrafast (Boulesbaa *et al.*, 2007). We aimed to take the advantage of this ultrafast electron-transfer process in fabricating photovoltaic devices, that is, our target was to make use of the electron-transfer process so that exciton dissociation may occur at each and every quantum dot. To do so, we

introduced some hybrid core-shell nanocrystals with an inorganic nanocrystal in the core and a layer of organic molecules as a shell layer. Upon photo-illumination, a photoinduced electron-transfer process was expected to occur from the inorganic core to an organic molecule on the shell resulting in exciton dissociation. With the hybrid core-shell nanocrystals in a hole-transporting polymer matrix, it is expected to have movement of electrons and holes towards the opposite electrodes that have different work-functions. In this way, we aim to convert the ultrafast photoinduced electron-transfer process into short-circuit current in the external circuit for efficient hybrid photovoltaic solar cells. Here, we choose the shell molecules in such a way that they formed a homogeneous interface with the host polymer. Moreover, the organic molecules formed type-II band-alignment or a staggered gap with the quantum dots, so that electron-transfer process becomes efficient. In other words, the semiconducting quantum dots decorated with suitable organic molecules can be considered as novel hybrid materials for efficient solar energy harvester (Guchhait and Pal, 2010; Guchhait *et al.*, 2009). A schematic representation of hybrid core-shell formation has been shown in Fig. 4A. While formation of hybrid core-shell structures was studied through optical absorption spectroscopy (Fig. 4B), photoinduced electron-transfer from the core to the shell was manifested by quenching of photoluminescence emission of the nanocrystals (Fig. 4C). The electro-transfer process upon formation of the organic shell layer was further supported by a sharp decrease in photoluminescence lifetime measured through time-correlated single photon counting (TCSPC) measurements spectroscopy.

Fig. 5A depicts a schematic representation of the device structure. Fig. 5B shows the results from a device where only CdSe nanoparticles were used. Results from the device based on hybrid core-shell nanoparticles are shown in Fig. 5C. In both the cases, we have added I - V characteristics under dark condition that were rectifying in nature. From the results under white light illumination, we find that with the use of hybrid core-shell nanoparticles, the device performance improved to a large extent. The short-circuit current of the latter device increased by 10

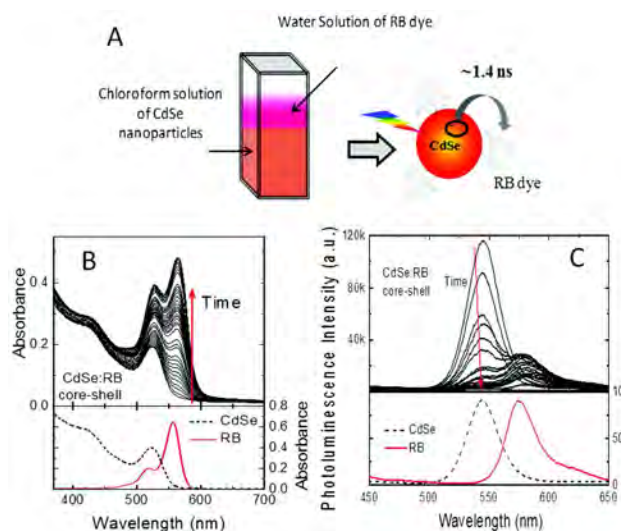


Fig. 4: A: Schematic presentation of hybrid core-shell formation, B: absorbance spectra of hybrid core-shell nanoparticles and C: photoluminescence spectra of the hybrid core-shell nanoparticles. In (B) and (C), red arrows indicate time evolution. Source: Guchhait *et al.* (2009)

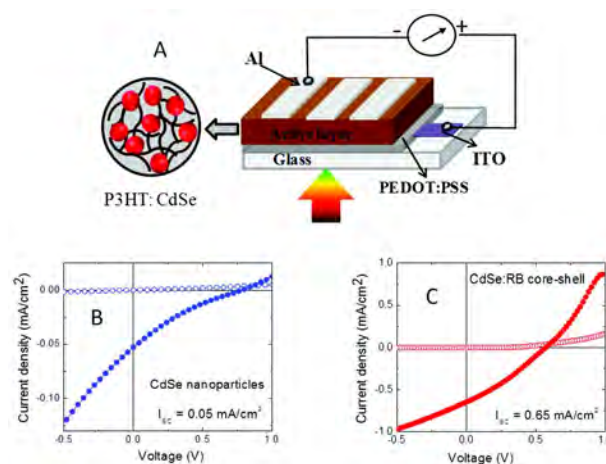


Fig. 5: A: Schematic presentation of a bulk heterojunction device. Current-voltage characteristics of a device based on B: only CdSe nanoparticles and C: CdSe-RB hybrid-core shell nanoparticles in P₃HT matrix under dark and white light illumination conditions. Source: Guchhait *et al.*, 2009

times as compared to that for the device with only CdSe nanoparticles.

We also observed that the rate of photoinduced electron-transfer process depends on the amount of dye present on the nanoparticle surface as well as on

the electron-accepting nature of the dye molecules. The rate of photoinduced electron-transfer process has been found to depend on the electron-accepting nature of the organic dye molecules in the shell layer. The device performance accordingly depended on the electron-transfer process. A one-to-one correspondence has been observed between the efficiency of the photovoltaic devices and the electron-accepting nature of the organic dye molecule (or decrease in lifetime of photoluminescence emission) of hybrid core-shell nanocrystals.

From the discussion, we could infer that introduction of hybrid core-shell nanoparticles in photovoltaic devices facilitates the use of inorganic nanoparticles in solar cell applications. Recently, researchers have introduced a range of hybrid nanocomposites in this direction. For example, Chang *et al.* have reported CdTe/SWNT nanostructures; photoinduced current in such nanostructures could be tuned by tailoring the nature of the semiconductor, morphology, and diameter of the CdTe nanostructures (Chang *et al.*, 2013). Mariani *et al.* have reported three-dimensional core-shell nanostructure for solar cell applications by using air-stable poly(3,4-ethylenedioxythiophene) (PEDOT) as a shell to periodic GaAs nanopillar arrays (Mariani *et al.*, 2012).

Organic/inorganic Hybrid *pn*-junctions

In the field of photovoltaic solar cells, researchers also search for environment-friendly or nontoxic elements with earth-abundance in fabricating high-efficient devices. The paths to achieve such a goal are not always unique, that is, a high-efficient device may often contain toxic elements, or green materials may not always return best solar cell parameters. Moreover, easiness of film-formation process should also be considered while choosing materials for fabricating solar cells. Finally, the mechanism of device-operation has remained worth-studying so that directions to improve device-performance can always be sought.

In such a complex scenario, new materials often bring fresh hopes. Earth-abundant $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) emerged as a promising absorber for thin-film solar cells (Shin *et al.*, 2013). CZTS is a quaternary kesterite

semiconductor with a direct band gap (~ 1.5 eV) and a large absorption coefficient ($\sim 10^4$ cm^{-1}). Thin-films of CZTS can be formed through various approaches. IBM Research (Yorktown, New York, USA) has already achieved the PCE of 11.1% in CZTS thin-film solar photovoltaic cells. The company also believes that these cells can be manufactured using ink-based techniques including printing or casting (<http://www.solarserver.com>, 2012). In the lab scale, thin films of *p*-type CZTS have generally been used in conjunction with a layer of *n*-type semiconductors such as CdS to fabricate *pn*-junction solar cells (Tanaka *et al.*, 2009). Recently, we have formed a *pn*-junction between a *p*-type CZTS layer and a fullerene derivative as the *n*-type material so that a solution-processed solar cell can be fabricated with materials based on earth-abundant and nontoxic elements that are more-importantly cadmium-free (Saha *et al.*, 2012). The junction can be termed as a hybrid *pn*-junction between layers of an inorganic semiconductor and an organic semiconductor. Here, we report characterization of CZTS/fullerene hybrid junctions under dark and illumination conditions evidencing solar cell applications to comment on the depletion region formed in *pn*-junction solar cells.

We have characterized the *pn*-junction devices based on CZTS nanoparticles and PCBM molecules. Schematic presentation of a *pn*-junction device structure and the equilibrium band-bending of the junction are shown in Fig. 6A&B, respectively. During the deposition of CZTS film, we have replaced the long-chain oleylamine ligands with short-chain pyridine by the layer-by-layer technique. This facilitated carrier transport through the CZTS nanoparticle film. In Fig. 6C&D, we have presented some results based on CZTS/PCBM junctions. In these ITO/CZTS/PCBM/Ca/Al devices under an illumination condition, excitons were photogenerated in both CZTS and PCBM layers. The excitons, which were generated within the depletion region at the CZTS/PCBM interface, would become easily dissociated into free carriers; the excitons, which are generated within the quasi-neutral region, might diffuse to the junction and become dissociated. Finally, the electrons move through the PCBM layer to the Ca/Al electrode and holes move through the CZTS layer to the ITO

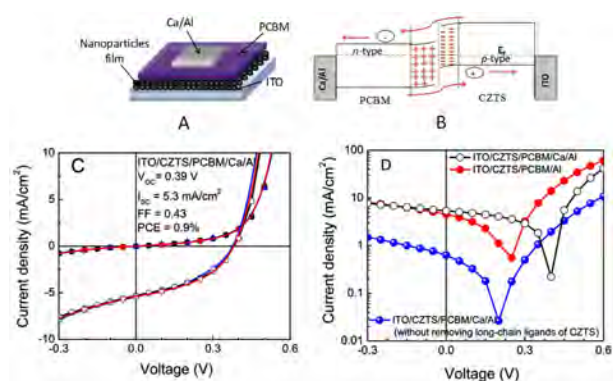


Fig. 6: A: Schematic presentation of a bilayer pn -junction device, B: energy band-bending of the junction under an equilibrium condition, C: current-voltage characteristics of the ITO/CZTS/PCBM/Ca/Al pn -junction device under dark and illumination conditions and D: characteristics under light of different devices as specified in the legend. Source: Saha *et al.* (2012)

electrode and yield photocurrent in the external circuit.

From C - V characteristics, we have determined the width of the depletion region and the density of carriers at the junction. A depleted and wider depletion-region has been observed in the CZTS/PCBM pn -junction as compared to those in Schottky devices. The results evidenced solar cell applications from nontoxic and earth-abundant materials forming hybrid pn -junctions.

***pn*-Junction Solar Cells Based on Inorganic Nanocrystals**

Solar cells can also be fabricated on basis of only inorganic nanocrystals, so that issues related to degradation of organic semiconductors do not arise. In this direction, we grew solar cells based on a layer of p -type nanocrystals and another layer of n -type nanocrystals to form a pn -junction. In such a junction under an illumination condition, separation of charge carriers occurs due to a drift of minority carriers through the depletion region. We hence formed a fully-depleted pn -junctions so that additional materials near the electrodes (“dead zones”) could be eliminated that would otherwise have increased the internal resistance of the solar cells without contributing to any photovoltaic response (Dasgupta *et al.*, 2014). In Fig.

7, we show that a fully-depleted device yields an improved solar cell performance as compared to thicker pn -junction devices comprising “dead zones”. Schematic representations of equilibrium band-bending of CZTS/AgInS₂@Cu pn -junction device structure and the fully depleted pn -junction are also shown.

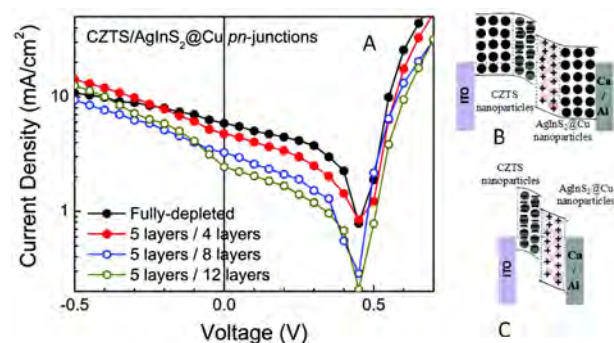


Fig. 7: Current-voltage characteristics of a fully-depleted and three other CZTS/AgInS₂@Cu pn -junctions under an illumination condition. Schematic representations of a conventional pn -junction and a fully-depleted pn -junction solar cell are also shown. Source: Dasgupta *et al.* (2014)

Future Avenues

As we must explore each and every form of renewable energy source, we must also continue to improve manufacturing/development of all types of solar cells. For the first generation solar cells, instead of aiming to improve efficiencies that may have reached saturation, reduction of the manufacturing-cost should be the goal. For the second generation solar cells, an improvement in efficiency would be beneficial to reduce the $\$/W$ value so that supply to the grid becomes economical. For the third and fourth generation solar cells, selection of suitable materials through materials engineering and at the same time simplifying the fabrication process of large-area solar cells are the two major directions that researchers should work in tandem.

As in other devices, the missing link between the lab and the plant has to be bridged. When a critical mass of researchers starts to work in this fascinating field, we will be able to comply with the societal aspect of research by making the renewable source of electricity a reality.

Conclusions

In conclusion, we have reviewed the evolution of solar (photovoltaic) cells based on a series of materials over the years. Solar cell materials ranging from crystalline silicon to most-recent inorganic quantum dot vs. organic hybrid systems for nanophotovoltaics have been discussed. We have shown how newer materials and materials engineering have allowed researchers to look beyond silicon as material for the future of solar cell technology. The importance of using earth-

abundant elements in choosing active materials for solar cells has been discussed to reduce the cost/Watt of electricity. Also, the need for using non-toxic elements in the selection of the active materials has been discussed in order to achieve environment-friendly and industrially viable solar cells for the future.

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