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Historic Developments, Current Technologies and Potential of Nanotechnology to Develop Next Generation Solar Cells with Improved Efficiency

Nisith Raval and Ajay Kumar Gupta*

Centre of Excellence in Nanotechnology (CoE-NT), Confederation of Indian Industry (CII), CII House, Gulbai Tekra Road, Near Panchavati, Ahmedabad - 380006. Gujarat, India.

Abstract: Sun is the continuous source of renewable energy, from where we can get abundant of solar energy. Concept of conversion of solar energy into heat was used back in 200 B.C. since then, the solar cells have been developed which can convert solar energy into the electrical energy and these systems have been produced commercially. The technologies to enhance the power conversion efficiency (PCE) have been continuously improved. Different technologies used for developing solar cells can be categorized either on the basis of material used or techniques of technology development which is further termed as 'first generation' (e.g. crystalline silicon), 'second generation' (thin films of Amorphous silicon, Copper indium gallium selenide, Cadmium telluride), 'Third generation' (Concentrated, Organic and Dye sensitize solar cell). These technologies give PCE up to 25% depending on the technology and the materials used. Nanotechnology enables the use of nanomaterial whose size is below 100 nm with extraordinary properties which has the capability to enhance the PCE to greater extent. Various nanomaterials like quantum dots, quantum well, carbon nanotubes, nanowire and graphene have been used to make efficient and economical solar cells, which not only provide high conversion efficiency economically but also are easy to produce. Today, by using nanotechnology, conversion efficiency up to 44.7 % has been achieved by Fraunhofer Institute at Germany. In this review article, we have reviewed the literature including various patents and publications, summarized the history of solar cell development, development of different technologies and rationale of their development highlighting the advantages and challenges involved in their development for commercial purpose. We have also included the recent developments in solar cell research where different nanomaterials have been designed and used successfully to prove their superiority over conventional systems.

Keywords: Solar cell, Nanotechnology, Renewable energy, Photovoltaic, Power conversion efficiency

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1. Solar cell: *historic developments and the current scenario*

By the year 2050, global energy demand will be more than two times and it may be three times by the end of this century. The Scope, to compete these increasing demand is the major challenges for achieving technological advancements, economic growth, and political stability. Advancement of existing technologies will not bridge the gaps between today's need and tomorrow's requirements. It must require additional source of energy and technologies to harvest the energy efficiency from these source over the next half-century with the capacity to double the today's energy output. The sun is the natural source of energy which delivers more energy to the earth in an hour than we use in a year from fossil, nuclear, and all other renewable sources together. Currently we are using only 0.1 % of our primary energy from sunlight.

In the last few decades, there had been growing research and developments in the area of solar cell technologies where the sunlight can be used as a source to generate electricity through photovoltaic effect. However this concept of solar technology is not new and find references as early as in centuries Before Christ (B.C.). In 3rd Century B.C., burning mirrors were

*Ajay Gupta: Phone: +917940279996; Fax : +917940279999
Email: ajay.gupta@cii.in

used to light torches by Greeks and Romans for religious purposes (Anuradha, Lovish & Pranjal 2013). Later, in 212 B.C., the Greek scientist, Archimedes used sunlight to set fire to wooden ships by using the reflective properties of bronze shields. During the era of 1st to 17th centuries, there were many reports indicating the use of solar energy in houses and public buildings for getting the warmth in winter seasons.

During the next two centuries (i.e. 18th and 19th century), there had been many developments and breakthroughs in the use of solar technologies. These developments are reported in the Table 1. All these milestones utilize different processes / technologies to harvest solar energy for use by the society (U.S Department of Energy 2015). However, still there was no scientific discovery or mechanism available which could be used at a commercial scale by mass public.

Table 1
History of solar cell (1700 – 1899)

Sr. No.	Year	Historical Developments / Milestones
1	1767	• World's first solar collector / cooker was developed to cook the foods by Swiss scientist Horace de Saussure.
2	1816	• Robert Stirling and Lord Kelvin developed a thermo-solar cell to concentrate sun's thermal energy to produce power.
3	1839	• French scientist Edmon Becquerel discovered the photovoltaic effect for the first time by using an electrolytic cell using electrolysis phenomenon.
4	1860	• French August Mouchet developed the solar powered steam engine for industrial applications.
5	1873	• W. Smith discovered the photoconductivity of selenium.
6	1876	• William Grylls Adams and Richard E. Day discovered the concept of selenium based solar cells and later in year 1883 Charles Fritts developed the first selenium wafer based solar cells.
7	1880	• Samuel P Langley invented bolometer to measure light from the sunrays.
8	1891	• C. Kemp patented the first commercial solar water heater.
9	1888 –1897	• Several scientists granted patents on solar cells.

However, at the same time (during the 18th and 19th century) several significant developments took place in the form of the industrial revolution which includes the machine based process, new chemical manufacturing, efficient hydro power production, increase the acceptance of steam and coal as a fuel source. However, as the industrialization progressed across the sectors, demand for the energy kept on rising. Earlier, the machines were operated manually which gradually started shifting to automatic operation where human intervention was minimal. These modern machines required energy (e.g. electrical, hydrothermal, steam engines, etc.). Due to this, there was growing need of energy for industry as well as society.

1.1 Birth of modern technology

In order to fulfil the future energy requirements, it was highly desirable to develop the technologies and devices which can capture the sun light and convert it into the form which can be put to use by the society. The beginning of 20th century brought more knowledge and improvement in the technologies used to harvest solar energy. Table 2 gives the glimpse of the developments happened during the century (U.S Department of Energy 2015; Affordable solar 2015; Wikipedia, Timeline of solar cell 2015; Experience 2015).

Table 2
History of solar cell (1900 – 2010)

Sr. No.	Year	Historical Developments / Milestones
1	1900 –1950	• Albert Einstein discovered the photo-electric effect (Year 1905). • Carnegie steel company invents copper coil based solar collector (year 1908). • Silicon (single crystalline) was developed by Jan Czochralski, a polish scientist (year 1918). • Photovoltaic effect was discovered in cadmium sulfide based solar cell by Audobert and Stora (year 1932). • Passive solar building in US was built (year 1947).
2	1951 – 1960	• Bell Labs invented solar cell (silicone) with about 6% efficiency to run daily equipment's (year 1954). • Western Electric licenses commercial solar cell technologies (year 1955). • Between years 1957 – 1960, Hoffman electronics achieved 8 – 14 % efficient in solar cell. • Silicon sensors started producing selenium and silicon solar cells (year 1960).
3	1961 – 1970	• The Telstar communications satellite is powered by solar cells (year 1962). • Sharp Corporation produces a module of silicon based solar cells (year 1963). • Japan installed a 242 watt solar cell array on a light house (year 1963) • First manned spacecraft (Soyuz 1) was powered by solar cells (year 1967). • Exon Corporation produced cheaper solar cells which could be used in remote locations where grid connections were not feasible (year 1970).
4	1971 – 1980	• First amorphous silicon solar cells were created by David Carlson and Christopher Wronski, with 1.1% efficiency (year 1976). • The world production of photovoltaic cells exceeded 500 kW (year 1977). • Salyut-1, Skylab, Florida Solar Energy Centre, The University of Delaware's "Solar One" residential building, Solar Energy Research

		Institute at Colorado, Solar panels in White House, USA, Calculators etc. powered by solar energy were developed in this decade. • First thin film solar cell was developed by University of Delaware with 10% efficiency using Cu_2S/CdS technology (year 1980).
5	1981 – 1990	• ARCO Solar produces > 1 MW of solar modules/year in California (year 1982). • Volkswagen, Germany tested solar arrays on the roof of Dasher station wagons (year 1982). • Global photovoltaic production exceeds 21.3 megawatts (year 1983). • Centre for Photovoltaic Engineering created 20% efficient silicon cells at the University of New South Wales (year 1985). • World's largest solar thermal facility located in Kramer Junction, CA, was commissioned (year 1986). • ARCO Solar released first thin film power module (year 1986). • Michael Gratzel and Brian O'Regan created world cheapest dye sensitize solar cell (year 1988). • Dr. Alvin Marks granted patents for Lepcon and Lumeloid (year 1988).
6	1991 – 2000	• National Renewable Energy Laboratory was established by President George H. W. Bush (year 1991 – 1994). • University of South Florida achieved 15.89 % efficient in thin-film cell (year 1992). • NREL achieve 30 % efficiency using GaInP/GaAs two - terminal concentrator cell (year 1994). • Graetzel, Switzerland achieves 11% efficient energy conversion using a photo electrochemical effect in dye-sensitized cells that (year 1996). • Total worldwide installed photovoltaic power reaches 1,000 megawatts (year 1999). • Spectrolabs, Inc. and NREL developed solar cells with an efficiency of 32.3% (year 1999). • NREL achieved 18.8% efficient in thin film solar cells (year 1999).
7	2001 – 2010	• BP Solarex developed highest solar modules of 10.8 % conversion efficiency achieved by 0.5 Sq. meter and 10.6 % achieved by 0.9 Sq. meter (year 2000). • Terra Sun LLC developed unique method holographic films to concentrate sunlight onto a solar cell (year2001). • Power Light Corporation developed word largest hybrid system (Wind and solar energy) to maximize the power generation (year 2001). • The University of Delaware achieved a new efficiency of 42.8% (year 2007). • China produced nearly half (1700 MW) of the world production (3800 MW) of solar panels (year 2007). • The installation cost of PV modules decreased from 16000 $/KW in 1990's to 6000 $/KW (year 2008). • World solar cell production reached 9,340 MW (year 2009).

Solar cell is an electrical device which converts the light energy into electric energy by photovoltaic effect. In simple words, upon exposure of solar cell with light, it can generate an electric current without being attached to any external voltage source. But do require an external load for power consumption. Recent technologies like screen printing and solar fabric can enable to install the solar cell inside the house, even on the roof. Today International market have opened up, in which solar panels manufacturer are now playing a key role in the solar power industry.

2. Solar Cell Technology

Photovoltaic (PV) is a similar term of solar cells, as an electronic devices that convert sunlight directly into electricity. The modern age solar cell was invented at Bell Telephone Laboratories in 1954. A solar cell are grouped together to form a solar module. Auxiliary components of solar cell (i.e. balance of system - BOS) comprise inverter, controls, etc. Today, solar cell is one of the fastest growing renewable energy technologies and in the present context, solar cell systems may be considered as one of the most abundant renewable technologies (IRENA 2012). This is because of the availability of innovative technologies, which makes it feasible to develop efficient modular size with ever increasing power conversion efficiency that they are within the reach of individuals, co-operative societies and small businesses who can install these modules for electricity generation and manage to lock-in prices. Over other conventional technologies solar cell technology offers additional benefits like renewable source of energy, readily available across the globe, small and highly modular sizes of solar devices can be installed anywhere at shade-free locations e.g. roofs, gardens etc. Solar cell generate electricity by harvesting sunlight and hence require no fossil fuels like nuclear, oil, coal, gas etc., thereby requires relatively low production, operation and maintenance costs. Today, wide ranges of technologies are available using different types of materials in solar cell. Hence with the huge scope, the future of solar cell is looking bright. Solar cell technologies are categories into three generations, viz. first-generation, second generation and third generation based on the material used.

2.1. First generation technologies

Silicon is a semi-conductive material widely use in solar cell applications. Energy band gap of crystalline silicon is about 1.1 eV, which make crystalline silicon more suitable for conversion of sun energy into electric energy. Out of all other materials tried till now, silicon have achieved conversion efficiency around 15 to 20 % at commercial scale (Kenneth & Paul 1982). This technology has a long history of reliable performance with lifetime of more than 25 years. First-generation solar systems use single types of material i.e. crystalline silicon (c-Si), either as single crystalline (SC-Si) or as multicrystalline (mc-Si). Single crystalline silicon wafers, which are cut from single crystal silicon ingots to make monocrystalline solar cell. Comparatively monocrystalline silicon has capacity to higher efficiency, but it is very difficult to produce from ingot silicon crystal. Hence it is very energy intensive and expensive to grow. While multicrystalline wafers are cut directionally solidified blocks or grown in thin sheet so it is easy to build up and they are less expensive. To prepare single crystal silicon from multicrystalline silicon, first and foremost requirement is molten state of silicon and follow by solidification in a manner to arrange the silicon atoms themselves in a perfect lattice as occur naturally. General procedure requires initial contact of single crystal seed of silicon with the molten state and enables to cool down slowly. As the single-crystal silicon is grown, appropriate substances or dopants are like to introduce to tune the material electric behavior as per requirement. Dopants like boron and phosphorus have been used to obtain electron donor and electron acceptor to complete the photoelectric circuit (Kenneth & Paul 1982). Advantages of monocrystalline silicon are that the monocrystalline cells have the highest efficiency, very stable and are simple type of solar cell. Drawback of these monocrystalline silicon based solar cells is that they are more expensive and they do not perform efficiently at elevated temperatures (Wide Bay Burnett Conservation Council Inc. WBBCC 2010). Crystalline silicon solar cells and modules have dominated photovoltaic technology from the beginning of solar cell history and contribute around 90 % in solar cell market. In 1996, electric output of single crystalline solar cell was 48.7 MW, which share 55 % of global solar cell market (Kenneth & Paul 1982). Multicrystalline solar cell output was 28.4 MW and occupies 32 % global solar cell market. In 2000, single crystalline cell output decreased to 32 % and for multicrystalline it increased to 51%. Such changes were observed because of expensive method of fabrication for single crystalline silicon solar cell. In 2004, china enters into the mass production of solar cell technology leads to capture 70 % of total market of solar cell technology. So in 2013, monocrystalline wafer based technology holds 90 % of total market, while multicrystalline about 55 % (Fraunhofer Institute of Solar Energy System 2014).

2.2. Second generation technologies

Thin film solar cell as second generation technology, was developed to produce low cost electricity as compared to first generation solar cell. Thin film solar cell technology involve the deposition of a thin layer of about 4 μm thickness of photovoltaic material on substrates like steel, glass or plastic. As a result, very less amount of photovoltaic material is required to produce solar cells with good conversion efficiency which makes them feasible for commercial production. Thin film solar cells technology utilize non-crystalline material, has lower conversion efficiency ranging from 4 to 12 %. Hence its power conversion efficiency is significantly lower in comparison with crystalline solar cells (International Energy Agency 2013). Photovoltaic materials like Amorphous silicon (a-si), Cadmium Telluride (CdTe), Copper indium selenide (CIS) and Copper Indium Gallium Diselenide (CIGS) are widely used to make thin film solar cell. Despite their lower efficiency, thin film solar cells enjoy good stability as well as good shelf-life comparable to c-Si module. In addition, they have short energy pay-back times which may be less than 1 year.

Amorphous silicon (a-Si)

In thin film solar cell technology, maximum efficiency was achieved with amorphous silicon as a photovoltaic material. Defective structure of amorphous silicon leads to high band gap 1.7 eV which in turn increases the absorptivity of sun light to almost 40 times as compared to monocrystalline silicon solar cell (Abdin et al. 2013). However, the main problem with amorphous silicon is the degradation of silicon in sun light, so overall efficiency of solar cell diminishes as a function of time. Various approaches have been utilized to overcome the above problems. One of the approach is the deposition of amorphous silicon material by plasma vapor deposition technique with as minimum thickness as possible as to strengthen the electric field across the material and its stability (Anas I.A.T. 2007). But as the thickness of the film decreases, light absorption capacity decreased and hence cell efficiency also got reduced. So to overcome the lower absorption and conversion efficiency, double, triple or multi junction thin film silicon solar cell approaches were explored. Such approaches comprised of the use of thin layer of amorphous silicon and subsequent layer of microcrystalline silicon on to the amorphous silicon. In year 2009, amorphous silicon panels achieved efficiency of 6-9 % (Green et al. 2011). Afterwards, Switzerland based company Oerlikon announced test panels that can reach power conversion efficiency of around 11 % using a multifunction technology (Greentechmedia 2009). Advantage of using amorphous silicon in producing thin film solar cell is that, it is not only very economical but also compatible with other materials.

Cadmium Telluride (CdTe)

Cadmium is a by-product of zinc during mining and tellurium is a by-product of copper processing. Cadmium telluride thin film is the most economical thin film technology out of currently available technologies. Its band gap is about 1.5 eV, which match with the solar spectrum. In 2011, CdTe thin film achieved very high efficiencies up to 16.7% with low production cost than other thin-film technologies (International Energy Agency 2013). Efficiency of CdTe solar cells depend on various parameters e.g. deposition technique, substrate and deposition temperature etc. Its band gap can be varied by using various approaches like hetero-junction or multi-junction solar cell which lead to increase in efficiency up to 18% (Noufi & Zweibel 2006). Various methods are available to deposit CdTe on substrate as mentioned in table 3 (Koch et al. 2011). A potential problem of cadmium telluride is the production quantity of telluride and availability, which is depend on extraction, refining and recycling yield of copper industry. Toxicity of telluride is another problem for solar cell industry.

Table 3
Thin Film deposition technique (Koch W et al 2011)

Sr. No.	Name of CdTe thin-film deposition techniques
1	Close space sublimation
2	Vapor transport deposition
3	Physical vapor deposition
4	Sputter deposition
5	Electrode deposition
6	Metal organic chemical vapor deposition
7	Spray deposition
8	Screen print deposition

Copper Indium Gallium Selenide (CIGS)

As CIGS is a new technology so still it is in developing stage and is set to compete with other technologies. Solar cells based on CIGS offer the highest efficiencies among all thin-film Solar cell technologies. Power conversion efficiency of solar cell have been achieved up to 20 % at laboratory scale and 7 to 16% was achieve at commercial scale which is close to that of crystalline Silicon cells (International Energy Agency 2013). In this case, band gap can be modified by varying the Group III cations from Indium, Gallium, and Aluminum and the anions between Selenium and Sulfur. Using combinations of different compositions enable to make wider the range of energy band gap. Semi conductive materials like $CuInSe_2$ (CIS), $Cu(InGa)Se_2$ (CIGS) and CdTe are widely accepted because of their high efficiency, long-term stable performance and potential for low-cost production (Noufi & Zweibel 2006). Thin layer of around 2 mm is sufficient enough to absorb the useful part of the solar spectrum because of its high absorbing power. As compared to other technologies, the manufacturing process is more complex and costly. Hence, by replacing indium with low cost materials could help to reduce the cost. Currently, researchers are more attracted towards the application of multicrystalline solar cell for space applications due to its excellent photovoltaic effect than silicon. However, thin film manufacturers start adopting modification in existing technology because of low cost crystalline silicon modules are available in the market. Four different types of thin film solar cell with power conversion efficiencies are described below in Fig 1 (EPIA- Europian Photovoltaic Industry Association 2011).

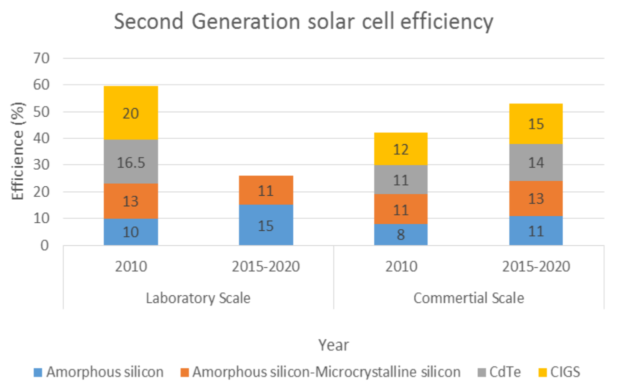

Fig 1: Second generation solar cell efficiency for laboratory scale and commercial scale.

2.3. Third generation solar cell

Third generation solar cell technologies includes concentrating PV (CPV), Dye sensitize solar cell and organic solar cells. Even with extensive efforts these technologies are still under demonstration and have not yet been widely commercialized.

Concentrated photovoltaic cell (CPV)

Concentrated photovoltaic (CPV) cell enable to concentrate a large amount of sunlight onto a small area of solar photovoltaic (PV) cells to generate electricity using optics as a main component which includes lenses or curved mirrors. A concentrator is usually made up of relatively inexpensive materials such as plastic / glass lenses to capture the sunlight falling on a large area and concentrate that energy onto absorbent (IRENA - International Renewable Energy Agency 2013). CPV technology has many advantages like it can operate at elevated temperature, produce more power in minimum time, have slow degradation compared to earlier generation solar technologies and have much higher power conversion efficiency. Mirrors or lenses decrease the cost of solar cell significantly than other expensive solar cell (IRENA - International Renewable Energy Agency 2013). CPV systems are classified according to the amount of the concentrated solar energy, measured in 'suns' (the square of the magnification): (I) Low concentration PV systems with a solar concentration of 2-100 suns, (II) Medium concentration PV systems with a solar concentrations of 100 to 300 suns and (III) High concentration photovoltaic (HCPV) systems with a solar concentrations of 1000 suns or more (Wikipedia, Concentrated photovoltaic 2015) . Today's CPV systems have system efficiencies almost 30%, which incorporate highly efficient III-V silicon solar-cells. The installation costs of CPV systems today are very competitive to flat-plate PV systems. At commercial scale silicon based CPV have achieved 20 to 25% power conversion efficiency (Robert & Vasilis 2012). At laboratory scale, more than 40% of power conversion efficiency was achieved using III-V semiconductors in multi-junction CPV. Their higher efficiency and the smaller PV surface area required may eventually reduce the overall costs. For techno-commercial reasons, the utility market is the most popular market for CPV companies. In 2008, according to a Green media survey there were 10, 38, and 46 companies available in the market with their CPV products in residential, commercial and utility segment respectively (Sorin, Elizabeth & Travis . 2008). SOITEC in Europe is another firm with multi junction cells announced for 4-junction devices, at 43.6% conversion efficiency under 319 suns (Solar server 2013). In 2012, the Fraunhofer Institute for Solar Energy Systems fabricated multi-junction photovoltaic cell with 44.7% power conversion efficiency and breaking its own record of 43.6% set just four months prior (Maria 2013).

Dye sensitized solar cell (DSSC)

Dye-sensitized solar cells combining the unique properties of both the organic compound and inorganic compound have attracted the attention of scientists in the recent years. In the conventional solar cell systems, semiconductor material plays the dual role of photon absorber and charge carrier. On the other hand, DSSC separate these two functions to two different materials, i.e. the organic molecule usually a dye as a sensitizer absorbs sunlight and the second inorganic molecule then transforms solar energy into electric energy. First, light is illuminated onto a dye which in turn excites electrons in the dye. The excited electrons further excite the electrons in titanium dioxide (TiO_2) film and ultimately reaching the electrode through diffusion. On the counter electrode, generated electrons reduce I_3^- ions to I^- ions and diffuse in the solution, reach the dye, give up electrons, and are oxidized forming I_3^- ions (Tomohiro & Hirohiko 2009). Numerous metal complexes and organic dyes have been used as sensitizers in solar cell. Photo excitation at a monolayer of organic dye results in the injection of an electron into the conduction band of oxide. Then, organic dye restores its original electron configuration by electron donation from the electrolyte, usually an organic system containing redox couples. N3 dye, RuL2(NCS)2, and Black dye, RuL(NCS)3, are the most commonly used as an organic dyes in DSCs. Main drawback with organic dye based DSSC is the toxicity of organic dye as well as the stability of electrolyte at elevated temperature. Such problem can be solved by using natural dye because they are biodegradable, cheap and abundant. By using synthetic organic dyes in DSSC, highest efficiency of 11-12 % have been achieved, while with natural dyes 9.8% was achieved. Natural dyes from flower, fruit or vegetable are capable to act as a photo sensitive material in DSSC. Highest efficiency of 7.6 % have been achieved by using coumarin as a natural dye (Souad et al. 2013). However DSSC have certain drawbacks e.g. low stability of dye and electrolyte solution at elevated temperature and lesser efficiency compared to other solar cell technologies. Need of the hours is to find out the solutions to increase the stability of dyes and electrolytes in these DSSC and at the same time increase the efficiency. Despite these problems, it is expected that the DSSC will become the future of solar cells technologies to provide the cheap energy due with high conversion efficiency.

Organic solar cell (OPV)

Within the last three decades, tremendous effort have been made to develop organic solar cells common materials used for photovoltaic devices are inorganic. The incorporation of semiconducting polymers into organic solar cells resulted in remarkable improvements within last few years. The sp^2-hybridization of carbon atom of semiconducting organic materials is responsible for the absorption of visible solar region and to transport the electrons to generate the electricity. Basically, four consecutive steps are involved towards working principle of organic solar cell i.e. light absorption, excitation, charge transport and collection (Myung 2009). Organic solar cells are classified on the bases of number of electron transporting layer available in the device namely single, double and triple layer organic solar cell (Daniel & Darren 2013). In 1994 A.D. R. N. Marks et al. prepared an organic solar cell having poly (p-phenylene vinylene) of 50-320 nm thickness in sandwiched manner between Indium titanium oxide (ITO) and cathode with 0.1% power conversion efficiency under 0.1mW/cm^2 intensity. The reason behind such low efficiency is due to intrinsically low mobility of charges through semiconducting organic. Organic solar cells have unique and significant advantage like these devices are not only low costs per module, but also their thinness and extremely small mass could also reduce the costs associated with transportation and installation of modules. So aim of the electronic segment is to set the application of electronics everywhere for the development of next generation. With these, semi conductive organic industry will play a vital role in upcoming future technologies. Multidisciplinary approach of organic solar cell with other components like batteries, in fuel cell etc. will enhance their production efficiency. This integration of organic solar cells into many products will be their technological advantage. Owing to the lack of scalable high performance donor materials, conversion efficiency of OPV is usually lower than other available solar technologies. Studies on mass-produced organic photovoltaic (OPV) devices lag far behind that on lab-scale devices. Power conversion efficiencies (PCE) of 6–7% have been achieved for OPV devices based on different active layers using different organic polymers. Recently it has been reported that 8.4% efficient fullerene-free organic solar cells were developed which exploited long-range exciton energy transfer. In one study PCE as high as 15% has also been reported and the technology was already patented by the inventors (Ning et al. 2013). Glimpse of power conversion efficiency (PCE) of all three generation technologies for solar cells in terms of laboratory scale and commercial scale as mentioned in Table 4 (Georg, Enrico, & Yoann 2012).

Table 4
The list of technologies with efficiency at laboratory Vs. commercial scale with their market share

Technology	Material	PCE at Laboratory scale (%)	PCE at Commercial scale (%)	Market share (%)
First generation	Crystalline Silicon (Multi crystalline and Mono crystalline)	28	16-20	85
Second generation	Amorphous Silicon	10	8	14
	CdTe	16	11	
	$Cu(InGa)Se_2$	20	12	
Third generation	Organic Solar cell	12	8	1
	Dye Sensitize solar cell (DSSC)	10 – 15	11	
	Concentrated Solar cell	43.6	31.8	

3. Current trends towards applications of Nanotechnology in solar cell

Current solar cell technologies have two major drawbacks i.e. low conversion efficiencies and high manufacturing cost for generation of electricity at commercial scale. Nanotechnology is an emerging technology that has the potential to provide solution to above problems. As the nanotechnology make use of materials, which are very small in size (less than 100 nm) having very large surface area. Such properties can enhance the efficiency manifold and also at the same time reduce the sizes of the devices. Currently, most commercial solar cell utilize silicon based semiconductor materials. But in the past few years, scientists have been investigating to increase the efficiency of solar cell using nanotechnology. Use of nanomaterial would provide the new ways to capture, store and exchange energy. Three basic advantage have been offered by nanotechnology based solar cell. First advantage is the large surface area offer enhanced solar absorption. Second, light generated electrons and holes need to travel over a much shorter path and thus recombination losses are greatly reduced. Third the tunable energy band gap by varying the size of nanoparticles. This allows for the much needed flexibility in designing of solar cells. Currently various nanomaterials have been explored to develop the solar cells. Among these materials quantum dots, quantum wells, carbon nanotubes and nanowires are most widely studied (Abdin et al. 2013).

3.1 Quantum dots (QDs)

Quantum dots are minute crystal composites of size less than 10 nm are having tremendous semi conductive properties. These properties are responsible due to their ability to enhance light absorption and absorb the infrared range. Quantum dots has potential to tune the band gap upto optimum value to enhance the maximum efficiency. It can be applied to single junction solar cells with different band gap to form a tandem cells. Due to significant properties like significant absorption of infrared radiation, at higher temperatures it increase the photo current and efficient radiation hardness. Theoritically it was predicted that the efficiency of QDs can be achieve up to ~64% for a well-adjusted intermediate band in a solar cell. A solar cell uses quantum dots as the light absorbing material can be use rather than known bulk materials such as silicon, copper indium gallium selenide (CIGS), TiO_2, ZnO or CdTe (Sethi, Mukesh, & Priti 2011).

Silicon based QDs have been proved to provide better power conversion efficiency as compare to bulk Silicon due to the following reasons that (Georg, Enrico, & Yoann 2012):

[1] Increase in the energy gap with decrease in the size of the QDs. Due to enhanced energy gap, widening in the distance between the energy states occurs. As a result, the relaxation of the excited carrier is slow down with respect to bulk silicon (Hot carrier solar cell).

[2] Si QDs exhibit strong photoluminescence in the visible red region of the solar spectrum. QDs can generate multiple excitons in silicon atom with twice or more energy than the band gap, thereby splitting the excited exciton into ‘n’ excitons without losing the excess energy in the form of heat.

QDs have many advantages like size dependent tunable energy band gap, strong photoluminescence, generation of multiple excitons etc. Various approaches have been tried by using QDs for solar cell in order to increase power conversion efficiency like (a) QDSSCs

(Quantum dot sensitize solar cell), here QDs act as an alternative to the dye molecule in Dye sensitized solar cell. (b) Crystal QDs.to combine the quantum dots inherent tunability with a simple manufacturing process in order to reduce the cost. (c) Multi junction solar cell (d) Organic solar cell:

Developments of solar cell using quantum dots (QDs)

According to US patent US20100012168, US20130042906, US8395042, a quantum dot sensitized solar cell including an anode, a cathode and an electrolyte is provided. The anode includes a semiconductor electrode adsorbed with a plurality of quantum dots. This include a tunable electron conductor that permits greater choices in quantum dots, thereby providing solar cells that can be constructed to utilize a broad light absorption range that covers the ultraviolet, visible and infrared regions leading to an improved conversion efficiency of the solar cell. The size and composition of a quantum dot can determine its band gap and Fermi level (Mihai, Viorel-Georgel, Cornel, Mircea , Bogdan-Catalin 2010; Ming-Way 2013; Neil, Friedrich, Timothy, & James, 2013). Various approaches have been explored to increase power conversion efficiency like QD's core-shell structure, QD's absorb light and emit red shifted light which can absorb by active layer and by depositing QD's on CNT/ Nanowire, 20nm ZnO mesoporous photo anode to achieve 12 % which was claimed by US patent application US2008/000183, US20120132891 and CN2011/000860 (Istvan et al 2006; Troy 2008; Prashant K. et al 2008; Mircea, Bogdan-Catalin, 2010; Leonard & Jeeseong, 2012; Robert et al 2012; Mihai, Viorel-Georgel, Cornel, Chunhui 2013). Material used for QD's solar cell are CdSe, ZnS, CdSe, InGaAs, InGa, InAs, Germanium, CdS, PdS and InP as per US8658889, US20110146772, US8072039, US20050155641, EP2442326 and US8574685 (Hiroaki 2011; Kyung-Sang, Byung-ki. 2011; Simon 2011; Anna, Zhi, Linan, Marilyn, 2013 & Jason, Xiaomei 2013; Kun-Ping 2014). Porphyrin-sensitized solar cells with cobalt (ii/iii)–based redox electrolyte and zinc porphyrin dye as sensitizer were succeeded to achieve 12.3% efficiency (Aswani et al. 2014).

Patent US7402832 claimed that core-shell defect free silicon quantum dot exhibits photoluminescence with power conversion efficiency is greater than 10 % (Howard & Hoon 2008). Light scattering Silicon and Gold Nanoparticle shown improved performance of quantum-well solar cells with a 17% power conversion efficiency (Derkacs et al. 2008). 94% of the light can absorb by 280 nm thick hydrogenated amorphous silicon (A-Si:h) layer in nano dome based solar cell. It is higher than the 65% absorption of flat film devices, due to efficient light management and self-cleaning concept (Ekins-daukes et al. 2010). Facilitation of significant electric interaction provided by P3HT−CdSe nanocomposites having well-defined interface. It also promoting the dispersion of CdSe within the P3HT matrix efficiently (Xu et al. 2007). Power conversion efficiency about 6 % was achieved using co-polymer, poly [n-9-hepta-decanyl-2, 7-carbazole-alt-5, 5-(4', 7'-di-2-thienyl-2', 1', 3'-benzothiadiazole) (PCDTBT) in bulk heterojunction composites with the fullerene derivative [6, 6]-phenyl c70-butyric acid methyl ester (PC70BM). Conversion of sunlight to electricity to supply for future generation is considered to be a major task. To address a future need of electricity, the cost of solar energy will have to be significantly lower and the efficiency will have to be increase significantly. So with these requirements, research on nanostructure Si QDs for application in solar cell has enormously increased. However, a deep scientific investigation of using these structures is required to outperform the C-Si solar cells to meet future energy needs.

3.2 Quantum well (QW)

Barnham and co-workers at Imperial College proposed and demonstrated the first quantum well solar cells (QWSCs) a decade ago. It was based on the hypothesis that quantum wells could extend the spectral response and increase the photocurrent of solar cells without degrading their voltage characteristics. Hence initial proposal for these devices was motivated by the goal of enhanced energy efficiency. Early experiments on AlGaAs-based cells indeed revealed that introduction of GaAs quantum wells enhanced both the photocurrent and power conversion efficiency under broadband illumination. These results motivate the researcher to explore quantum well phenomenon to enhance power conversion efficiency (Keith et al. 1997).

In the past few years researcher are more attracted towards quantum well solar cells (QWSC). Quantum well solar cells (QWSC) is a thin layer of material posing a lower band gap than the surrounding barrier or host material. Quantum well must be sufficient thin to bring about quantum effect through the confinement of electron and holes, so its dimension is in range of few nanometers. Hence its novel structure has potential to achieve high efficiency if the absorption spectra of absorbing material is wide by photo-generated electrons and holes escape from the wells and increase the output current. A QWSC consists of a p–i–n-junction constructed from high band-gap semiconductor with thin layers of lower band-gap semiconductor to form potential wells, as shown in Fig 2. By the recombination in the bulk material, the open circuit voltage can be still controlled which is known as barriers. While the sections of lower band-gap material absorb low-energy photons that the barrier material which is known as well. For light with energy greater than the band-gap (E) the quantum-well (QW) cell behave like a conventional solar cell. However, light with energy below and above the energy band-gap (Eg), can be absorbed in the quantum wells.

In 2009, a single junction GaAsP/InGaAs quantum well solar cell attained a peak efficiency of 28.3% under solar concentration (Ekins-Daukes et al. 2013). Major benefit of incorporating a quantum well stack into a multi-junction solar cell is to increase the photocurrent up to 40 % with InGaP/ MQW/Ge. Hence additional current flow through the top and middle cells to increase the efficiency. Presently, QWSC efficiencies of approximately 20–25% are achievable. While in future, it can be expected that 35% efficiency or beyond is achievable using strain-balanced tandem QWSC in order to extend the spectral range (Rault & Zahed 2003). For single junction QWSC optical band gap can tune the thickness and composition to get highest efficiency efficiencies.

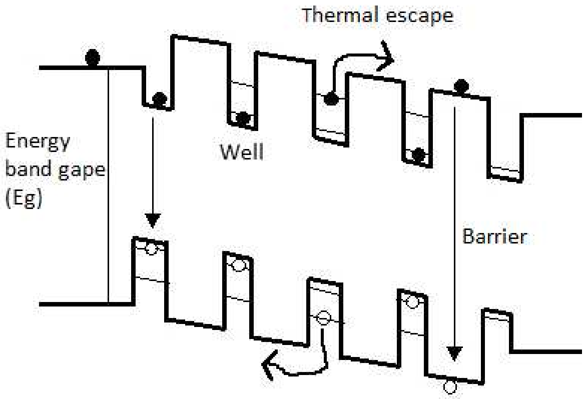

Fig 2: Quantum well based solar cell.

Development of solar cell using quantum well (QW)

Prof Keith Barnham of Imperial College London invented the QW solar cell in 1989, which operated at high current and was made of alternating layers of InGaAs and GaAsP wile p and n layer are made from GaAs. In 2009, Prof Keith Barnham achieved the highest efficiency of a nano structure solar cell at 30.6 % obtained from a tandem junction QW solar cell at a concentration of 54 suns (Mazzer et al 2006).

US patent US5496415 and US4688068 describe a solar cell formed from a semiconductor having a relative wide band-gap characterized by a multi-quantum well system incorporated in the depletion region of the cell. These quantum wells comprise regions of semiconductor with a smaller band gap. Material used for smaller band gap is InGaA, GaAs, GaP, and GaN (Gordon 1986; Keith 1996; Alexandre 2000; Liang, Ilyas & Masud 2013; Roger). These kinds of quantum well were able to achieve 12 % power conversion efficiency. It has been also discovered that the power conversion efficiency of InGaN/GaN based quantum well sola cell are inversely proportional to temperature (Ramesh et al 2013). InGaN/GaN multiple quantum well (MQW) solar cells with enhanced power conversion efficiency using colloidal CdS quantum dots (QDs) and back-side distributed Bragg reflectors (DBRs) up to 20.7% (Yu-Lin et al. 2013).

Patent US20120167973, EP2595193 and US8101856 describe that solar cell were designed by using quantum well which is made up of polycrystalline silicon, germanium or GaP-Si. By incorporating hydrogenated nano crystalline silicon (nc-Si:H) and a-Si:H (nc-Si:H/a-Si:H) multiple quantum wells (MQW) in the intrinsic region, absorption coefficient increases in three steps starting from 1.0 × 104 cm^{-1} to 3.0 × 104 cm^{-1} for photon energy of 1.2 eV to 1.4 eV, respectively. Therefore number of incorporation is directly related with the efficiency of solar cell (Ankur, Manvendra, Pratibha 2014).

The mitigation of the thermal scattering as well as the control of the light absorption range of quantum energy level is considered as a driving force for next generation solar cell. Multiple quantum wells (MQW) utilize absorbing material with multiple band gap to achieve higher conversion efficiency. This MQW thickness of the well layer (5-10 nm) is important to form quantized energy state in the well. MQW based solar cells demonstrate good temperature stability because of multi band gap structures. Due to this feature of MQWs they are also suitable thermo-photovoltaic applications, where heat generated from combustion process can be converted into electricity. These cells can also be used for spaces applications (Seung 2007).

3.3 Carbon nanotube (CNT)

Carbon nano tube (CNT) is made up of graphite sheet, which are rolled like a straw. It may be single rolled sheet single wall carbon nano tube (SWCNT) or multiple rolled sheet i.e. multiple wall carbon nano tube (MWCNT). Carbon nanotubes is considered as ideal material for solar cell due to wide range of direct band gaps from infrared to ultraviolet and high carrier mobility with reduced carrier transport scattering, which make themselves ideal photovoltaic material. Secondary advantage of carbon nanotubes is earth abundant, possess high optical absorption, and superior thermal and photo stability. The extraordinary properties of CNTs such as light weight, excellent mechanical strength, three dimensional flexibility and outstanding electro catalytic property, can improve the performance of solar cells. CNT nanostructured surface can also enhance the performance of both charge separation and electron transportation, so they can be applied as either a working electrode or counter electrode, or even as the conductive substrate as shown in fig 3. Electron mobility's on the order of 10,000 cm^2/Vs have been measured for both metallic and semiconducting tubes. These extraordinary electronic properties are due to low defect density and the one dimensional geometry (Yan et al. 2013).

Utilizing the concept of the photo induced charge transfer between organic conjugated polymers as a donor and nanotubes as acceptor, CNTs and different polymers have been used extensively with an aim to increase the efficiency by three times. Hence CNT are considering as a promising candidate for solar cell by increasing conversion efficiency, increasing stability and decreasing cost (Maciej et al. 2011).

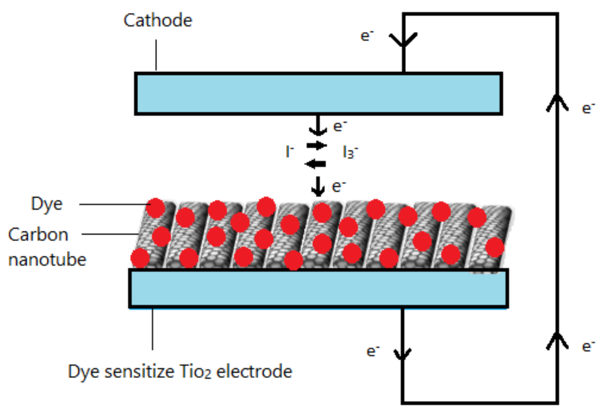

Fig 3: Dye sensitize solar cell containing CNT as charge transfer layer

Development of solar cell using carbon nanotube (CNT)

Their low-cost processing is expected to become a method for commercially realistic energy conversion efficiency and the most probable technology to significantly contribute to renewable electricity generation in the coming years. Due to their electro catalytic properties carbon nanotube as an electrode increase power energy conversion of solar cell up to 7-9 % (Chen et al. 2012). Recently, a dye-sensitized solar cell with a tube like structure achieves 4.16 % conversion efficiency, which is different from the sandwich structure of the traditional dye-sensitized solar cell (Yongping et al. 2012).

So far, CNTs have been utilized in solar cell as a substitute of TiO_2 either in counter electrode or photo anode with simple mixing in solid state electrolyte and with an engineered interfacial layer. Recently various approaches utilizing CNTs have been explored to increase the conversion efficiency of solar cell. TiO_2 is considered to be a versatile candidate for the photo electrochemical (PECH) application due to its ability to improve the light absorption in visible region (Cheng et al. 2013). A titanium dioxide nanoparticle is dispersed on single wall carbon nanotube (SWCNT) films to improve photo induced charge separation and transport of carriers to the collecting electrode surface. As far as photoelectron-chemical is concern, charge equilibrium between TiO_2 and single wall carbon nanotube is a prime important factor to improve the efficiency of solar cell (Yongping et al. 2012). However, in case of Multi Wall Carbon Nano Tube (MWCNT), a controlled layer of multi-wall carbon nanotubes (MWCNT) is usually grown directly on top of fluorine-doped tin oxide (FTO) or other glass electrodes as a surface modifier for improving the performance of organic solar cells by 2% (Capassoa et al. 2014). Charge transport properties enhance the charge collection efficiency of dye sensitized solar cells (DSSC) by incorporating oriented TiO_2 nanotube arrays consisting of closely packed nanotubes having several micrometers in length with typical wall thicknesses, inter tube spacing of 8–10 nm and pore size diameters of about 30 nm (Kai et al. 2007). Recent patent applications (IN2010/000023 and JP2013118127) describe that using TiO_2 carbon nano tube (MWCNT) nanocomposites comprised DSSC prepared by using hydrothermal route leads to the increased efficiency of the DSSC (Brian et al. 2005; Subas, Vivek, Sarfraj, Mujavar, 2010; Kiyoshige 2013).

Recently, several polymers having conducting properties have gained popularity in designing cheap, lightweight, flexible and affordable solar cells. Several investigations in this regard have been done by various researchers. For example, single-wall carbon nanotube (SWCNT)–polymer solar cells were constructed with region regular poly (3-octylthiophene)-(P3OT) with purity >95% w/w, laser-generated SWNTS (Michael c/o Stuttgart Technology Center Dürr, Gabriele c/o Stuttgart Technology Center Nelles, Akio Stuttgart Technology Center Yasuda 2005). Another invention mentioned in Patent EP1507298 describes that solar cell comprising carbon nanotubes (CNT) as an electron conductor and organic substance like polymethacrylate's for hole's to get photovoltaic effect (Michael c/o Stuttgart Technology Center Dürr, Gabriele c/o Stuttgart Technology Center Nelles, Akio Stuttgart Technology Center Yasuda 2005). In another such research, by using concentric electro spinning of poly (methyl methacrylate) as a core precursor and polyacrylonitrile as a shell precursor to prepare a hollow active carbon nanofiber have been used. Such nanofiber with 190 and 270 nm for core and shell diameter showed excellent mesoporous structure, and 1-D conducting pathway in employing as catalysts of counter electrodes (CEs) for dye-sensitized solar cells (DSSC). In other developments involving the development of high efficiency solar cells various semiconducting materials have been deployed. Patent US20130092236 and US2011/054301 describe such devices where absorbing layer are composed of Gallium Arsenide (GaAs), Copper Indium Selenide (CuInSe) etc. to achieve high efficiency with low cost (Ranga, Christopher, Claire, Bhaskar, Omkaram, Srikant, Gaurav, Sanjayan, Kaushal; Robert 2012). It was also demonstrated in one of the study that acid infiltration of nanotube networks significantly boosts the cell efficiency to enhance charge separation and transport by reducing the internal resistance to improve the fill factor and by forming photo-electrochemical units. Here the efficiency of about 13.8% was achieved by combining carbon nanotubes and silicon (Yi et al. 2011). Other materials such as silver, palladium, Germanium, Platinum etc. were also used as conductive adhesives. Conductive adhesive enables interconnection of new cells and interconnector concepts, such as heterojunction solar cells with their heat sensitive surface (Zemena et al 2013). Palladium nanocrystallite decorated TiO_2 nanotubes (Pd/TNTs) improve the light absorption in visible region which enhance photo catalytic activity of solar cells (Cheng et al. 2013). In another study a composite film composed of platinum nanoparticles and carbon fibers was coated on FTO glass as a counter electrode in dye-sensitized solar cell (DSSC) shown 7.77% efficiency (Cai, Chen & Peng 2010). Patent No 20100089447 describes the use of conductive layers prepared of Silver nanoparticles or Magnesium nano layer (1-20 nm) thereof mixture (Takahito, Chihaya, 2007; Bulent, Burak, Richard, 2010). The purpose of carbon nanotube (CNT) based conductive adhesive was to increase the reliability and also to replace these costly heavy metals.

Defect rich edge planes of bamboo like structure carbon nanotube enable the electron transfer kinetics at the interface of counter electrode and electrolyte and result in improvement of fill factor due to low charge transfer resistance. So in combination with a dye-sensitized TiO_2 photo anode and an organic liquid electrolyte, a multi-wall carbon nanotube (CNT) counter-electrode DSSC shows 7.7% energy conversion efficiency. Uniform distribution of multiwall carbon nanotubes within the heterojunction organic solar cell are shown to increase in cell fill factor of 50–60% (Anthony, Ross, Ravi 2006). It has been reported that CNT incorporated with TiO_2 structure could play an important role in transporting the photo generated electrons towards the conductive supports, with the addition of SWCNTs, the incident power conversion efficiency 7.3 % to 16 %. CNTs can be used for the development of flat solar cells and flexible solar cells, where the latter are light weight and have the advantage for signal transmission and PV self-power generation. In the flexible solar cells, rigid substrate made of transparent conducting oxides (TCO) has been replaced and it has more power conversion efficiency. The flexible solar cells can be generated through carbon fibers, wire shaped CNT-CNT solar cell and carbon nanoyarn. In addition, the carbon nanostructures due to their efficient power conversion efficiency and 3D bendable structure can be used for various engineering applications such as fiber textile, composites etc. A further research is required, where new designs functional materials with smaller band gaps may enhance power conversion efficiency. Wire shaped DSSCs with above mentioned characteristics and stability under different environments may be used for various engineering applications.

3.4 Nanowire (NW)

Nanowires are defined as metallic or semiconducting particles having a cross sectional diameters <1 nm, and submicron size length. Ideal material for nanowires would have a band gap of around 1.55 eV (Qifeng, et al. 2012). The nanowire geometry provides potential advantages like optimum tunable band gap, better light trapping, increase defect tolerance and reduce reflection to increase the efficiency and reduce the cost. 1-D nanowire arrays as photo-electrodes have been widely investigated to provide a rapid collection of carriers and affording large junction areas with less reflectance loss. Nanowires are composed of n-type and p-type material, arrange in such a way that one material rolled over another material, so as an when photons irradiate on it then hole and charge move in equal and opposite direction as shown in Fig 4.

Nanowires of Si, Ge, GaN and InAs have high electron mobility in the axial direction. Therefore nanowires show comparable to or even over the best reported for solar cell efficiency (Benjamin & Peidong 2009). One of the most successful methods employed for nanowire synthesis is based on chemical vapor deposition (CVD). Nanowires grown by CVD employ a so called vapor liquid Solid (VLS) growth mechanism. Vertically aligned oxide nanowire comprising solar cell allows the light to be absorbed in the vertical direction and prevent exciton diffusion to improve the efficiency. In addition, the use of inexpensive, environmentally benign, and stable oxide materials suggests that a device constructed in this manner could have an excellent working lifetime at a fraction of the cost of existing solar cells.

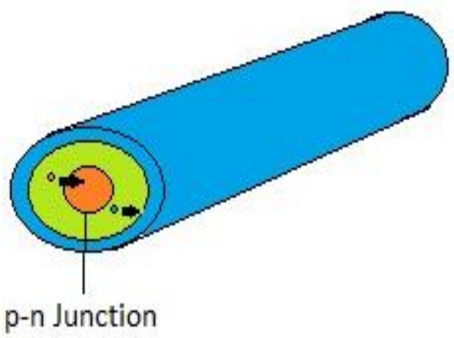

Figure 4. Charge Transfer in Nanowire based solar cell

The x and y axis directions are much smaller than z axis direction of nanowire, which enable to impart nanowires with various applications in electronic and optoelectronic devices. It was found in dye sensitized solar cells (DSSC) that, the nanowires provide electron transport 100 times faster than conventional cell by providing direct pathways for electron conduction. Semiconducting nanowire (NWs) present a fascinating potential opportunity for developing high efficiency, low-cost solar cells by decoupling light absorption and carrier separation. Ordered arrays of vertical nanowires with radial junctions has advantages like optical, electrical, strain relaxation, charge separation mechanisms and product cost than thin film solar cell with planner junction. In addition to playing a role in providing direct pathways for electron transport, compared to planar film, the nanowires contribute to enhancing the optical absorption and hence increase the solar cells efficiency (Sharma & Juhi 2013).

Development of solar cell using Nanowire (NW)

According to patent US7893348, solar cell comprising silicon (si) nanowires as active elements have been designed (Bastiaan & Loucas 2011). Patent US201102847230 describe that patterning planar photo-absorbing materials into arrays of nanowires is demonstrated as a method for increasing the total photon absorption in a given thickness of absorbing material (Chang & Yue, 2010; Robert & William 2011). By varying the wire length alters the wire filling ratio required to achieve the same amount of light absorption. Optimal designs for antireflective Silicon nanowire based solar cells achieve 11% power conversion efficiency (Jin et al 2013). Radial growth of hydrogenated amorphous silicon over p-doped crystalline silicon nanowires using plasma enhanced chemical vapor deposition technique on glass substrates achieves 5.6 % efficiency (Erik & Peidong 2010).

As with CNTs, solar cells have been fabricated using various other materials like Silver, Gold, Titanium, ZnO, TiO_2, InGaN, GaN, GaAs, and GaInP etc. or in combination with silicon nanowires (Fei, Siguang, Kang, 2007; Lars, Martin, Federico, 2009; Juneui, Jihyun, Sangwoo 2010; Yijie, Anjia, James, Shu, Paul 2012; Siegfried, 2012; Tae, Joo, Jae, Jae, Won 2012; Zetian 2013). By using TiO2 and Germanium Arsenide (GaAs) nanowire either with polymer as composite or as an electrode it can achieve even higher power conversion efficiency of 9.2 % (Jiun, Shu, Ching 2012; Hong, Shu, Ching 2012; Sin K. et al 2014). Patent applications IB2013/050943 and US20120202314 describe that solar cell comprised of a layer of p/n-doped semiconductor nanowires with embedded polymer layer (Samson, Hao, Felix, 2012; Silke, Boer, Gerhardus, 2013). Based on a heterojunction between the vertically aligned GaAs/ Ag nanowires and polymers like poly (3, 4-ethylenedioxythiophene): poly (styrenesulfonate) and/or incorporating poly (3-hexylthiophene) electron blocking layer have been designed to achieved power conversion efficiency of 9.2% (Jiun, Shu, Ching 2012; Hong, Shu, Ching 2012). In another breakthrough, highly flexible and cost-efficient brush painting of flexible organic solar cells (FOSCs) used same material.

In addition, it provides an opportunities to fabricate complex single crystalline semi-conductors devices directly in low cost subtract and electrodes such as Al foil, stainless-steel and conductive glass. Nano wire based solar cell can be fabricated using a wide variety of materials ranging from Si, Zn, CdTe, CuO_2, Tio_2, in and many other polymer NW combination. Power conversion efficiency from these nanowires can be achieved close to 10%. These nanowire provide high efficiency due to their unique geometry for example (a) Periodic array of nanowire with radial junctions give the advantage such as reduced reflation, maximum light trapping, radial charge separation and single crystalline synthesis on known epitaxial subtracts (b) Axial junction loss the radial charge separation benefit but keep the others. (C) Substrate junction lack the radial charge separation benefit and cannot be removed the substrate for testing as single nanowire solar cell. These nanowire have been synthesized by using two most common techniques i.e. chemical vapor deposition and pattern chemical etching. The surface property of the materials, dopant profiling and incorporation of catalyst during growth of NWs has been found to affect the electrical properties, charge mobility and diameters. The above factors promised to lower the cost of solar cell by reducing the amount of material needed. It is expected that the cost of multifunction solar cell fabrication using nanowire can be as low as to that of traditional thin film solar cell cost without compromising the power conversion efficiency. However there are many challenges which needs to be addressed before the benefits can be realized commercially, These challenges includes surface characteristics of the material, mechanical and chemical stability, doping control, nanowire array uniformity and scalability.

3.5 Graphene

Graphene is the two dimensional (2D) building block for Sp^2 carbon allotropes. A flat monolayer of carbon atoms tightly packed into a two dimensional (2D) honeycomb lattice is known as Graphene. It is generally wrapped up into zero dimension (0D) fullerenes, rolled into one dimension (1D) nanotubes or stacked into 3D graphite. Hence it can be used as a lubricant due to its loosely bonded layered planar structure with the planes of carbon atoms.

History of Graphene

History of Graphene is incomplete without describing Graphene oxide (GO). Graphene are called as reduced Graphene oxide. Which was extensively studied in back 1840s (Daniel, Rodney, Christopher 2010). Timeline of selected events occurred in the history of Graphene as mentioned below Table 5.

Table 5
Historical development of Graphene for solar cell (Daniel, Rodney, Christopher 2010)

Year	Events
1987	The name "Graphene" was first mentioned by S. Mouras and co-workers to describe the graphite layers that had various compounds inserted between them forming the so-called Graphite Intercalation compounds or GIC's.
1999	Ruoff and coworkers micromechanically exfoliate

	Graphene into thin lamella comprised of multiple layer of Graphene.
2003	In 2003, Andre and Kostya succeeded in producing the first isolated Graphene flakes and this work was published in 2004.
2005	The first major result on the electronic properties was the anomalous quantum Hall effect in Graphene reported around the same time by Andre and Kostya and by Philip Kim's group at Columbia University.
2010	Andre and Kostya were awarded the 2010 Nobel prize in physics for this work and are continuing to unveil new and exciting properties in graphene and other related two dimensional crystal materials.
2014	Jonathan Coleman and colleagues from Trinity College Dublin were able to create Graphene by mixing the proper amount of graphite powder, water and dishwashing liquid in a high-powered blender.

Potential for solar cell

Graphene has very high electrical conductivity due to it contains both holes and electrons as charge carriers. The Graphene with each absorb photon it generate an electron hole pair. It was said that graphene's electrons has similar mobility as photon due to their lack of mass. Graphene electrons require to travel sub-micrometer distances without scattering i.e. ballistic transport phenomenon. Graphene is used as a light absorbent can able to increase efficiency of solar cell by enhancing absorption capacity. Graphene is the strongest material ever discovered with a tensile strength of 300 x 108 Pascal's which is 4 x 108 times stronger than A36 structural steel. The reason behind its strength is 0.142 Nm-long carbon bonds. Hence graphene is a strong candidate for solar cell (Yanwu et al. 2010).

Development of solar cell using Graphene

Stanford University scientists have developed the first solar cell made entirely of carbon, which is a cheaper alternative to the expensive, silicon based solar cell (Standford 2012). Bao and her colleagues use Graphene sheets as dual material (active layer and electrode). It primarily absorbs near-infrared wavelengths of light so it power conversion efficiency is less than 1% (Standford 2012). The University of Florida achieves 8.6 % power conversion efficiency by using graphene doped with trifluoromethanesulfonyl-amide (TFSA) coated silicon wafer material. With celebrative research of universitat Jaume I in Castello and Oxford University, they claimed 15.6% power conversion efficiency by combining titanium oxide and graphene as a charge collector and perovskite as a sunlight absorber. Its production costs are very low, enable to make it possible for the technology to be used on flexible plastics (Gizma 2015). If plasmonic nanostructures of graphene were optimized, it should be possible for falling photon on graphene is converted into current and increase the efficiency of solar cell. That is what industry want to produce said by Alexander Grigorenko of Manchester (Physic world 2011).

Soitec Germany- As recently developed, a word class four junction solar cell grown on different III-V compound materials using CPV technology gives an outstanding 43.6 % PCE. This technology was developed in collaboration with the Fraunhofer institute of solar energy system and the Helmholt zentrum fur materialien und Energie in berline. This allows optimal band gap combinations to capture the maximum sunlight's. Recently, multi-junction solar cells with concentrator photovoltaic (CPV) systems have demonstrated solar conversion efficiency over 40. It is cost effective because of broad geographic areas for solar absorption. For metamorphic 3-junction GaInP/GaInAs/Ge solar cell, its power conversion efficiency was about 41.6% at 484 suns, the highest efficiency yet demonstrated for this type of cells.

Professor Ravi Silva from the University of Surrey outlined his definition for 4^{th} generation (4G) solar cells, capable to improve the power conversion efficiency of existing 3rd generation solar cell. 4^{th} generation (4G) solar cells comprise single layer of conducting polymer films (organic) i.e. cheap and flexibility with novel nanostructures (inorganic) i.e. lifetime stability (Anthony, Ross, Ravi 2006).

3.6 Nanofabrication: Roll to Roll process

Three dimensional (3-D) nanomaterial has potential to boost up the performance of solar cell owing to the power conversion efficiency. However the cost effective production with mass production having unchanged optical and physical properties are still remain challenge for the present technology. Though, polymeric solar cell up to some extent are able to overcome the current challenges like high manufacturing cost, lack of ability for mass production or restricted application etc. So in modern scenario, researchers are adopting multidisciplinary approach by combining the nanofabrication technique and polymeric solar cell concept to beneficiate the solar industry. Nanofabrication is the technique to manipulate the component or material in controllable manner at nanometer scale in 1, 2 or 3 dimension. Such technique gives value addition to the manufacturing process due to change in electronic property of the material at nanometer scale. In last few years, electronic industry has attracted much towards the nanofabrication technique to produce electronic circuits or boards with extraordinary electric performance. Now a day's same concept was applied for solar cell using roll to roll process. Roll to roll is the process to deposit, assemble or coat the material on substrate for mass production of industrial product. It has been already used by coating industry to beneficiate of time saving mass production. While in solar industry, roll to roll process is unable to fulfill the prior requirement of power conversion efficiency. By coupling nanofabrication and roll to roll method it is possible to open a wide scope of opportunity for manufacturing paradigm and industrial requirements. Nanofabricated roll to roll technique provides a flexible, transparent and light weight substrate for the manufacturing of solar cell. At development stage, materials like silicon, group I-V and polymeric nanoparticles have been investigated as an absorbing component, while plastic or metal strip have been used as a substrate of solar cell. As roll to roll technology for solar cell industry is less mature enough technology than other technologies and hence the power conversion efficiency of solar device achieved very low. The list of different methods of roll to roll process are comprising nanofabrication with their power conversion efficiency in solar cell as shown in Table 11. With extensive research and development in last few years power conversion efficiency of flexible solar cell using CIGS is 14.1 %, CdTe is 11.4 %, a-silicon is 12 % and TiO_2 is 8 % on plastic substrate at laboratory scale. While at industrial scale for CIGS is 17.5 %, CdTe is 8 % and a-silicon is 8 % (Razykov et al 2011). However inherent stability and less production cost indicate a promising potential for these technology. Various types of nanofabrication process are available like nano-imprinting, nano-lithography, self-assembling, molecular engineering etc. Hence, large scale flexible solar cell will grove into a billion dollars industry over the next few years and will change our view of electronics. The photo-electric market in 2010 with about 2 billion USD of which 20% is flexible. It was projected that by 2020, it rises to almost 60 billion USD, of which 75 % is of flexible (IDTechEx 2009-2029 market report 2009).

Table 6
List of roll to roll methods with their PCE (%) (Markus H. 2013)

Sr. no.	Technology	Material	Power conversion efficiency (%)
1	Slot die coating	PEDOT:PSS, P3HT:PCBM	1.74
2	Doctor blading	POD2T-DTBT:PCBM	6.74
3	Spray Coating	P1:PCBM	5.1
4	Screen printing	Ag	20.3
5	Flexo printing	Ag	18.1
6	Gravure printing	PEDOT:PSS, P3HT:PCBM	2.8
7	Inkjet printing	Ag	4.91

4. Future aspects

Researchers succeed to demonstrate the conversion of solar energy to electric energy after the extensive research of 60 year. Today also we are facing crucial limitations like manufacturing cost and poor power conversion efficiency. Hence, it is not sufficient to replace the consumption demand of fossil fuel with solar energy. Innovative solar cell technologies that utilize nanostructured materials offer great technological potential due to their attractive properties. The late noble physicist Richard smalley saw a potential in nanomaterial to bring revolution in energy sector by modifying the fundamentals component of solar cell using value adding property of nanotechnology to make better solar cell. To overcome the problem of reflection, anti-reflecting coating has been used, which increase the cost of solar cell. Recently, nonporous material was coated on solar cell surface which is known as black silicon. It increased the 20% power conversion efficiency from conventional solar cell. However, efficiency of solar cell is not only the advantage of nanotechnology. Another value addition of nanotechnology is to produce ultra-thin and flexible solar cell, which cross limit of rooftop solar panels. New solar cells are based on films formed by roll-to-roll process technology of nanomaterial enabling high surface area, transparency, excellent stability and good electrical conductivity and are ideal for solar applications. It also opens the opportunity to produce cheaper and environmental friendly solar cells. Availability of electricity is the major challenge for developing countries, due to lack of fossil fuel and high global price of crude oil. So, nanotechnology has potential to decrease the cost of solar cell and allow to achieve good power conversion efficiency. It also enables to meet the increasing demand of electricity and also accessible for those people. Today researchers started exploring nanotechnology in different way to develop the solar cell. Therefore, the use of nanotechnology appears to provide a ladder to develop newer solar cell with much high PCE at cheaper cost and bring revolution in the solar cell industry in future.

5. Acknowledgement

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